GROUNDWATER CHEMISTRY OF SHALLOW AND DEEP GROUNDWATER SOURCES OF A COASTAL SEGMENT OF KERALA: A STUDY OF ARATTUPUZHA VILLAGE, ALAPPUZHA, INDIA

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By

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Certificate

Certified that the work presented in the thesis entitled **"Groundwater Chemistry of Shallow and Deep Groundwater Sources of a Coastal Segment of Kerala: A Study of Arattupuzha Village, Alappuzha, India"** is an authentic record of research work carried out by Ms. Regi George T under my supervision and guidance in the School of Environmental Studies, Cochin University of Science and Technology, Kochi-682022 and that this work has not been included in any other thesis submitted previously for the award of any degree.

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Declaration

I hereby declared that the work presented in this thesis entitled **"Groundwater Chemistry of Shallow and Deep Groundwater Sources of a Coastal Segment of Kerala: A Study of Arattupuzha Village, Alappuzha, India"** is based on the original work done by me under the supervision of **Dr. V. Sivanandan Achari**, Associate Professor, 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 and most gifted resource of the natural environment. It is considered as least polluted and protected compared to other inland water resources. The major problem with the groundwater is that once contaminated, it is difficult to restore its pristine quality. Preservation and rational use of water resources are considered most important for economic stability, sustainable development and social well being.

Principles of inorganic geochemistry and analytical chemistry form the background of groundwater quality studies. For evaluating hydrogeophysical features of a region's groundwater, physico - chemical and trace metal studies are significant. Chemical analysis of groundwater generates the fundamental data essential for the determination of groundwater quality.

Present study area is on environmentally significant and ecologically sensitive Arattupuzha coastal village in Alappuzha District, Kerala, India. This region has been severely affected by 26th December 2004 Indian Ocean Tsunami. The district has a tropical humid climate with oppressive summers and plentiful seasonal rainfall. The sand and silt form the lithological feature of the study area. The coastal alluvial soils are seen along the coast which has been developed from recent marine and estuarine deposits.

This bound research work comprises study of the groundwater chemistry of shallow and deep groundwater sources along this ecologically sensitive coastal segment for the last 5 years. Sampling at selected shallow and deep groundwater stations started in January 2012 and continued in each month till December 2012. Sampling and analysis were done in the subsequent years, 2013, 2014, 2015 & 2016. A comparison with the post tsunami study data available for the year 2005 and that reported for year 2001 regarded as pre-tsunami condition, are done for a critical evaluation of the hydrogeochemistry of the region. Hence, this makes an extensive study on the groundwater chemistry intermittently for a period 2001-2016.

Water quality standards for drinking purpose, domestic, agricultural and industrial use, published by various agencies are used for evaluating the groundwater quality in this study. Presentation of results in graphical forms and supported by GIS maps help determine temporal and spatial variation of constituents. Results of chemical analysis are statistically evaluated by correlation studies which help to hypothesise relationship among parameters. Water quality index calculated using WHO standards are discussed to identifying nature and quality of groundwater. The ratio of sodium and chloride concentrations are particularly important because they give insights regarding the prominence of the groundwater processes; *ion exchange* and *reverse ion exchange*. Hill-Piper Trilinear diagrams are used to infer hydrogeochemical facies of the water sources. Gibb's plot is used to evaluate the prominent hydrogeochemical processes occurring. Different parameters used for irrigational quality evaluation are sodium adsorption ratio (SAR), sodium percentage (Na %), magnesium adsorption ratio (MAR), residual sodium carbonate (RSC), permeability index (PI) and kelly's ratio (KR). USSL and WILCOX diagrams are presented to classify water based on irrigation suitability. Saturation indices are reported in the study to distinguish the industrial use of water with respect to aggressiveness.

The thesis comprises testing and evaluation of the hypotheses: whether there is any significant difference in water quality parameters between stations, months, years and also between strata such as control well (CW), dug well (DW) & bore well (BW) groundwater sources. Also, whether the water quality index differ between strata and between time periods. Findings are critically evaluated and inferences are summarized with sound interpretation based on the principles of analytical chemistry and statistical methods.

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List of Abbreviations

CW	-	Control well
DW	-	Dug well
BW	-	Bore well
BIS	-	Bureau of Indian Standards
WHO	-	World Health Organisation
DBU	-	Designated Best Use
CPCB	-	Central Pollution Control Board
WQI	-	Water Quality Index
GIS	-	Geographic Information System
CI	-	Confidence Interval
DO	-	Dissolved Oxygen
BOD	-	Biochemical Oxygen Demand
EC	-	Electrical Conductivity
TH	-	Total Hardness
TDS	-	Total Dissolved Solids
KR	-	Kelly’s Ratio
MAR	-	Magnesium Adsorption Ratio
PI	-	Permeability Index
SAR	-	Sodium Adsorption Ratio
RSC	-	Residual Sodium Carbonate
USSL	-	United States Salinity Laboratory
AI	-	Aggressiveness Index
LSI	-	Langelier Saturation Index
RSI	-	Ryznar Stability index

* * *

Chapter 1

INTRODUCTION

Long-term studies of groundwater composition of coastal areas prone to natural disasters like tsunami require considerable detailed sampling and analysis which is expensive in money and professional talent [1-10].

1.1 Groundwater Science

Groundwater is more than a resource. It is an important feature of the natural environment. 94% of the earth's water rests in the oceans and seas at high levels of salinity. Groundwater accounts for about two-thirds of the freshwater resources of the world. It is the only utilizable fresh water since the rest is present as icecaps and glaciers. The fresh water breakdown comes to: groundwater- 95%, lakes, swamps, reservoirs and river channels- 3.5% and soil moisture-1.5% [11].

The term groundwater is usually referred to the subsurface water that occurs beneath the earth surface, constitute water table in soils and geological formations that are fully saturated. Study of groundwater rest on an understanding of the subsurface water chemistry and fresh water availability in a region and is regarded as an interdisciplinary subject [12]. Knowledge of geology, hydrology, meteorology, physics, chemistry, biology, environment etc. are necessary in studying groundwater science.

1.1.1 Geochemical Environment

Various parts of the earth being studied are important in a greater perspective of groundwater chemistry. The lithosphere (rocks), pedosphere (soils), biosphere (living organisms), atmosphere (air), hydrosphere (water), anthroposphere (man’s effect on the spheres) are the common systems of the earth. One of the major processes occurring in these spheres is the cyclic distribution of water on the planet earth [hydrologic cycle]. The natural quality of groundwater is controlled by the geochemistry of the lithosphere and the hydrochemistry of the hydrosphere.

The initial composition of groundwater originates from rainfall, which may be considered to be diluted seawater. During its return path to the ocean, the water composition is altered by rock weathering, evaporation and aeration. Thus in hydrologic cycle, water circulate through hydrosphere, atmosphere and upper part of lithosphere (upto 3km).

Lithosphere

A knowledge of rock composition is essential to understand the chemical composition of groundwater. Earth has iron-rich core surrounded by a thick mantle made up of magnesium and iron rich silicates and a thin outer crust made up of rather extensively reworked silicates and other minerals. The outer crust of earth exerts a direct influence on the composition of groundwater. 95% of Earth's crust to a depth of 16km is igneous rock. Most recoverable groundwater occurs at depths of less than 2km below the land surface where sedimentary rocks are more prevalent. Sedimentary rocks results from consolidation of loose sediments, or a chemical rock formed by precipitation from solution, and an organic rock consisting of the remains of plants and animals. Common sedimentary rocks include sandstones, shale, limestone and evaporates which consist quartz, clay, calcite, iron oxide, dolomite, gypsum, anhydrite and halite.

Cementation of sedimentary rocks usually results in low porosity.

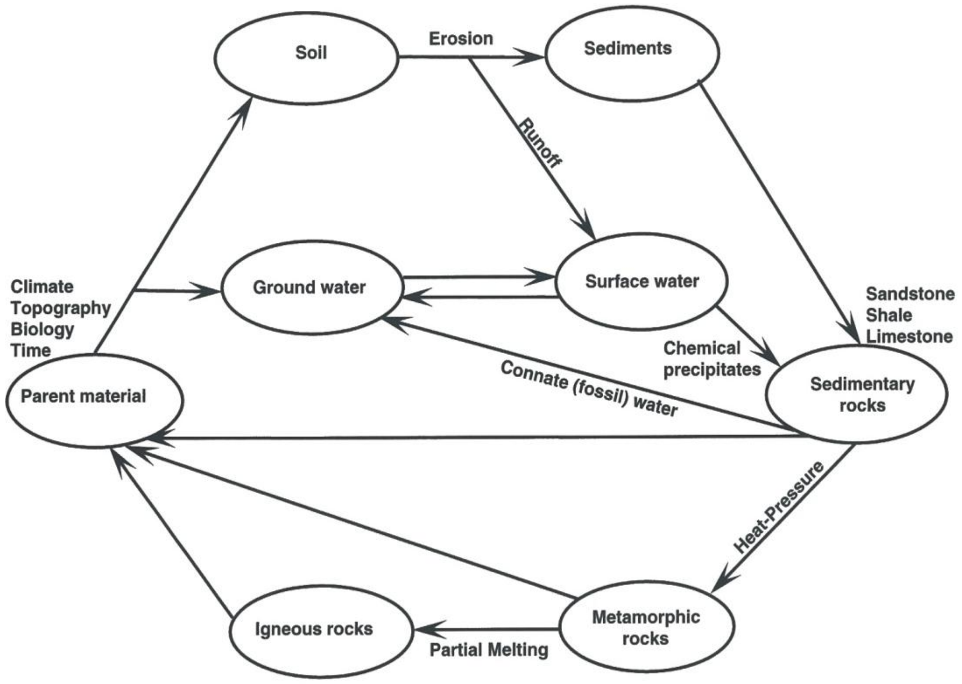

Figure 1.1: Hydrologic and geologic cycles (Hounslow AW 1995) [13]

Table 1.1: Generalized geological succession along Kerala Coast [14, 15]

Period	Epoch	Formation	Lithology & areal distribution
Quaternary	Recent	Alluvium	Sand and clay seen along the coast and the flood plain deposits of Kuttanad and Kole lands
	Sub-recent	Laterite	Laterite capping on the sedimentary formations
Tertiary	Lower Miocene	Warkali	Sandstones and clays with thin band of lignite, south of Cochin all along the coast & western portion of Kuttanad
		Quilon	Limestone and clays, south of Cochin
	Oligocene to Eocene	Vaikom	Sandstones with pebbles and gravel beds, clay and thin band of lignite, all along the sedimentary basin.
	Eocene	Alleppey	Carbonaceous clay and sands, encountered only in boreholes in Alappuzha coast
Precambrian	Archaean		Crystalline basement of khondalites and charnockites.

Environmental Factors

In addition to rock composition, other spheres of Earth have strong influence on the composition of groundwater [16-19]. Hydrosphere consists of vapour, liquid and solid water present at and near the land surface and its dissolved constituents. Ocean constitute about 98% of the hydrosphere. Atmosphere consists of mainly nitrogen (78.09%), oxygen (20.95%), Argon (0.93%) and CO_2 (0.03%). Minor constituents include oxides of carbon, nitrogen, sulphur and other gases. The supply of liquid water is replenished by precipitation. The components of regional climate like the amount and rate of rainfall, runoff, evaporation and the temperature of the systems are important factors that control groundwater composition. The microbiological population affects the biodegradation reactions, as well as catalyzes many of the redox reactions. Plants in the biosphere help in the identification of trace metal anomalies, particularly for Ag, Au, Cu, Sn, Se and U. Humic substances are produced by the chemical and biological degradation of plant and animal residues and from the synthetic activities of microorganisms. They form water soluble and water insoluble complexes with metal ions and hydrous oxides and interact with clay minerals and organic compounds. Human activities may modify water composition extensively through direct effects of pollution and indirect results of water development, such as intrusion of seawater in groundwater aquifers.

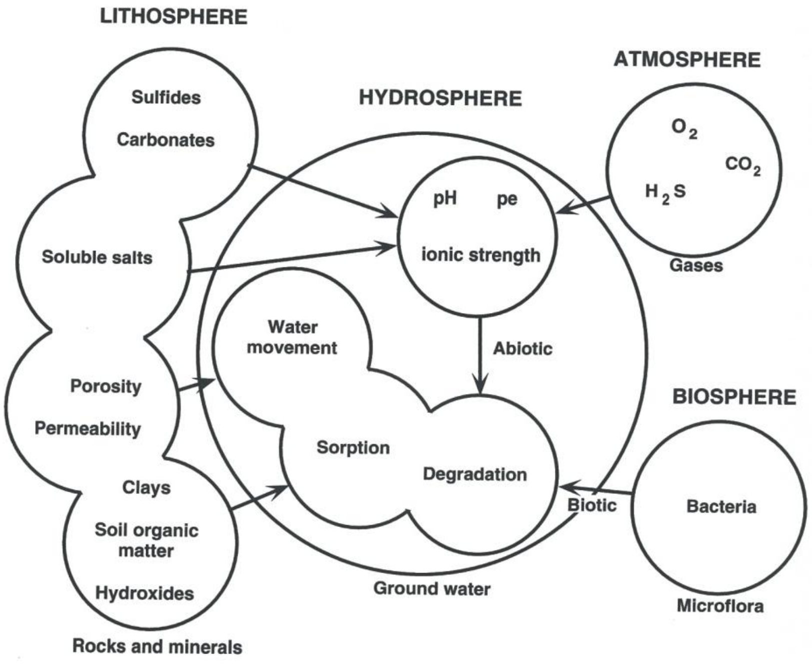

Figure 1.2: Groundwater Chemistry (Hounslow AW 1995)

1.1.2 Aquifers

A rock formation, sequence of formations or part of a formation which yields appreciable quantities of groundwater is called an *aquifer*. If the upper surface of an aquifer is defined by the water table, it is called an *unconfined* or *phreatic* aquifer. A confined aquifer is separated from the atmosphere by a relatively impermeable confining rock. Major fluctuations in piezometric-level are related to seasonal rainfall and pumpage.

The texture and rock type determine the porosity and permeability of the rocks & hence their aquifer characteristics. Most of the world’s regional aquifers are of sedimentary origin. Igneous and metamorphic rocks have low porosity and permeability and they do not form important aquifers. Unconsolidated materials in which inter-granular flow dominates are restricted to relatively shallow depths and are very important as aquifers. They are characterized by generally good water quality because of the short to moderate residence times and regular recharge mainly in humid areas, but are often highly vulnerable to anthropogenic influences.

In *shallow phreatic aquifers* in thickly populated areas, changes in environmental pressure and anthropogenic pollutants threaten groundwater quality. In the case of coastal aquifers, the degree of sea water contamination, defined by seawater-freshwater interface depends on the hydraulic gradient or the height of the fresh water column over the mean sea level.

Aquifer recharge occurs by various process like direct infiltration of surface water, seepage, direct and deep infiltration of rainwater and groundwater flow which result from the lateral discharge of an adjacent aquifer. The recharge varies with time and space. The regional recharge in a year and over years may range from zero to very high values based on the time distribution of rainfall.

1.1.3 Weathering

The weathering of rocks involves the reactions of their constituent minerals with atmospheric gases and water. The products of secondary weathering depends on the environmental conditions such as temperature, precipitation, biological activity etc. and other factors like drainage. Presence of humic and fulvic acids increase the amount of rock dissolved. The fluids (leachate) from this environment carry a variety of ions into surface and groundwater systems. Weathering leads to inorganic constituents which can be classified based on their behaviour in the secondary environment.

1) *Resistates:* which are resistant to chemical and mechanical breakdown, and include soils containing the minerals quartz(Si), zircon(Zr), tourmaline(B), rutile(Ti), cassiterite(Sn), and gold(Au).
2) *Hydrolysates*: which are products of chemical breakdown of aluminosilicates like feldspar, and form shales, soils or bauxites.They adsorb elements like potassium.
3) *Oxidates*: which are the oxidation products of iron and ferric hydroxide and include redbeds, laterites or soils
4) *Reduzates*: which consist of organic material and sedimentary sulphides.
5) *Carbonates*: which are products of organic or inorganic precipitation of calcite, aragonite and dolomite, and form limestones, dolomites, and travertines.
6) *Evaporates*: which are relatively soluble salts that accumulate in oceans and later evaporate to form evaporates, and contain halite (NaCl), sylvite, gypsum and carnallite.

The effectiveness of water in weathering rocks is increased by its ability to wet mineral surfaces and penetrate into small openings.

Thus the chemical quality of groundwater depends on the host rock constituting the aquifers. Interstices in rocks can store water or allow water to move through. These properties of rocks differ depending on origin, mineralogical composition, geological history and climatological factors. Depending on the surface and subsurface environment, the moving groundwater may dissolve, transport and deposit mineral matter. Between the land surfaces that are not continually covered with water and the underlying groundwater body there is an intermediate zone where openings and pore spaces are filled mainly with air. The water that is added to this zone by rainfall or by irrigation or by the portion that is not returned by evapotranspiration to the atmosphere can move downward towards the groundwater table. If the groundwater is under unconfined conditions this percolation becomes a major means of recharge. Movement of solutes are even slower due to the interaction of ions in the water films on mineral surfaces and surface charge sites [12]. Considering the geochemistry of groundwater, the chemical species of cations derive mainly from the lithological (geogenic) sources, while those of anions from the non-lithological (anthropogenic) sources. Depending upon the occurrence of source material under climatic conditions, the quality of groundwater varies from place to place. The expected controlling chemical processes in the groundwater are mineral dissolution, leaching of ions, ion exchange, precipitation of ions, evaporation, etc.

1.1.4 Principles of chemical processes in groundwater

Principles of inorganic geochemistry form the background of groundwater quality study [12]. In evaluating pollution problems organic compounds and trace metal studies are required.

Thermodynamics

There are several chemical processes occurring in the transfer of solid or gaseous components of the Earth and atmosphere into the liquid water of the hydrosphere. Thermodynamic principles can be used to explain these processes. These principles form a basis for evaluating quantitatively the feasibility of various possible chemical processes in natural water systems, for predicting the direction in which chemical reactions may go, and in many instances for predicting the actual dissolved concentrations of reaction products that should be present in the water. The total energy in a groundwater system includes components of gravitational, thermal, and chemical energy.

Reversible and irreversible reactions

Groundwater system can be considered as dilute and heterogeneous. Depending on kinetic factors, physical features and thermodynamics, groundwater reactions can be reversible or irreversible. Dissociation of dissolved carbondioxide is an example of reversible and homogeneous reaction.

$$H_2CO_3(aq) = HCO_3^- + H^+ = CO_3^{2-} + H^+ \quad \text{.......................................} \quad (1.1)$$

Heterogeneous reactions such as dissolution of unreactive gases are readily reversible. Many sorption-desorption or ion-exchange reactions are readily reversible.

$$Na_2\text{-clay} + Ca^{2+} = 2Na^+ + Ca\text{-clay} \quad \text{...} \quad (1.2)$$

Homogeneous and heterogeneous redox reactions involving iron are less reversible. Energy barriers of various kinds may inhibit reversibility.

Chemical Equilibrium

The study of chemical equilibria is based on the law of mass action. Mass-law calculations are used for system of dissolution of calcite.

$CaCO_{3(s)}+H^{+}=Ca^{2+}+HCO_3^{-}$ .... (1.3)

Equilibrium constant, K is calculated using the activities of various species in moles per litre. The activity of solid is taken as unity.

$K=\frac{[Ca^{2+}][HCO_3]}{[CaCO_3][H^{+}]}$ .... (1.4)

A large number of equilibrium constants as functions of temperature, and of pressure in some instances, are available in equilibrium computer programs. K calculation are helpful to test whether a given water is unsaturated and can dissolve more calcite, is supersaturated and can precipitate calcite, or is at equilibrium.

Chemical Kinetics

Some processes may involve several steps. In redox reaction involving iron, oxidation of ferrous iron occur,

$Fe^{2+}=Fe^{3+}+e^{-}$ .... (1.5)

Reduction of aqueous oxygen is a complex reaction involving steps.

$O_{2(aq)}+4H^{+}+4e^{-}=2H_2O(l)$ .... (1.6)

In the case such complex reactions involving a series of stepwise reactions, a kinetic model applied to a summarizing equilibrium reaction is not likely to be meaningful or useful. Instead, the reaction mechanism must be looked at in detail, and kinetic data must be derived for the significant parts of it.

Solubility

A solubility product is an equilibrium constant for the solution of a compound that dissociates into ions. The chemical equation representing the dissolution of gypsum is

$CaSO_4\ 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$ .... (1.7)

and the corresponding solubility product expression is ,

$[Ca^{2+}]\,[SO_4^{2-}] = Ksp$ .... (1.8)

Solubility and solubility products have been determined for many inorganic compounds of interest in natural-water chemistry.

Interfaces

Physical and chemical processes occurring at liquid-gas and liquid-solid interfaces are of importance in studies of water quality. Dissolution of gases O_2, CO_2 etc. in water are depends on such physical and chemical characteristics as area of interface, mechanisms of transport away from interface, temperature, and pressure. The occurrence, solution, and transport of oxygen are important to the study of biochemical processes relating to water pollution. The process of photosynthesis is a major source of oxygen in some water bodies. Carbon dioxide dissolves in water and participate in many geochemical processes. By Henry's law, the solubility of a gas in water at constant temperature is proportional to the pressure, in atmospheres, of the gas phase in contact with the water. For a mixture of gases, the effective pressure of each component is proportional to its mole fraction.

Adsorption

In adsorption processes, the solute species at the interface may be removed or exchanged for other solutes without greatly affecting the properties of the solid surface. This transition from the solution phase to the solid phase can be represented in terms of energy, and this has useful implications in solution or deposition processes. A very finely divided precipitate may have a greater solubility than a precipitate that is identical in composition and structure but is present in larger crystals. This difference can be assigned to the surface free energy of the solid. Adsorption is pH dependent.

Cation-exchange capacity (CEC), represents the total number of negative charge sites in a given amount of solid at which reversible cation adsorption and desorption can occur. If both cations have same charge, constant selectivity coefficient values are obtained.

Electrical Double Layer

A mineral solid immersed in a solution normally has a net negative electrostatic charge that attracts cations from the solution to maintain electro- neutrality. Thus a fixed layer of immobilized cation is formed at the solid surface. A diffuse layer of oppositely charged ions is also produced. Thus the concept of electrical double layer is of importance in groundwater study.

Membrane Effects

Since cell walls and many forms of biological membranes are semi permeable, osmosis is particularly important in biological and biochemical processes. Due to osmosis a pressure difference is generated which is called osmotic pressure. From Raoult’s law vapour pressure measurements are possible. It permit the calculation of solvent activities which in turn help the computation of osmotic pressure for systems exhibiting ideal behaviour. As the water becomes saline, due to high osmotic pressure, it becomes more difficult for plants to obtain moisture from the soil, because the plants must overcome this pressure.

Thus several principles of chemistry are of much relevance in groundwater studies. The rate of geochemical processes like oxidation/ reduction, ion exchange, dissolution, evaporation, precipitation etc. and microbiological process are to be considered in evaluating the hydrogeochemistry of groundwater.

1.2 Groundwater Quality

Groundwater has emerged as the primary democratic water source and poverty reduction tool. Due to its low capital cost, it is the most preferred source of water in India. More than 85% of India’s rural domestic water requirements, 50% of its urban water requirements and more than 50% of its irrigation requirements are met from groundwater resources. Coastal aquifers prove to be an important source of groundwater resources. Stress on groundwater, both in terms of quality and quantity, are increasing rapidly due to growing demands, significant changes in land use pattern, sea water intrusion, industrial effluent, domestic effluent etc. A major concern with water quality is human health and disease. Cancer may result from excessive Cd, Ni & Pb. Cardiovascular disease is also of interest, and this involve the study of Ca, Mg & water softening. Urolithiasis, the occurrence of kidney stones, because of the build-up of Ca oxalates and Ca phosphates is also of continuing interest. The need to assess the groundwater quality is becoming increasingly important. Mathematical models provide a quantitative frame work for analysing data from monitoring and assess quantitative responses of the groundwater systems subjected to external stresses.

Significant water quality parameters

Major constituents (>5mg/l) of water are sodium, calcium, magnesium, chloride, sulphate, bicarbonate and silica.

Minor constituents (0.01-10mg/l) of water are potassium, strontium, Iron, carbonate, fluoride and nitrate.

Trace constituents (<0.1 mg/l) of water are aluminium, arsenic, barium, bromide, cadmium, chromium, cobalt, copper, iodide, lead, lithium, manganese, molybdenum, phosphate, selenium, uranium and zinc. Pollution from anthropogenic sources result in the presence of harmful trace elements.

In a typical water, the major ions existing in solution are

Na^+, K^+,Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- and CO_3^-.

Other determinations include pH, Redox potential (Eh), Electrical Conductivity (EC), SiO_2, Total Dissolved Solids (TDS), Hardness, Alkalinity, Dissolved oxygen, Total Carbon (TC), Total Organic Carbon (TOC), Total Inorganic Carbon (TIC) etc.

Biological analysis include Biochemical Oxygen Demand (BOD), MPN analysis, E. Coli analysis etc.

pH

pH is a measure of hydrogen ion activity, $pH= -\log_{10}[H^+]$

Three main sources of hydrogen ion in groundwater are hydrolysis, dissociation of H_2CO_3 and oxidation of FeS_2. Other sources include humic and fulvic acids, acid rain etc. The pH of natural water is a useful index of the status of equilibrium reactions in which the water participates. Neutral pH at 30°C would be 6.92. If the system contain calcite ($CaCO_3$) and if the gas phase is ordinary air, the pH at 25°C will be 8.4. Temperature has a strong effect on hydrogen-ion behaviour. In moderately alkaline environments carbonates are precipitated and many trace metals co-precipitate with them. Seawater has a pH of about 8.1.

Redox Potential (Eh)

It measure the potential of electron flow. $Eh=pe/16.9$

The usefulness of the Nernst equation and the pH-Eh diagram in generalized theoretical studies of redox equilibria in natural water is well established. The diagram is an indication of limiting conditions and is a clear, simple, and convenient means of evaluating the chemical equilibrium status of multivalent elements in a specified environment.

Electrical Conductivity (EC)

It is the reciprocal of resistivity and is temperature dependent. EC is the most important parameter of water which tell much about its quality. Dissolved salts increase the current carrying capacity of water. EC is related to many other parameters. Conductivity is a good estimator of Total Dissolved Solids (TDS) because TDS in mg/l is proportional to the conductivity in micromhos. It is an important parameter in irrigation quality study.

Calcium and Magnesium (Ca & Mg)

Water Ca &Mg result from decomposition of Ca & Mg aluminosilicates and at higher concentration from dissolution of limestone, magnesite, gypsum and others. Reverse ion exchange is also a source of these ions. They are removed by ion exchange and by the precipitation of calcite and gypsum. They contribute to hardness of water and total hardness is expressed as calcium carbonate ($CaCO_3$). Mg is found in the Earth's crust in much lower amounts as compared with Ca. In natural waters, the content of calcium is 3-4 fold higher than that of Mg, where as waters which are more heavily salted like seawater contain 3-4 fold more Mg.

Sodium and Potassium (Na & K)

Major sources of sodium are halite, sea spray, hot springs, brines etc. and that of potassium are potash feldspar, mica etc. The only common sink for sodium is reverse ion exchange and for potassium are plants and clays. Maintenance of optimum soil fertility entails providing a supply of available potassium. The element is present in plant material and is lost from agricultural soil by crop harvesting and removal as well as by leaching and runoff acting on organic residues. In dilute natural waters in which the sum of sodium and potassium is less than 10 mg/L, it is not unusual for the potassium concentration to equal or even exceed the sodium concentration. Water containing *10 to 20 mg/L* of sodium and nearly equal concentrations of potassium appears to be fairly common. However, in most other freshwater aquifers, if the sodium concentration substantially exceeds 10 mg/L the potassium concentration commonly is half or a tenth that of sodium. Seawater contains 390 mg/L of potassium.

Bicarbonate (HCO_3^-)

Major source are rock weathering, sulphate reduction, pyrite oxidation and neutralisation etc. and sink is calcite. Most surface streams contain less than 200 mg/L, but in groundwaters somewhat higher concentrations are not uncommon. Concentrations over 1,000 mg/L occur in some waters that are low in calcium and magnesium, especially where processes releasing carbon dioxide (such as sulfate reduction) are occurring in the ground-water reservoir.

Chloride (Cl^-)

Natural source of chloride is sedimentary rock (evaporates) which contain halite (NaCl), sea spray, brines and hot springs. Cl^- occurs in all types of natural waters. High concentration of chloride is an indication of pollution.

Dissolved Oxygen (DO)

Sources of oxygen in water are atmospheric aeration and photosynthesis, while oxygen sinks are respiration, decomposition of organic matter and losses to atmosphere. Based on Henry's law and percentage of oxygen in the atmosphere, the calculated DO at 100% saturation at sea level at 20^oC is 9.03mg/l. Gas saturation decreases by 10% per meter increase in depth due to hydrostatic pressure. DO levels are constantly affected by diffusion, aeration, photosynthesis, respiration and decomposition. DO levels can range from less than 1mg/l to more than 20mg/l. DO concentration will vary by season, location and water depth. Do decreases exponentially as salt level increases. Salt water hold about 20% less DO than fresh water.

Biological characteristics

Biochemical oxygen demand (BOD) is the amount of DO needed by aerobic biological organisms to break down organic material present in a given water sample at certain temperature over a specific time period. Microbiological processes that transform both organic and inorganic constituents of groundwater hasten geochemical processes. The organisms first use dissolved oxygen. When it is depleted some can use nitrate, sulphate and carbondioxide. Microbiological activity affect some metals mainly iron and manganese. The health hazard caused by faecal contamination has principal concern. Soil effectively defends the transmission of faecal organisms. Microbiological processes may influence groundwater quality both positively and negatively [20, 21].

1.3 Groundwater quality monitoring

The international standard organization (ISO) has defined monitoring as “The programmed process of samplings, measurements and subsequent recording or signalling or both, of various water characteristics, often with the aim of assessing, conformity to specified objectives”. A systematic plan for conducting water quality monitoring is called monitoring programme, which include monitoring network design, preliminary survey, resource estimation, sampling, analysis, data management & reporting. Through such monitoring programmes information on chemical quality of different hydro geological units can be gathered. It also helps in sustainable development and provides important information for water management [22]. Water quality monitoring is necessary in industrial sectors because incrustation and corrosion can create adverse effects on processing, steaming and cooling units if bad quality waters are used.

The most common types of national or regional assessment of groundwater quality cover large areas, with sampling points tens to hundreds of kilometres apart. In contrast, emergency or impact monitoring may be limited to a small area. Design of a programme consists of the choice of sampling stations, sampling frequency, range of variables, methods of data production and interpretative approaches required to produce the information needed for decision making.

1.4 Review of Literature

Chemical principles and environmental factors form the basis of groundwater chemistry [23-29]. Groundwater plays an important role in supplying water to much of the global population for use in drinking water, agriculture and industrial purposes. Studies related to various aspects of groundwater science are conducted in various parts of the world. Physical and economic water scarcity occurs in all of the populated continents.

Hydrogeochemical features of groundwater resources in Tabriz Plain, Northwest of Iran suggest Mixed Ca–Mg–Cl and Na–Cl type of groundwater is predominant in the study area. The concentrations of some major ions in groundwater are above the permissible limit for drinking and domestic purpose except for a few locations. The scatter plots of different ions are analyzed to identify the interrelationships between the ions and possible chemical reactions which may occur . Na and Cl^- are strongly correlated with TDS, which represent that these ions are the most effective in the mineralization and salinization of the groundwater of the study area [30]

Assessment of physico-chemical quality of borehole and spring water sources supplied to Robe Town, Oromia Region, Ethiopia shows that most of the physico-chemical parameters analyzed comply with national and international drinking water guidelines, except pH, iron and manganese. The highest iron and manganese concentration are recorded in the three borehole water sources and so the water quality of borehole water sources differ from that of spring water source. The borehole water sources were found to be slightly acidic and have high TDS, EC, TH, Ca etc. [31]. The study of physico-chemical quality of boreholes in Densu Basin of Ghana reveal that the groundwater contain iron and manganese [32].

Groundwater and spring waters from carbonate aquifers of southern Latium region, Central Italy, were investigated to evaluate the water quality for drinking and irrigation purposes [33]. The results suggest fresh to brackish, slightly acidic to alkaline and hard to very hard nature of water. The types of water that predominates in the study area are (1) Ca–Mg–HCO_3, (2) mixed facies between Ca–HCO_3 and Na–Cl, (3) Na–Cl and (4) Ca–Cl, suggesting influence of water–rock interaction and seawater intrusion in coastal area.

The interpretation of the hydrochemical analysis results of 42 water samples from hand dug wells in wadi Sayyah area in Western Saudi Arabia reveals that the groundwater in this area ranges from fresh to brackish and alkaline in nature [34]. The dominated hydrochemical facies of groundwater are Ca-Cl, and mixed Ca-Mg-Cl. Gibb’s diagram indicates that rock weathering and evaporation are the dominant process controlling groundwater quality in the area. In a study of water quality assessment and hydrochemical characterization of Zamzam groundwater, Saudi Arabia, a direct relationship between Zamzam groundwater salinity and rainfall is recorded.

An investigation of hydrochemical characteristics of groundwater in the Harzandat Aquifer, Northwest of Iran suggest that salinity is the principal problem concerning irrigated agriculture in the area. Special management for salinity control is required and plants with good salt tolerance should be selected. Maintaining soil organic matter levels and appropriate leaching is necessary to avoid the build-up of salts over time [35].

Hydrochemical analysis and evaluation of groundwater quality, especially for irrigation, in El Eulma Area, Algeria, which is an agricultural area is conducted. In most of the samples alkaline earths significantly exceed the alkalis and weak acids exceed the strong acids [36]. US salinity laboratory diagram for irrigation water suggest that most of the samples fall in C3S1 quality with high salinity hazard and low sodium hazard and based on RSC all the samples are suitable for irrigation.

Hydrochemical study of surface water and groundwater in the shale bedrock of the Cross River Basin and Niger Delta Region, Nigeria, suggest dissolution of halite and gypsum, ion exchange, silicate weathering and pyrite oxidation as the major processes contributing to water composition [37].

A study for groundwater characterization and selection of suitable water type for irrigation is carried out in the western region of Bangladesh. Among four water types, Na–Ca–Cl type of water does not satisfy Sodium Percentage and Kelly's Ratio criteria for irrigation quality and Na–Ca–Mg does not satisfy Sodium Percentage. Therefore, these two water types are required to be monitored for future chemical status change. Other two groups, i.e., Ca– Na–Mg and Ca–Na–Mg–Cl water types are suitable to be used for irrigation [38].

There are many other reported studies available from different parts of the world [39-43] regarding the groundwater quality and its chemistry.

Groundwater and surface water are often closely linked, and changes to quality or quantity in one resource frequently creates an impact on the other. Groundwater contributes to streams, lakes and wetlands, and is particularly significant in maintaining these surface water ecosystems in dry periods.

To understand the general water quality situation, the time series data of selected water quality parameters were analyzed in an urban river in Peninsular

Malaysia. The two way ANOVA showed significant difference among different stations. The quality of river water primarily depends on the Waste Assimilative Capacity (WAC) of the water. The low DO levels will lead to the mortality of aquatic flora/fauna [44]. Hydrochemical Assessment of Water Quality of the Medjerda River in Tunisia suggest that the only suitable point for irrigation from Medjerda mainstream is located in the mid-valley. Mid-tolerant crops should be encouraged in such areas. For the remaining locations, only plants tolerant to salt could be grown. This survey would assist managers to prioritize and make rational decisions for improving water quality used for irrigation. Some solutions can be recommended in accordance [45].

Surface water quality can affect groundwater quality through seepage and where surface water directly enters groundwater. Protection of surface water quality is often considered to be of paramount importance. Studies of water quality of various rivers is available in the literature [46-54].

Limited availability of quality fresh water is one of the most critical environmental issues of the 21st century. It has been estimated that the requirement of groundwater in 2050 will be about more than 3 times the present level due to the population growth and growing demand. Groundwater is an important water resource for domestic and agriculture uses in both rural and urban parts of India. Enough literature is available on studies conducted in different states of India [55-69].

In groundwater which represents a multi component system, chemical elements exist primarily not in the form of simple cations and anions but as associated compounds of different complexity and stability. The frequency distribution of concentrations in groundwater was used to determine the natural groundwater quality in aquifers.

Study of geochemical evaluation of groundwater in the western delta region of river Godavari, Andhra Pradesh reveal that certain parameters like EC, TDS, Na, K, Cl^-, HCO_3^- and NO_3^- , show a higher range of standard deviations, while others (Ca, Mg and SO_4^{2-}) have a lower range of standard deviations suggesting the inter-mixing of chemical processes caused by geogenic, anthropogenic and marine origin along water flow path. The concentrations of Na and K increase simultaneously with the increase of Cl^- and SO_4^{2-}, indicating a common source of these ions [70]. The study of groundwater quality and its suitability for drinking and irrigational use in the southern Tiruchirappalli district, Tamil Nadu inferred that the groundwater in the study area is slightly alkaline and hard in nature. Na, Ca, HCO_3, and Cl are the dominant ions and 45 % of the study area exceeded the recommended limits of TDS. Based on the Gibb's diagram, evaporation dominance and rock– water interaction dominance are the two main contributors to change in the water quality of the study area. The correlation matrix and principal component analysis indicate that the over exploitation of groundwater and anthropogenic inputs are high in the study area. Comparison of geochemical data shows that majority of the groundwater samples are suitable for drinking and irrigation purposes [71]. From the results of groundwater quality characterization around Jawaharnagar open dumpsite, Telangana, the moderately high concentration of TDS, TA,TH, Mg, Ca, Cl^-, SO_4^{2-},F^- indicates contamination. The correlation coefficient and regression method are also used for the study.

Recently, there has been overall development in various fields such as agriculture, industry and urbanization in India. This has lead to increase in the demand of water supply which is met mostly from exploitation of groundwater resources. Hydrochemical study is a useful tool to identify the suitability of the groundwater for various puroses

India has about 7517km long coastline. Coastal zone is an area of interaction between land and sea and thus both terrestrial and marine environments influence this zone. The population of coastal districts is currently about 15% of the total population of India. High evaporation and low and erratic rainfall depleted the groundwater level and available groundwater quantity, especially in the coastal areas, and resulted in seawater intrusion [72]. Accurate and reliable groundwater level forecasting models can help ensure the sustainable use of a watershed's aquifers for urban and rural water supply. A study by Yang Q. et.al. demonstrates a case study on how to utilize time series analysis to predict groundwater table in a coastal island, South China using three time series models [73]. GIS-based assessment of groundwater quality in the coastal aquifers of Tuticorin Corporation, Tamilnadu, is carried out to understand the groundwater quality in the coastal area. GIS is utilized to locate groundwater quality zones suitable for different usages such as irrigation and domestic. High hardness level is noticed in the study area. Chloride concentrations is the major factor that makes up the TDS in the groundwater, and plays an important role in the determination of the quality of groundwater. Groundwater in a part of the lower Palar river basin,Tamil Nadu, southern India is dominated by Na, Ca and HCO_3 ions. Groundwater in the weathered rocks of the area has relatively high Na concentration while groundwater occurring in the alluvial formations has high Ca content. The cation exchange process and silicate weathering control the groundwater chemistry in this area. Several studies on coastal area groundwater quality are available in literature [74-80].

The approach to groundwater quality protection and enhancement varies not only between States but also within them. The monitoring of groundwater quality is one of the important tools for sustainable development and provides important information for water management. Anthropogenic activities like explosion of population, industrial growth, inputs of fertilizers, pesticides and irrigation has been a crucial factor for determining the quality of groundwater. Essentially all activities carried out on land have the potential to contaminate the groundwater, whether associated with urban, industrial or agricultural activities. Large scale concentrated sources of pollution such as industrial discharges, landfills & subsurface injection of chemicals &hazardous wastes are an obvious source of groundwater pollution. These concentrated sources can be easily detected & regulated but the more difficult problem is associated with diffuse source of pollution like leaching of agrochemicals & animal wastes ,subsurface discharges from latrines & septic tanks & infiltration of polluted urban runoff & sewage where sewerage does not exists or defunct. Diffuse sources can affect entire aquifers, which is difficult to control and treat.

1.5 Present Study

The coastal region is a unique natural environment where land, sea and atmosphere interact. Coastal zones are the most fragile, dynamic and productive ecosystem. But they are often under pressure from both anthropogenic activities and natural processes. It supports a large amount of floral and faunal biodiversity. Human settlements are often more concentrated in the coastal zone because of the economic benefits that accrue from access to ocean navigation, coastal fisheries, tourism, recreation and industrialization. Erosion and accretion, inundation due to sea level rise and storm surge, shifting of shoreline caused by natural or anthropogenic forces, such as construction of artificial structure, port and harbours leads to changes in the coastal zone and its environment. Thus, regular monitoring of coastal zone is indispensable.

About 35% of Indians live within 100 km of the country's coast line measuring 7517 km. Present study is conducted along a coastal segment of Kerala, which is in Alappuzha district Alappuzha is the smallest district in the state in terms of area (*3.64*% of area of the state). As a result of the long coast line Alappuzha occupies a very important position in the fisheries map of Kerala. The Vembanad and Kayamkulam backwaters and network of canals and streams that flow into them have enriched the water potential and the fishery wealth of the region. Total population of Alappuzha district as per 2011 Census is *2127789*, which is 6.37 % of total population of the state and the district is placed at the 9th position as far as population size is considered.

The traditional industrial sector of Alappuzha include coir and coconut oil. They have potentials for flourishing because coir related products are gaining importance as an alternative to plastic products under the name geotextiles. Other small scale industries of importance to Alappuzha are umbrella parts manufacture and processing of spices and other agro based industries. More than 20% of the total area of the district is waterlogged and the vast area of Kari lands and Paddy fields are suitable for pisciculture. As the area is water logged and the groundwater table high, open wells in this area are highly polluted by salinity and are contaminated. Hence they cannot be considered as a prime source for water supply. The surface and shallow groundwater are not potable because of organic pollution. Another problem in coastal areas is sea water intrusion. As sea water intrusion progress, existing pumping wells especially close to the coast become saline and have to be abandoned, thus reduce the value of aquifer as a source of fresh water.

The coastal erosion in this stretch is one of the recurring natural hazards. Kayamkulam Estuary is a shallow brackish water lagoon streaching between Panmana and Karthikapally. It has an outlet to the Arabian sea at Kayamkulam barrage. A massive earthquake that triggered the Indian Ocean tsunami on the morning of 26 December 2004 affected the coastal segment in Arattupuzha village of Alappuzha district, Kerala, India which is the area selected for the present study.

Figure 1.3: Picture of Arattupuzha coast, Alappuzha, Kerala, India.

The borehole lithology at Pallippuram in Alappuzha district indicates that the unconsolidated Quaternary sediments comprising sands constitute the upper layer underlain by clay, clayey sand, laterites, clay with limestone, clay with few sand, sandy clay, etc. However, towards the coastal side (western part), the Quaternary sedimentary sequence, consisting of alternate layers of sand and clay, has a total depth of 445 m at Arthungal [81].

Figure 1.4: Pictures of 26th December 2004 Indian Ocean Tsunami impact on Arattupuzha coast, Alappuzha, Kerala, India.

1.6 Significance of the study

Present research work evaluate the groundwater chemistry of shallow and deep groundwater sources along an ecologically sensitive coastal segment, Arattupuzha in Alappuzha district, for the last 5 years. Sampling at these stations started in 2012 January and continued in each month of 2012. In the subsequent years, 2013, 2014, 2015 & 2016, sampling and analysis were done towards the end of the year. This work is conducted in an area which was inundated by the 26th December 2004 Indian Ocean Tsunami. Post-tsunamic studies of the region were conducted in 2005 [82-85]. Thus a comparison with the post tsunami study data that available for year 2001, helps in generating a database of over 16 years along the study area. The study is planned to continue in future.

Through a preliminary reconnaissance survey carried out in January 2012, sampling stations were selected. Majority of them are those studied during post tsunamic period. One dug well (temple well at Kuriappassery), is selected as the control well (CW), as it maintained good quality water throughout the period of study. The other sampling stations are classified into 2 based on depth profile.

1) Dug well strata (DW) which consist of 6 shallow groundwater sources (2m depth)
2) Bore well strata (BW) which consist of 7 deep groundwater sources (25-100m depth)

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

1.7 Objectives

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

1) To establish the temporal groundwater quality variation profile of a coastal segment of Kerala in Alappuzha district intermittently for a period 2001-2016.
2) To study the variation of the groundwater quality profile of the study area with respect to depth profile of groundwater sources

classified as dug wells (DW) of average depth 2m and bore wells of average depth 25-100m.

3) To study the groundwater chemistry and monthly variation of major groundwater quality parameters of shallow and deep groundwater sources of the study area during year 2012.
4) 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.
5) To analyse the trace element content of shallow and deep groundwater sources.
6) To evaluate the statistical relationship between the water quality parameters using Pearson correlation matrix.
7) To compute the monthly water quality index of each groundwater source by giving adequate weightage to significant water quality parameters.
8) To evaluate ionic ratios (sodium-chloride) and to study the major processes occurring in the study region.
9) To study the major processes controlling the groundwater quality of the study area using Gibb's plot.
10) To study in detail the irrigational quality of various groundwater sources by using the parameters Sodium Adsorption Ratio (SAR), Sodium Percentage (Na %), Magnesium Adsorption Ratio (MAR), Residual Sodium Carbonate (RSC), Permeability Index (PI) and Kelly's ratio (KR).
11) To classify water based on irrigation suitability by using graphical plots such as USSL and WILCOX diagrams.

12) To understand the hydrogeochemical facies of the study area by using Hill-Piper Trilinear diagrams.
13) To evaluate saturation indices for studying industrial utility of various groundwater sources.
14) To study the groundwater quality parameters and to evaluate other interpretation parameters of the groundwater sources in the years 2013, 2014, 2015 & 2016.
15) To suggest recommendations for management of groundwater quality problems.

1.8 Hypothesis

Hypothesis to be tested are,

a) Whether there is any significant difference between mean values of various parameters in control well (CW) stratum at different months of 2012.
b) Whether there is any significant difference between the values of various parameters of dug well (DW) strata in April, 2012.
c) Whether there is any significant difference between the values of various parameters of dug well (DW) strata in July 2012.
d) Whether there is any significant difference between the values of various parameters of dug well (DW) strata in December 2012.
e) Whether there is any significant difference between mean values of various parameters of dug well (DW) strata in each month of year 2012.
f) Whether there is any significant difference between mean values of various parameters of dug well (DW) and control well (CW) strata in each month of year 2012.

g) Whether there is any significant difference between mean values of water quality index of dug well (DW) strata in each month of year 2012.

h) Whether there is any significant difference between water quality index of control well (CW) and dug well (DW) strata in year 2012.

i) Whether there is any significant difference between water quality parameters between control well (CW) and bore well (BW) for the months of 2012.

j) Whether there is any significant difference between water quality index for different bore well stations for the months of 2012.

k) Whether there is any significant difference in the mean values of the parameters in dug well (DW) strata at different time periods (2001-2016).

l) Whether the water quality index for dug well (DW) strata differ significantly for the years 2013-2016.

m) Whether the water quality index for dug well (DW) strata differ significantly in the months of 2005 for 5 stations DW1, DW2, DW3, DW4, DW5.

n) Whether there is any significant difference in the mean values of the parameters in bore well (BW) strata at different time periods (2001-2016).

o) Whether the water quality index for bore well (BW) strata differ significantly for the years 2013-2016.

p) Whether there is any significant difference in the mean of the water quality parameters between dug well (DW) and bore well (BW) strata.

q) Whether mean water quality index of dug well (DW) and bore well (BW) strata differ significantly over the last 16 years.

1.9 Structure of the Thesis

Chapter 1 is a concise introduction of the thesis. It briefly introduce the topic groundwater science, which is an interdisciplinary subject. In order to explain the geochemical environment various spheres of Earth and their importance in hydrologic cycle are discussed. As the background of groundwater study is that of inorganic geochemistry, the principles and processes in chemistry which are relevant in the groundwater perspective are briefly introduced. The various parameters of groundwater quality, monitoring programme and studies reported in literature form a major part of this chapter. The background of the research study starting with the geographical importance of the coastal areas of Kerala especially the study area, relevance of the current study, objectives of study and hypothesis form the remaining part of this chapter.

Chapter 2 is materials and methods. It mainly describes methodology followed for this research study. Description of the study area with GIS maps and locations of the sampling stations form the initial part of the chapter. It is followed by materials and methods, instrumentation, sampling protocols, standard operating procedures. Analytical chemistry and hydro analytical methods followed for the estimation of each parameter is briefly described. This is followed by a detailed description of other interpretation methods, diagrammatical plots, statistical tools used for the study.

Chapter 3 explains hydrogeochemistry of shallow groundwater sources of the study area. It comprises the results and discussions on the monthly variation of water quality parameters and other interpretation methods of the shallow groundwater sources of the study area during year 2012. Monthly variation of individual parameters with graphical representation form the major part of this chapter. It is followed by trace element study, statistical study using Pearson correlation matrix, water quality index determination, sodium-chloride ratio interpretation, irrigation quality evaluation, saturation indices determination, Hill-Piper Trilinear plot evaluation, Gibb's plot evaluation and comparison with standards. This chapter ends with statistical interpretation of the results with a conclusion.

Chapter 4 explains hydrogeochemistry of deep groundwater sources of the study area. It comprises the results and discussion on the monthly variation of water quality parameters and other interpretation methods of the deep groundwater sources of the study area during year 2012. Monthly variation of individual parameters with graphical representation form the major part of this chapter. It is followed by trace element study, statistical study using Pearson correlation matrix, water quality index determination, sodium-chloride ratio interpretation, irrigation quality evaluation, saturation indices determination, Hill-Piper Trilinear plot evaluation, Gibb's plot evaluation and comparison with standards. This chapter also ends with statistical interpretation of the results with a conclusion.

Chapter 5 discusses the temporal variation of major groundwater quality parameters of shallow groundwater sources of the study area intermittently for the last 16 years (2001-2016). 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, irrigation quality and Hill-Piper Trilinear plot are presented for shallow groundwater sources of the study area in view of pre and post tsunami situations. The chapter ends with statistical interpretation of the results with a conclusion.

Chapter 6 discusses the temporal variation of major groundwater quality parameters of deep groundwater sources of the study area intermittently for the last 16 years (2001-2016). Graphical representations of major water quality parameters of deep bore well stations form major part of the chapter. Interpretation of water quality index, ionic ratio, irrigation quality and Hill-Piper Trilinear plot for hydrochemical facies are critically presented for deep groundwater sources of the study area in the background of pre and post tsunami situations. This chapter ends with statistical interpretation of the results with a conclusion.

Chapter 7 is the overall summary and conclusions of the study presented. The hypotheses suggested in the introduction chapter are tested by various statistical methods and their results are discussed in this chapter followed by future scope of the study.

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Chapter 2

MATERIALS AND METHODS

2.1 Introduction

Water quality determines the ‘goodness’ of water for particular purposes. By testing water over a period of time, the changes in the quality of the water can be seen. Observations of water quality mainly refer to concentrations of dissolved constituents in the water in terms of physical (like turbidity, conductivity etc.), chemical (like sodium, potassium, cadmium etc.) and biological parameters (like algae, bacteria etc.). Data on water quality requires collection of a water sample followed by analysis (measurement) for specific water quality parameters. Some of these water quality parameters can be measured at site, the so-called field parameters. . Bureau of Indian Standards (BIS 2012) in drinking water specification defines “drinking water intended for human consumption for drinking and cooking purposes from any source. It include water (treated or untreated) supplied by any means for human consumption”. Also Indian standard requires water shall comply with the requirements given in tables.

1) Organoleptic and physical parameters 2) General parameters concerning substances undesirable in excessive amounts 3) Parameters concerning toxic substances 4) Parameters concerning radioactive substances 5) Pesticide residue limit and test methods 6) Bacteriological quality of drinking water.

Considering the present study area, the sea coast of south Alappuzha and a stretch of Kollam districts are rich in mineral sand called 'black sand' in common parlance [1]. The sand contains several heavy minerals like, monazite, ilmanite, rutile and zircon. Ilmanite and rutile are used for production of white pigment, titanium metal and as flux for welding electrodes. Zircon is used in ceramic and refractory industries besides acting as basic raw material for the production of metal and alloys for use as structural materials in nuclear power reactors. The mineral 'monazite' is radioactive as it contains thorium and uranium. The study area is continuously/intermittently subjected to study with respect to the hydrogeochemistry of the shallow and deep groundwater for the period 2001-2016. In 2012 January onwards 6 different shallow groundwater sources and 7 deep bore well waters are analysed.

2.2 Study Area

Alappuzha (Alleppey) is one of the well-developed coastal districts in southern part of Kerala state covering an area of 1,414 sq.km and is the smallest district accounting 3.64% of the area of the state. The area selected for the present study (coastal area of Aartupuzha village) lies between north latitudes *9°7'41" & 9°11'26"* and east longitudes *76°26'25" & 76°28'23"*.

According to 2011 census, the district has a population of 2121943. The population density is 1501 persons/sq.km, the highest among all the districts of the State [2].

2.2.1 Climate and Rainfall

The district has a tropical humid climate with oppressive summers and plentiful seasonal rainfall.

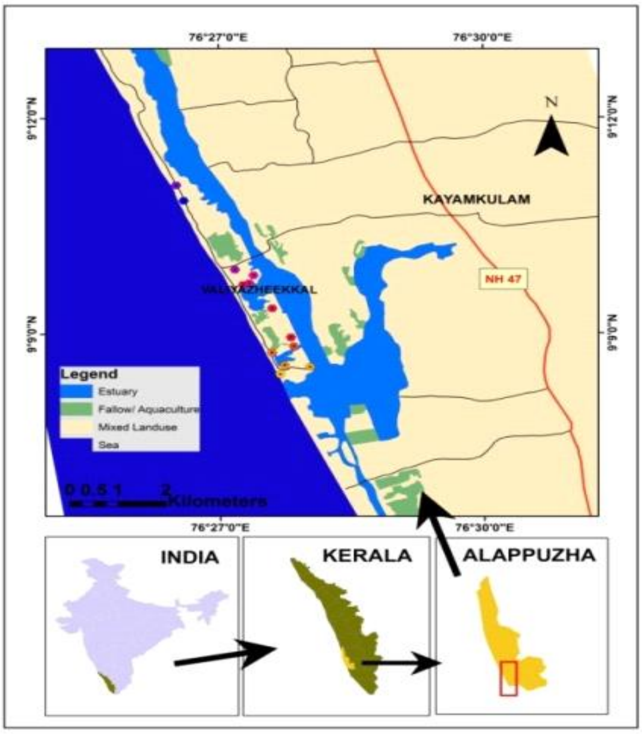
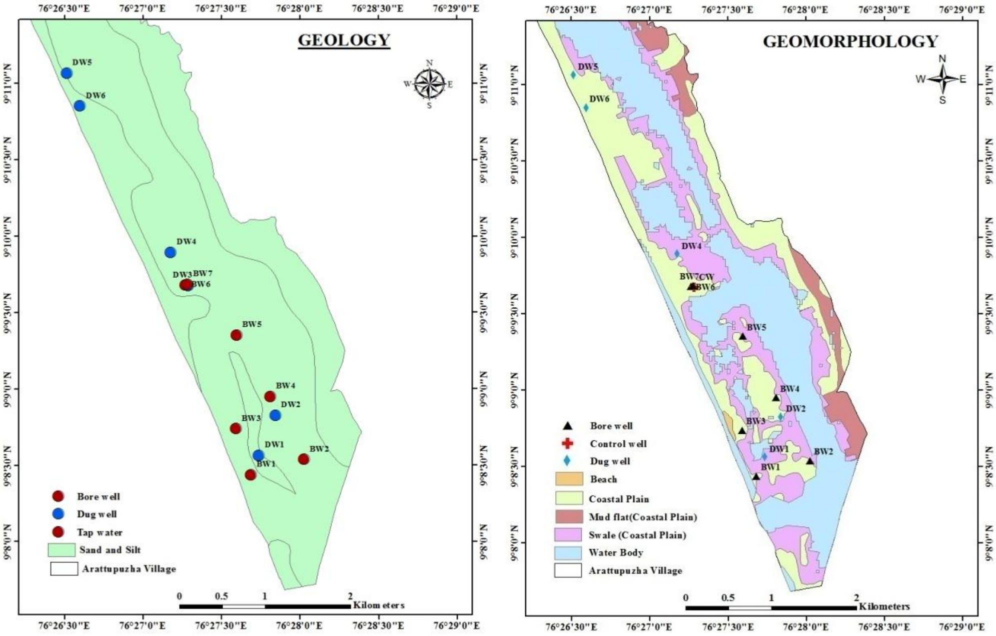


Figure 2.1: Location Map of the study area, Arattupuzha coast, Alappuzha, Kerala, India.

The period from March to the end of May is the hot season. This is followed by the southwest monsoon season, from June till the end of September, which contributes nearly 60.3% of the annual rainfall. This is followed by the northeast monsoon season from October to December, which contributes about 20.9% of the annual rainfall, and the balance 18.8% is received during the period from January to May months. The district receives an average annual rainfall of 2965.4 mm. At Alappuzha the maximum temperature ranges from 28.8 to 32.7ºC whereas the minimum temperature ranges from 22.6 to 25.5ºC. The average annual maximum temperature is 30.7ºC and the average annual minimum temperature is 23.9 ºC.

2.2.2 Geology and Geomorphology

The sand and silt is the lithological (Figure 2.2 a) feature of the study area.

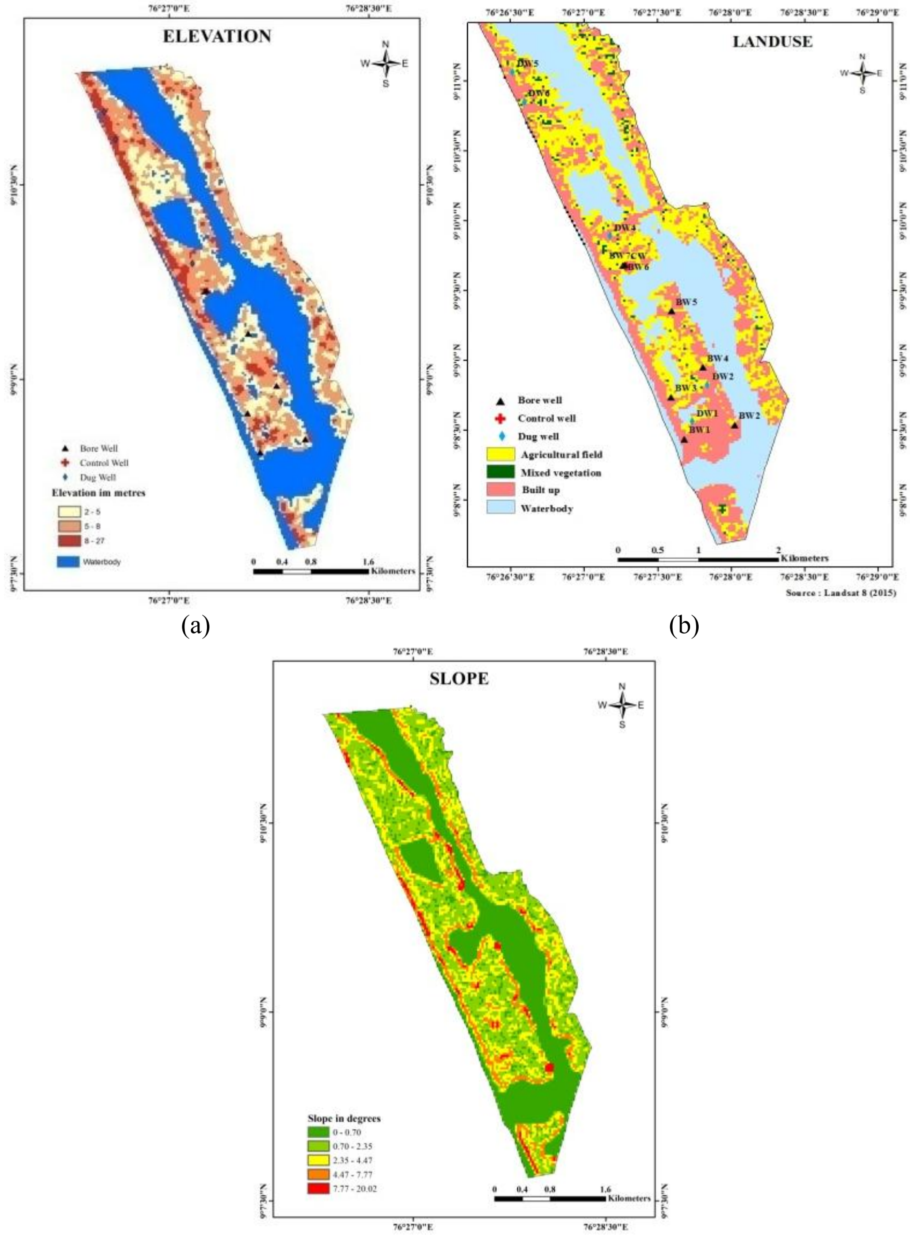


(a) (b)

Figure 2.2 (a) Geology (b) Geomorphology of the study area, Arattupuzha coast, Alappuzha, Kerala, India.

A major part of the district forms part of the coastal plains. The coastal alluvial soils are seen along the coast which has been developed from recent marine and estuarine deposits. The texture is dominated by sand fraction and is extensively drained with very high permeability. These soils have low content of organic matter and of low fertility level.

The geomorphology of the area includes beach, mudflat, coastal plains and water body (Figure 2.2 b). The beach ridges are suggestive of marine regression. Beach is very narrow and straight. The absence of extensive tidal plain and the intensive coastal erosion may be indicative of neo-tectonic activity.



Source : Landsat 8 (2015)

(a)

(b)

(c)

Figure 2.3: (a) Elevation (b) Land use pattern and (c) slope of the study area, Arattupuzha coast, Alappuzha, Kerala, India

The general elevation of the area is less than 6 m above mean sea level (Figure 2.3a). The land use of the area includes agricultural field, mixed vegetation, built up and water body (Figure 2.3 b).

2.2.3 Hydrogeology

Alappuzha district consists of coastal alluvium comprising sand and clay along the coastal region and flood plain deposits in Kuttanad region. Residual laterite formations are encountered in the south-eastern parts of the district and granites are encountered in and around Chengannur area. charnockite, khondalite and granites form the basement. They are overlain by tertiary sedimentary formations.

The tertiary formations constitute the major aquifer in the coastal area with total thickness of sediments ranging from 90.0 to more than 600 m. They are underlain by crystalline basement and overlain by laterite and unconsolidated formations. Tertiary formations consist of Aleppey beds, Vaikom beds, Quilon beds and Warkali beds. Of these, Warkali beds is the most extensively developed aquifer in the district [3-5].

The bottom most unit of Tertiary sedimentary formations, the Aleppey bed, comprise of highly carbonaceous clay with intercalations of sand. The formation water is brackish in quality and hence no wells are constructed tapping this formation. Vaikom beds overlying the Aleppey bed with thickness varying from 25 to 238 m, is the most potential aquifer among the tertiary formations of the district. They comprise gravel, coarse sand, clay and seams of lignite. The water from Vaikom aquifer in coastal zone is highly mineralized. General groundwater flow in this aquifer is from south to north. Compared to the underlying Vaikom beds, the groundwater potential from the Quilon bed is not very promising. The thickness of granular zones tapped in this aquifer is between *6 to 10* m and is composed of fine sand. The Warkali aquifer overlying the Quilon bed is composed of medium to fine grained sand with an effective grain size of *0.21 to 0.30* mm. Groundwater occurs in semi-confined to confined conditions with the cumulative thickness of granular zone varying from 6 to 44 m. The Recent unconsolidated formations constitute an important phreatic aquifer comprising coastal sands all along the coast. A large number of shallow dug wells and tube wells for domestic use and to a limited extent for irrigation and industrial purpose tap this aquifer. The water table is generally shallow. Depth of wells tapping coastal sediments ranges between 2.75 to 10.60 m bgl with depth to water level in the range of 1.0 to 2.0 m bgl. Among the deeper confined aquifers of tertiary group, Warkali and Vaikom aquifers are potential and groundwater development is mostly restricted to these aquifers.

Extensive groundwater development is taking place over years and the recharge during monsoon season is not enough to compensate groundwater reserve. Coastal erosion is one of the grave natural hazards affecting the district and extensive coastal erosion is taking place in the coastal areas. The wave intensity is generally found to be slightly higher at Thrikunnapuzha, which is attributed to the relatively steeper slope of inner shelf at this location. Erosion is prevalent in the southern sector while accretion is dominant in the zone north of Cochin inlet. The southernmost sector from Kayamkulam to Arattupuzha is to be a critically eroding coast. The most critically eroding sector of the coast line encompasses Arattupuzha and Trikkunnapuzha. It is advisable to leave the coast as such and plan the land use appropriately so that the impact of pollution from land based activities is controlled and constructions close to the beach are discouraged [6,7].

2.3 Groundwater Study: Monitoring Strategy and Sampling Protocol

A sample collected at a particular time and space can represent only the composition of the source at that time and place. Grab samples collected at suitable intervals and analysed separately can document the extend, frequency and spatial variations. Seasonal variation in natural systems necessitates sampling for several months over an annual cycle.

Monitoring of groundwater regime is an effort to obtain information on groundwater levels and chemical quality through representative sampling. Most of the physical factors that promote mixing of surface waters are absent or are much less effective in ground-water systems. Even in thick sand of uniform permeability, the movement of water in the zone of saturation is slow and mixing is poor. In most sediment, the horizontal permeability is greater than the vertical permeability. This inhibits vertical movement of water, and water in a particular stratum may develop chemical characteristics that are substantially different from water in strata above or below. Means of studying differing composition of water in different parts of the saturated zone are not entirely adequate. Wells commonly obtain water from a considerable thickness of saturated material and from several different strata. These components are mixed by the turbulent flow of water in the well before they reach the surface of the land and become available for drawing/sampling. Although one rarely can be certain that a sample from a well represents exactly the composition of all the water in the vertical section at that point, it is usually a useful indication of the average composition of available water at that point. Where a considerable number of wells reaching the same aquifer are available for sampling and show similar composition, the investigator usually is justified in assuming homogeneity in drawing some conclusions about the chemistry of the groundwater in the aquifer. If a well penetrates a large, relatively homogeneous aquifer, the composition of the pumped water generally will not change much over long periods of time. Areal variations in ground-water quality are evaluated by sampling wells distributed over the study area.

The differences in water quality with depth is evaluated in the present study by discussing dug well and bore well stations in separate chapters. The study of this coastal area starts just after the 26th December 2004 Indian Ocean Tsunami. In 2005, monthly sampling and analysis were carried out. Three years later in 2008 also, the water quality was assessed [8, 9]. A pre-tsunami groundwater quality data of the area is obtained from Central Groundwater Board (CGWB) which is of 2001 April.

The present work begins in 2012 January. Sampling stations were fixed with respect to regular spatial intervals. One shallow dug well, Kuriappassery temple well, which kept a good water quality throughout the study period is taken as the control well (CW). Six shallow dug wells (DW) and 7 deep bore wells (BW) were selected for the study (Table 2.1 & 2.2). In 2012 monthly sampling and analysis were carried out. The water quality monitoring continued in the subsequent years 2013, 2014, 2015 & 2016. Thus a long term data of groundwater quality of the area can be generated.

Table 2.1: Dug well (DW) sampling stations along the study area, Arattupuzha coast, Alappuzha, Kerala, India.

Sl. No.	Station	Description	Remarks	Location
1	DW1	Valiyazheekal temple	Dug well DW1 Away from the sea	09^{o} 08’ 33 N, 76^{o} 27’43E
2	DW2	Palliyara Sree Parvathy temple	Dug well DW2 Saline intrusion	09^{o} 08’ 49 N, 76^{o} 27’49E
3	DW3	Kuriappassery temple	Dug well DW3 Taken as the control well CW	09^{o} 09’ 40 N, 76^{o} 27’16E
4	DW4	Panackal temple	Dug well DW4 Away from the sea	09^{o} 09’ 53 N, 76^{o} 27’10E
5	DW5	Bhaskaran vattachal – house owner	Dug well DW5 Near to the sea	09^{o} 10’ 51 N, 76^{o} 26’35E
6	DW6	Mohanan vattachal – house owner	Dug well DW6 Near to the sea	09^{o} 11’ 03 N, 76^{o} 26’30E

Table 2.2: Bore well (BW) sampling stations along the study area, Arattupuzha coast, Alappuzha, Kerala, India

Sl. No.	Station	Description	Remarks	Location
1	BW1	Thara – house owner	Bore well BW1	09^{o} 08’ 26 N, 76^{o} 27’41E
2	BW2	Valiyazheekal pump - jetty	Bore well BW2	09^{o} 08’ 32 N, 76^{o} 28’01E
3	BW3	Prown shed	Bore well BW3	09^{o} 08’ 43 N, 76^{o} 27’35E
4	BW4	Yuvasakthi	Bore well BW4	09^{o} 08’ 56 N, 76^{o} 27’48E
5	BW5	Baiju –house owner	Bore well BW5	09^{o} 09’ 21 N, 76^{o} 27’35E
6	BW6	Kuriappassery –pipe water	Bore well BW6	09^{o} 09’ 40 N, 76^{o} 27’15E
7	BW7	Kuriappassery –Pump house	Bore well BW7	09^{o} 09’ 40 N, 76^{o} 27’16E

Standard methods were followed in the full gamut of activities including sampling and analysis [10, 11]. Preservation of the samples were not required since all the unstable parameters were analyzed well within

3 hours of sampling. Hence, the samples collected were not split nor were they subjected to pH control, chemical addition, refrigeration, filtration, freezing or bottling in amber colored or opaque containers [1, 9]. The sampling sites were less than three hours away from the laboratory.

The chain–of-custody report, as is required of a systematic sample analysis, is also not relevant in the present context as samples were collected, transported and analyzed by the self-same hands. All samples were collected in the morning without fail. Mostly around 8.00a.m when photosynthetic activity is not yet established and ambient temperature has not reached its zenith [9].

During the sampling field trips, groundwater samples were collected from the selected shallow dug wells and deep bore wells in clean polythene bottles. The samples for DO analysis, Iron estimation and biological analysis were collected separately. The grab sampler and the containers were rinsed thrice with the sample and the DO was fixed in situ. Bacteriological sampling bottles were opened under water. On every field trip, the conspicuous visual features observed were noted, especially the status of floating vegetation, colour variations, cases of fish kill, construction/ destruction of temporary bunds, evolution of H_2S and presence of mosquito larvae etc [8].

In the field diary date of sampling, time of sampling and temperature of sample were entered at the sampling site. Samples were collected from the surface water. It is assumed that vertical mixing is completed that stratification is non-existent. Once back in the laboratory, where reagents had in advance been prepared and the instruments calibrated, the analyses were carried out immediately.

(a) (b)

(c) (d)

(e) (f)

Figure 2.4: Photograph of some sampling stations along the study area, Arattupuzha coast, Alappuzha, Kerala, India:- (a & b) –Station DW1, Valiyazheekal temple (c & d) – Station BW2, Valiyazheekal pump & jetty (e) – Station DW5, Bhaskaran, Vattachal, House well (f) – Station DW6, Mohanan, Vattachal, House well

2.4 Laboratory quality control checks

Groundwater monitoring program was done strictly to ascertain the quality of data generated. To ensure the quality of primary data the generally accepted quality control aspects were ensured. To avoid any deviation in analytical procedures a standard operating procedure (SOP) was prepared for this groundwater quality-monitoring program.

Quality assurance procedures for data entry were routinely followed during field and laboratory analysis. Any changes made to data on bench sheets/ records were initialled by the researcher. Raw data for outliers and questionable entries, if any, were immediately verified. Final data were entered on a master data book and thereafter, systematically fed to the computer.

In this study the distance between two consecutive sampling locations, as a general rule, was fixed to be 1km. Accessibility and the nature of the groundwater sources were the deciding factors in this flexible rule. Field trips were undertaken towards the end of the month (as the first sampling started towards the end of December 2004) and this remained unaltered, through out the study. The parameters monitored were pH, Eh, Alkalinity, Electrical Conductivity, Turbidity DO, BOD, Chloride, Total Hardness, Calcium Hardness, Phosphate, Sulfate, Total iron, Nitrate, Total organic carbon and Trace metals.

pH, EC, Eh and hardness, chloride and sodium were chosen as a regular parameter to be monitored because it is indicative of the degree of the saline water intrusion, bio-geochemical processes and contamination. Deep groundwater is generally acidic where as seawater is alkaline.

Alkalinity, conductivity, chloride, hardness and sulphate are directly related to saline intrusion in the study area. Nitrate and phosphate are the essential plant nutrients and their ratio is indicative of sewage or external contamination. Solubility of iron is directly related to pH and DO. DO and BOD are the most important parameters required to define the quality of a groundwater body. Percentage saturation of DO is a direct measure of the purity of water.

2.5 Methods

2.5.1 Water quality analysis; Methods followed: APHA 2012 [11]

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). To calibrate and check the instrument, the cell constant is measured from time to time using standard KCl. Hardness (Method: 2340 C EDTA Titrimetric Method). Water Hardness: The complexometric method using EDTA was used for the determination of Ca and Mg ions present in the water samples. The titration of the water using Eriochrome Black -T indicator was followed to determine Total hardness, and murexide indicator (ammonium purpurate- this indicator changes from pink to purple at the end point) to determine Calcium and Magnesium hardness. Turbidity (Method: 2130 B; Nephelometric Method). Standard Nephelometric method using formazin suspension (hydrazine sulphate and hexamine mixture) as standard was followed to measure the turbidity in NTU using single beam turbidimeter. Nepheloturbidimeter: 131 SYSTRONICS make (Range: 1 to 1000NTU) was used to measure the light scattered measured in turbidity unit.

Alkalinity (Method: 2320 B; Titration Method). Alkalinity of water (is a measure of titrable bases) is determined by acid titration using mixed indicator (Bromocresol green and methyl red) as a measure of total titrable bases. Dissolved oxygen (Method: 4500 - O C; Azide Modification Method). Dissolved oxygen content of the water has been determined following the above method most suitable for water analysis. Total Iron (Method: 3500 Fe - B; Phenanthroline Method). Iron present in the groundwater samples were analysed forming into the Fe- phenanthroline chelate – orange red complex spectrophotometrically measured at 510nm. Water is first treated with acid – hydroxylamine and treated with 1-10, Phenanthroline to make any iron present into the dissolved form. Chloride (Method: 4500 Cl^- - B; Argentometric method). The Chloride content of the water samples were analyzed by argentometric method were the titration of water against with $Ag\ NO_3$ will precipitate out AgCl fully before the red coloured $Ag_2(CrO_4)$ reacts. This could indicate the completion of the titration procedure. 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). Dissolved nitrate present in the water samples were determined quantitatively by reducing to nitrite by passing through a packed tubular reactor containing cadmium filings treated with copper sulphate. The nitrite thus produced is determined by diazotizing with sulfanilamide and coupling with N- (1-naphthyl) - ethylene diamine to form a highly colored azo dye which is quantitatively measured colourimetrically as per the above cited standard method. Sulphate (Method: 4500- SO_4^{2-} E; Turbidimetric Method). Groundwater samples containing sulphate has been determined by precipitating in acetic acid medium in presence of barium chloride as uniform crystals of sulphate get measured photometrically and the results are extracted against a standard calibration curve. Phosphate (Method: 4500 – P E; Ascorbic Acid Method). Spectrophotometric method is followed for measuring orthophosphate content of the groundwater where water forms heteropoly acid- phosphomolybdic acid that is insitu reduced to intensely coloured molybdenum blue by ascorbic acid. 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. Because, most of the time the sampling location was away from the laboratory hence the time lag between collection, transportation and analysis was not avoidable at any instance of sampling.

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. It is performed in 3 steps namely presumptive test (screening test for the presence of coliform organisms), confirmatory test and completed test.

The analytical data can be used for the classification of water for utilitarian purposes and for ascertaining various factors on which the chemical characteristics of water depend.

2.5.2 Trace Element Study

Inductively Coupled Plasma–Mass Spectrometer— Instrument capable of scanning the mass range 5 to 250 amu with a minimum resolution capability of 1 amu peak width at 5 % peak height is used in the present study to analyse the trace elements lithium, rubidium, caesium, strontium, barium, vanadium, chromium, manganese, cobalt, nickel, copper, zinc, silver, cadmium, aluminium, gallium, indium, lead, arsenic, bismuth and selenium.

Sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are detected by a continuous dynode electron multiplier assembly and the ion information processed by a data handling system. Interferences relating to the technique are recognized and corrected.

2.5.3 Geographic information system (GIS)

In addition to the existing effective water quality monitoring, Geographic Information System (GIS) are applied for scientific investigations. Satellite data provide quick and useful baseline information about the factors controlling the occurrence and movement of groundwater like geology, lithology, geomorphology, soils, land use/cover, drainage patterns, lineaments, etc. differences in surface temperature (resulting from near-surface groundwater) measured by remote sensing have also been used to identify alluvial deposits, shallow groundwater, and springs or seeps. GIS provide a wide range of possibilities in studying the processes happening in the natural environment, which are important for environmental protection [12-20].

In the present study, using Geographic Information System (GIS) spatial distribution of various parameters along the study area are plotted.

Hydrochemical analysis can give the quality of the isolated patches only, but GIS maps can give the concentration at unknown points by using Inverse Distance Weighed (IDW) algorithm. IDW is a method of interpolation that estimates cell values by averaging the values of sample data points in the neighbourhood of each processing cell. The closer a point is to the centre of the cell being estimated, the more influence or weight it has in the averaging process.

2.5.4 Statistical Analysis

Different statistical methods are widely applied in groundwater studies [21-25].

Characteristics of groundwater resource data are : lower limit of zero and no negative values are possible; presence of 'outliers'; positive skewness; non-normal distribution of data; data reported only as below or above some threshold (censored data); seasonal patterns; autocorrelation; dependence on other uncontrolled variables.

Graphs provide visual summaries of data which more quickly and completely describe essential information than do tables of numbers. So graphical method is extensively applied in the present study. Other statistical methods applied include,

t-test

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

$$\mu = \bar{x} \pm ts/\sqrt{n} \qquad \text{...(2.1)}$$

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 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.

two sets of data consisting of n_1 and n_2 measurements (with averages x_1 and x_2) whose *t* value is calculated using the formula,

$$t = \frac{\overline{x_1} - \overline{x_2}}{s_{pooled}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}} \qquad \text{... (2.2)}$$

$$s_{pooled} = \sqrt{\frac{s^2{}_1(n_1 - 1) + s^2{}_2(n_2 - 1)}{n_1 + n_2 - 2}} \qquad \text{... (2.3)}$$

s_{pooled} is a pooled standard deviation making use of both sets of data. The value of *t* calculated is compared with standard value of student's *t* for $(n_1+n_2 - 2)$ degrees of freedom in the table. If the calculated *t* is greater than the tabulated *t* at the 95% confidence level, the two results are considered to be 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

$$r = \frac{1}{n-1}\Sigma^{n}{}_{i=1}\left(\frac{x_i-\bar{x}}{s_x}\right)\left(\frac{y_i-\bar{y}}{s_y}\right) \quad \text{..} \quad (2.4)$$

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

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

2.5.5 Water Quality Index

The water quality index is a modern method that reflects the quality of any water body under study by means of a single number, calculated by considering combined effect of important physico-chemical parameters. WQIs are the only medium by which the highly multi-attribute and multivariate concept of water quality can be conveyed to the lay persons in the form of a single score [26-29]. Different methods are used for water quality index calculation, like National Sanitation Foundation Water Quality Index (NSFWQI), Canadian Council of Ministries of the Environment

Water Quality Index (CCMEWQI), Oregon Water Quality Index (OWQI) and Weighted Arithmetic Water Quality Index Method (WAWQI). In the present study estimation of water quality index is done using weighted arithmetic water quality index method developed by *Brown* et al. (1972) [26] using the parameters pH, EC, Total Hardness (TH), Ca, Mg, Na, K, HCO_3^-, Cl^- & SO_4^{2-}. This method includes following steps

1) The values of ten parameters for each groundwater source or mean value of the parameters is determined.

2) Quality rating scale of each parameter is calculated by using formula

$$Q_i = \left[\left(V_o - V_i\right)/\left(V_s - V_i\right)\right]100 \quad \ldots\ldots\ldots\ldots (2.5)$$

Where Qi= Quality rating of the i^{th} parameter, V_o=observed value or mean value of the observed values of any parameter, V_i=ideal value of particular parameter [V_i=0 for all parameter except pH and DO. Vi for pH=7 and for DO Vi=14.6mg/L.], Vs= Standard permissible value of a particular parameter determined by WHO.

3). Calculation of relative unit weight (w_i)

The relative unit weight of any parameter (w_i) $\propto 1/Vs$

$$w_i = \frac{K}{V_s} \quad \ldots\ldots\ldots\ldots (2..6)$$

Where K=Proportionality constant. For the sake of simplicity,
K is taken as 1

4). Finally water quality index (**WQI**) = $\mathbf{w_iQ_i/Q_i}$ ....(2.7)

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

Table 2.4: Classification of groundwater on the basis of Water Quality Index,WQI (Brown et al. 1972) [26].

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

In other words

a) $0 < WQI < 100$ Fit for human use
b) $0 > WQI > 100$ Unfit for drinking use

2.5.6 Ionic Ratios

Ionic ratios give important information regarding processes occurring in groundwater [30]. In the present study concentration of sodium and chloride are used for ionic ratio calculations. If *Na/Na+Cl*> 0.5 and if *Na/Cl* > 1.0, ion exchange is occurring. . In ion exchange process Ca & Mg in water replaces Na in clays. Since Ca & Mg are removed from water this process is also called *natural softening*. In *reverse ion exchange* the opposite change occur and it is observed when highly saline waters come in contact with calcium rich clays.

2.5.7 Irrigation Quality Evaluation

Neutral salts in water may accumulate in soils according to the intensity of irrigation. It causes toxic damage to plants and reduces the availability of water for plants through a high osmotic pressure of the soil solution or through changes in soil structure and texture properties. High Cl^- content generally affect tissues and plant leaves. Different crops require different irrigation water qualities. Therefore, testing the irrigation water is prior to contribute to effective management and utilization of the groundwater resources [34, 35].

Three major water quality parameters EC, TH, & TDS are important to evaluate the irrigation quality of water [31]. Classification of water based on these parameters is given in Table 2.5.

Table 2.5: Irrigation quality classification of groundwater on the basis of Electrical Conductivity (EC), Total Hardness (TH) & Total Dissolved Solids (TDS)

EC µS/cm		**TH mg/l**		**TDS mg/l**	
<250	Excellent (E)	<75	Soft(S)	<1000	Fresh(F)
250-750	Good (G)	75-150	Moderately hard(MH)	1,000-3,000	Slightly saline(SS)
750-2000	Permissible (P)	150-300	Hard(H)	3,000-10,000	Moderately saline(MS)
2000-3000	Doubtful (D)	>300	Very hard(VH)	10,000-35,000	High saline(HS)
>3000	Unsuitable (U)				

The irrigation quality can be evaluated by various calculated parameters such as Sodium Adsorption Ratio (SAR), Sodium Percentage (Na %), Magnesium Adsorption Ratio (MAR), Residual Sodium Carbonate (RSC), Permeability Index (PI) and Kelly's ratio (KR). Concentrations of various ions obtained from chemical analysis are converted to milli equivalents per litre (meq/L) and the different parameters are calculated as per the equations given below.

Kelly's Ratio (KR) [32]

$$KR = \frac{Na^{+}}{\left(Ca^{2+} + Mg^{2+}\right)} \quad \text{...} \ (2.8)$$

Magnesium Adsorption Ratio (MAR)

$$MAR = \frac{Mg^{2+} \text{ x } 100}{Ca^{2+} + Mg^{2+}} \quad \text{...} \ (2.9)$$

Permeability Index (PI) [33]

$$PI = \frac{Na^{+} + \sqrt{HCO_3^{-}}}{Ca^{2+} + Mg^{2+} + Na^{+}} \times 100 \quad \ldots\ldots\ldots (2.10)$$

Sodium Adsorption Ratio (SAR) [36]

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \quad \ldots\ldots\ldots (2.11)$$

Residual Sodium Carbonate (RSC)

$$RSC = (CO_3^{2-} + HCO_3^{-}) - \left(Ca^{2+} + Mg^{2+}\right) \quad \ldots\ldots\ldots (2.12)$$

Sodium Percentage (Na%)

$$Na\% = \frac{Na^{+} \text{ x } 100}{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}} \quad \ldots\ldots\ldots (2.13)$$

The following tables give the classification of water based on these parameters.

Table 2.6: Classification of groundwater on the basis of Kelly's ratio (KR), Magnesium Adsorption Ratio (MAR) & Permeability index (PI).

Parameters						
KR*		**MAR****		**PI*****		
<1	Suitable(S)	<50	Suitable (S)	Class I	>75%	Good for irrigation (G)
>1	Unsuitable (US)	>50	Unsuitable (US)	Class II	25-75%	Good for irrigation(G)
				Class III	<25%	Unsuitable for irrigation (US)

* $KR = Na^{+} / \left(Ca^{2+} + Mg^{2+}\right)$; ** $MAR = Mg^{2+} \text{ x } 100 / \left(Ca^{2+} + Mg^{2+}\right)$;

*** $PI = [Na^{+} + \left(HCO_3\right)^{1/2}] \text{ x } 100 / [\ Ca^{2+} + Mg^{2+} + Na^{+}]$

Table 2.7: Classification of groundwater on the basis of Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC) and Soluble Sodium Percentage (SSP)

Parameters					
SAR[*]		**RSC**[**]		**Na%**[***]	
<10	Excellent(E)	<1.25	Good(G)	<20	Excellent(E)
10-18	Good(G)	1.25-2.50	Doubtful(D)	20-40	Good(G)
18-26	Doubtful(D)	>2.5	Unsuitable(US)	40-60	Permissible(P)
>26	Unsuitable(US)			60-80	Doubtful(D)
				>80	Unsuitable(US)

[*] $SAR = Na^+ / [(Ca^{2+} + Mg^{2+}) / 2]^{1/2}$; [**] $RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$; [***] $Na\% = Na^+ \times 100 / (Ca^{2+} + Mg^{2+} + Na^+ + K^+)$

USSL Diagram

In USSL diagram, Sodium Adsorption Ratios (SAR) are plotted against Electrical Conductivity (EC) along Y-axis and X-axis respectively to classify water samples [37]. SAR measures the degree to which sodium in irrigation water replaces the adsorbed (Ca^{2+} + Mg^{2+}) in the soil clays and thus damages the soil structure. Irrigation waters are usually classified in terms of salinity hazard (conductivity or TDS) and sodium hazard (SAR). Figure 2.5 is the SAR conductivity plot where the salinity hazard dividing points are 250, 750 and 2250 µmhos, resulting in four categories:

a) <250 µmho- Low-salinity water [C1],
b) 250-750 µmho- Medium-salinity water [C2],
c) 750-2250 µmho- High- salinity water [C3]
d) >2250 µmho - Very high- salinity [C4].

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

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

Where S is the SAR and C is the conductivity.

The resulting four categories are

- S1 - Low-sodium water
- S2 - Medium-sodium water
- S3 - High-sodium water
- S4 - Very high-sodium water

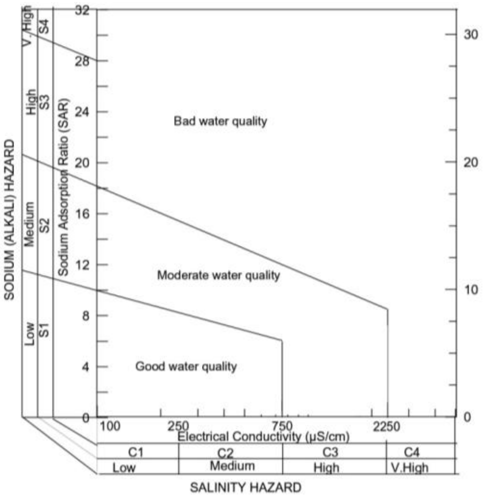


Figure 2.5: USSL Diagram for classification of water based on SAR and EC

Wilcox diagram

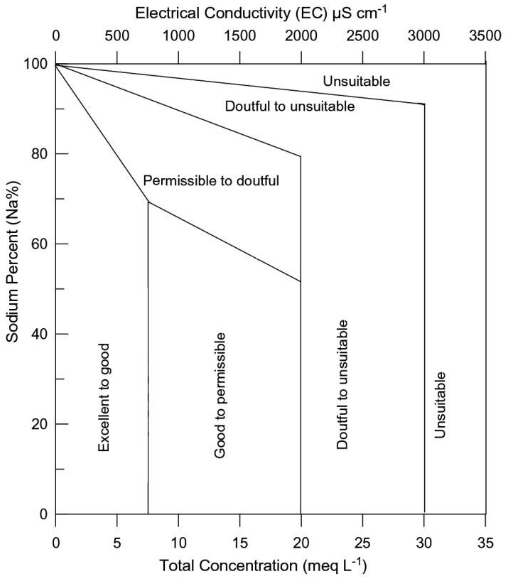


Figure 2.6: Wilcox Diagram for classification of water based on Na% and EC

Sodium percentage (Na %) is plotted against electrical conductivity (EC) in Wilcox diagram [38]. From the diagram inferences can be drawn about the irrigational quality of water.

2.5.8 Corrosion Study

Corrosion indices are useful to predict the potential for corrosion or scale-formation of water [39, 40]. They are derived from chemical equilibrium equations for the $CaCO_{3(s)}$ system (Table 2.8).

Aggressiveness Index (AI)

This empirical indicator formula was developed by the American Water Works Association for a water's aggressiveness towards the corrosion of Asbestos-Cement pipes.

Aggressiveness Index (AI) is calculated as

$$\mathrm{AI} = \mathrm{pH} + \log\left(\mathrm{AH}\right) \quad \text{......} \quad (2.14)$$

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

Saturation Indices

The water quality conditions at a specific site requires careful consideration of several key indicators like pH, DO, H_2S, TDS, CO_2, Cl. Using the results of laboratory analyses of these indicators, corrosion indices are determined, which forecast the potential for corrosion or scale-formation that the groundwater possess. Scaling is one of the most critical water quality issues in India

Two indices commonly used in the water treatment industry to evaluate the nature of a water source are the Langelier Saturation Index (LSI or Saturation index) and the Ryznar Stability Index (RSI or Stability index). In both cases these indices are based upon a calculated pH of saturation for calcium carbonate (pHs). The pHs value is then used in conjunction with the water's actual pH to calculate the value of the index as follows:

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

$$\mathrm{RSI = 2pHs - pH} \quad \text{.......... (2.16)}$$

The fundamental reaction in the LSI calculation is:

$$\mathrm{CaCO_{3(s)} + H^+ = Ca^{2+} + HCO_3^-} \quad \text{.......... (2.17)}$$

When equilibrium is reached:

$$\mathrm{K} = \frac{\left[\mathrm{Ca^{2+}}\right]\left[\mathrm{HCO_3^-}\right]}{\left[\mathrm{H^+}\right]} \quad \text{.......... (2.18)}$$

Rearranging, taking logs

$$\mathrm{pH_s = pCa^{2+} + pHCO_3^- + pK} \quad \text{.......... (2.19)}$$

Where $\mathrm{pH_s}$ = equilibrium pH value $\mathrm{pCa^{2+}}$ = equilibrium calcium content

$\mathrm{pHCO_3^-}$ = total alkalinity when the pH value is less than 9.5

pK = arithmetic difference between $\mathrm{pK_2}$ (second protolysis constant for $\mathrm{H_2CO_3}$) and $\mathrm{pK_s}$ (solubility product constant for $\mathrm{CaCO_{3(s)}}$) i.e., $\mathrm{pK = pK_2 - pK_s}$

Thus, the $\mathrm{pH_s}$ is a calculated value from three terms. By subtracting pHs from actual pH, Langelier saturation index (LSI) is calculated.

Calculation of the value for pHs can be done using the nomograph or through the use of the following equation

$$\text{pHs} = (9.3 + A + B) - (C + D) \quad \text{...} \quad (2.20)$$

Where:

A = [log (TDS) -1)/10], TDS in ppm
B = [-13.12 log (T + 273)) + 34.55], Temperature, T in ^{o}C
C = [log (calcium hardness) - 0.4], Ca hardness in ppm (as $CaCO_3$)
D = log (alkalinity), alkalinity in ppm (as $CaCO_3$)

It is apparent that the temperature at which the calculation is made has considerable impact upon the results. The classification of groundwater on the basis of corrosion indices, Aggressiveness index (AI), Langelier Saturation Index (LSI) & Ryznar Stability index (RSI) is given in Table 2.8.

Table 2.8: Classification of groundwater on the basis of corrosion indices, Aggressiveness index (AI), Langelier Saturation Index (LSI) & Ryznar Stability index (RSI)

AI[*]	**Tendency of water**	**LSI**[**]	**Tendency of water**	**RSI**[***]	**Tendency of water**
< 10.0	Highly aggressive (HA)	< ¯2	Intolerable corrosion (IC)	4.0 – 5.0	Heavy scale (HS)
		¯2 - ¯0.5	Serious corrosion (SC)	5.0 – 6.0	Light scale (LS)
10.0-11.9	Moderately aggressive (MA)	¯0.5 - 0	Slightly corrosive but non scale forming (SCNSF)	6.0 – 7.0	Little scale or corrosion (LSC)
		0	Balanced but pitting (BP)	7.0 – 7.5	Corrosion significant (CS)
> 12.0	Non-aggressive (NA)	0 – 0.5	Slightly scale forming and corrosive (SSFC)	7.5 – 9.0	Heavy corrosion (HC)
		0.5 - 2	Scale forming but non corrosive (SFNC)		

[*] $AI = pH + \log(AH)$ [**] $LSI = pH - pHs$ [***] $RSI = 2pHs - pH$

Water with a Langelier saturation index of 1.0 is one pH unit above saturation. Reducing the pH by 1.0 unit will bring the water into equilibrium. This occurs because the portion of total alkalinity present as CO_3^{2-}decreases as the pH decreases, according to the equilibria describing the dissociation of carbonic acid.

2.5.8 Hill-Piper Trilinear Diagram

A piper plot is a way of visualizing the chemistry of a rock, soil, or water sample [41]. It comprise three pieces: a ternary diagram in the lower left representing the cations (calcium, magnesium and sodium+potassium), a ternary diagram in the lower right representing the anions (carbonate+ bicarbonate, chloride and sulphate), and a diamond plot in the middle representing a combination of the two. The position of an analysis that is plotted on the Piper diagram can be used to make a tentative conclusion as to the origin of the represented by the analysis.

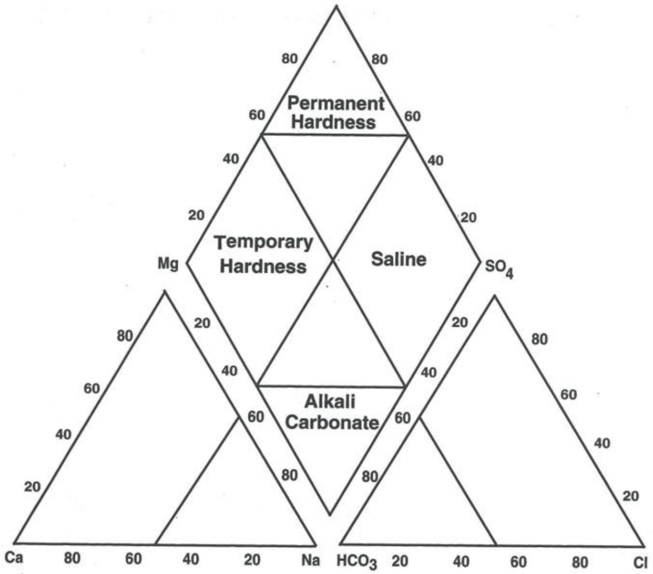


Figure 2.7: Water type classification as per diamond portion of Hill-Piper Trilinear diagram

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

(i) *Permanent hardness:* Water with plot data at top of the diamond, i.e. high in both [Ca^{2+} +Mg^{2+}] and [Cl^- +SO_4^{2-}] ions indicates character of permanent hardness.

(ii) *Temporary hardness:* Water with plot values at left corners of the diamond has character of temporary hardness. Ions [Ca^{2+} +Mg^{2+} and HCO_3^-] are prominent.

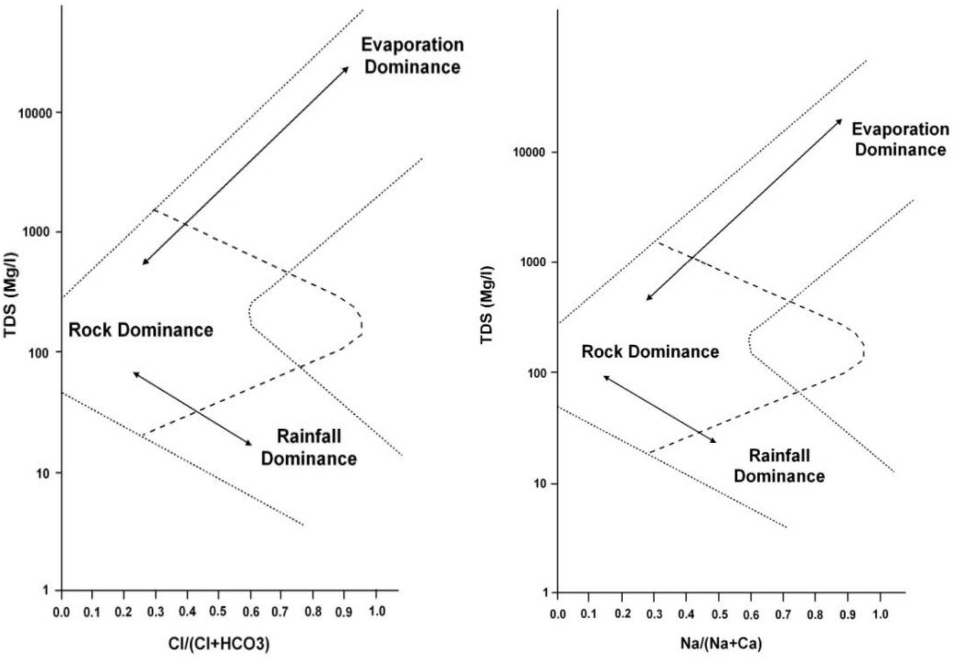
(iii) *Hardness due to soft-ions:* Water with plot data at lower corner of the diamond has hardness due to soft ions due to alkali carbonates [Na^+ +K^+] and [HCO_3^- + CO_3^{2-}] ions.

(iv) *Hardness due to saline ions:* water with plot data at right corners are classified as saline [Na^+ +K^+] and [Cl^- +SO_4^{2-}] ions are prominent.

The percentage composition of different anions and cations can be evaluated from the position of corresponding data points in the 2 triangles.

2.5.9 Gibb’s Plot

Using Gibb’s plot, the chemical composition of the groundwater is plotted to assess the influence of precipitation (rainfall), rock weathering and evaporation on groundwater system [42]. In Gibb’s plot of anion ratio, ($Cl/Cl+HCO_3$) is plotted against total dissolved solids (TDS) and in cation ratio (Na/Na+Ca) is plotted against TDS in mg/l. From the position of the point in the diagram inferences can be drawn.



(a) (b)

Figure 2.8: Gibb's plot for a)anion and b) cation ratios

2.6 CPCB Classification

As per the eleventh five year plan document of India (2007-12), "there are about 2.17 lakh inhabitants in our country affected by water quality problems. More than half of them affected with excess iron, followed by fluoride, salinity, nitrate and arsenic in order. Further, approximately, 10 million cases of diarrhoea, more than 7.2 lakh typhoid cases and 1.5 lakh viral hepatitis cases occur every year. A majority of which are contributed by unclean water supply and poor sanitation".

Standards are set by the Bureau of Indian Standards, which specifies the acceptable limits and the permissible limits in the absence of alternate source, of various water quality parameters. In cases where WHO guidelines are not available, the standards available from other countries have been examined and incorporated, taking in view the Indian conditions.

Open wells of Kerala are under threat of bacteriological contamination. In Kerala about 60% of the population relies on groundwater for drinking. At the same time studies have shown that fecal contamination is present in 90% of drinking water wells. The open character of the wells, and conventional maintenance habits, and use of buckets and pulley rope to draw water, kitchen wastes and pit latrines with average family load factor (5 members) at a distance of less than 5 meters from wells are some of the factors, which are contributing to the bacteriological contamination.

Faecal contamination of water is routinely detected by microbiological analysis. The presence of the indicator organisms, that inhabit the gut in large numbers and are excreted in human faeces, in water is evidence of faecal contamination and, therefore, of a risk that pathogens are present. The term “total coli forms” refers to a large group of Gram-negative, rod-shaped bacteria that share several characteristics. The group includes thermo tolerant coli forms and bacteria of faecal origin, as well as some bacteria that may be isolated from environmental sources. Thus the presence of total coli forms may or may not indicate faecal contamination. The most probable number (MPN) of coli forms in 100 ml of the water sample is estimated.

More than 95 per cent of thermo tolerant coli forms isolated from water are the gut organism Escherichia coli, the presence of which is definitive proof of faecal contamination.

Table 2.9: 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**

In India, CPCB has identified water quality requirements in terms of a few chemical characteristics, known as primary water quality criteria [43-45]. Central Pollution Control Board classified the water into five class i.e.; from A to E on the basis of their designated best use (Table 2.9). The classification has been made in such a manner that with the degradation in quality, the water quality requirement becomes progressively lower from A to E.

Biological examination is of value in determining the causes of objectionable tastes and odours in water and controlling remedial treatments, in helping to interpret the results of various chemical analysis, and in explaining the causes of clogging in distribution pipes and filters.

2.7 Conclusions

The significant features of the study area selected, protocols followed for the sampling and analysis of the groundwater samples from the study area, the relevance of the prominent water quality parameters selected, statistical and interpretation methods followed, diagrammatical plots used and basis of Central Pollution Control Board (CPCB), BIS and WHO classification are scientifically presented through the sections placed above. The results, outcome and inference are presented in the following chapters.

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Chapter 3

HYDROGEOCHEMISTRY OF SHALLOW GROUNDWATER SOURCES OF ARATTUPUZHA COAST, ALAPPUZHA, KERALA, INDIA

Contents

3.1 Introduction

Study of groundwater properties rest on an understanding of the subsurface water chemistry, quality and fresh water availability in a region is recently significant in the case of post disaster impact study of water sources [1]. In India groundwater is an important water resource for domestic and agriculture uses in both rural and urban areas and economy of the country is most dependant on the freshwater availability [2, 3]. The need to assess the groundwater quality is becoming increasingly important in a local perspective [4]. Primary standards and treatment techniques protect public health by limiting the levels of contaminants in drinking water and is possible through unfailing research initiatives region wise. Several publications are available reporting the groundwater quality in India [5-10] and water conservation initiatives are planned based on the data available. India has about 7517km long coastline and a complete groundwater quality profile of these regions comprising physico-chemical and biological parameters over a period of 12 months is rare. Present study is focused on a coastal segment of Kerala-Arattupuzha coast (10. 41 82^0N 76.2262^0 E) in Alappuzha district, Kerala, India [11]. This district has a flat unbroken coastline of 82km length which constitutes 13.9 percent of the total coast of the state of Kerala. Water level data determined by groundwater department for the period since 1987 shows declining trend [12]. This indicates that extensive groundwater extraction is taking place over the years and the recharge during monsoon season is not enough to compensate. Rainfall recharge occurs mainly from June till the end of September and comparatively high evaporation occurs from the month of March to May. These two factors play a major role for the seasonal variation of major ions [13]. Monsoon result in decrease in ionic concentrations due to the dilution. The recharge process reduces the ionic concentration of groundwater. During the non-monsoon period, usually increase in major ion concentration is observed, due to the lowering of water level and the evaporation process. Coastal erosion is one of the grave natural hazards affecting the coasts of Alappuzha district and extensive coastal erosion is taking place in the present study area (Figure 3.1). The study area focussed, the Arattupuzha coast is devastated by 26th December 2004 Indian Ocean Tsunami [14, 15] with a number of human and property loss and has many significant features resulted by rich mineral sand deposits; mostly ilmenite, rutile and monazite regarded as the valuable beach sand resource of Kerala.

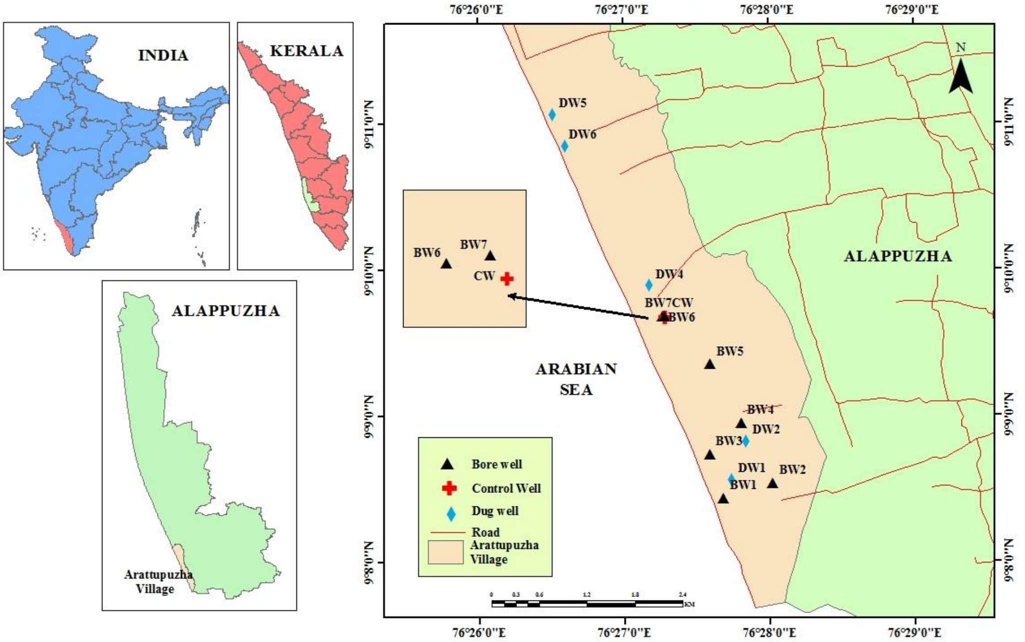

Figure 3.1: Groundwater sampling locations in 26th December 2004 Indian Ocean Tsunami affected coastal areas of Arattupuzha village, Alappuzha, Kerala, India.

Chemical analysis of water generate the fundamental data essential for the determination of groundwater quality [16-19]. Major constituents are measured in milligrams per litre and trace constituents in microgram per litre. Water quality standards for domestic, agricultural and industrial use, published by various agencies are used for evaluating the water quality of the present study area. Presentation of results in graphical forms helps studying temporal and spatial variation of constituents. Results of chemical analysis are statistically evaluated by correlation study which helps to identify relationship among parameters [20-23]. Water Quality Index calculated using WHO standards help in easily identifying the quality of water [24-27]. The ratios of sodium and chloride concentrations are particularly important because they give suggestions regarding the groundwater processes like ion exchange and reverse ion exchange [28]. Hill-Piper Trilinear diagrams are particularly useful to infer hydro geochemical facies [29, 30]. Gibb's plot is another diagrammatical method to evaluate the prominent hydro geochemical processes occurring in the study area [31]. Different parameters used for irrigational quality evaluation are Sodium Adsorption Ratio (SAR), Sodium Percentage (Na %), Magnesium Adsorption Ratio (MAR), Residual Sodium Carbonate (RSC), Permeability Index (PI) and Kelly's ratio (KR).USSL and WILCOX diagrams are graphical plots to classify water samples based on irrigation suitability [32, 33]. Saturation indices calculation helps in evaluating the industrial use of water [34].

The study taken up under this chapter elaborately discusses the monthly variation of water quality parameters and hydro geochemistry of shallow groundwaters in the coastal alluvial soil of Arattupuzha village in Alappuzha district during year 2012.The sampling stations and their locations are given in Table 3.1 and are marked as dugwell sources (DW) in the thesis.

Table 3.1: Dug well sampling stations along Arattupuzha coast, Alappuzha, Kerala, India

No	Station	Description	Remarks	Location
1	DW1	Valiyazheekal temple	Dug well DW1 Away from the sea	09^{o} 08' 33 N, 76^{o} 27'43E
2	DW2	Palliyara Sree Parvathy temple	Dug well DW2 Saline intrusion	09^{o} 08' 49 N, 76^{o} 27'49E
3	DW3	Kuriappaserry temple	Dug well DW3 as the control well CW	09^{o} 09' 40 N, 76^{o} 27'16E
4	DW4	Panackal temple	Dug well DW4 Away from the sea	09^{o} 09' 53 N, 76^{o} 27'10E
5	DW5	Bhaskaranvattachal – house owner	Dug well DW5 Near to the sea	09^{o} 10' 51 N, 76^{o} 26'35E
6	DW6	Mohananvattachal – house owner	Dug well DW6 Near to the sea	09^{o} 11' 03 N, 76^{o} 26'30E

3.2 Water Quality Parameters

The work presented in the following section of the thesis comprises the major results and discussions on the water quality parameters of the shallow groundwater sources of the study area during year 2012 and their groundwater chemistry. It is done in continuation of a research study initiated in January 2005 as a part of post tsunami impact study of the coastal regions of Kerala. In graphical plots, the variation of the parameter in control well (CW) is represented along with the mean value of dug well (DW) strata with error bar.

3.2.1 pH

The notation "pH" is taken to mean hydrogen-ion activity. Temperature has a strong effect on hydrogen-ion behaviour [35]. In the present study, the 2012 annual mean temperature of water samples of shallow dug wells is 29.9±1.1^{o}C.

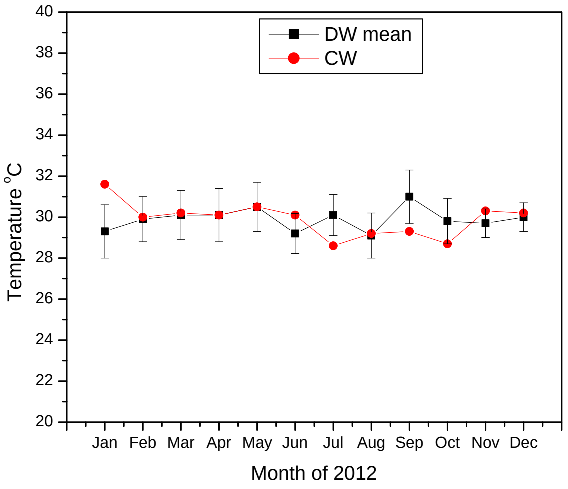

Figure 3.2: Monthly variation of Temperature of dug well (DW) groundwater sources & control well (CW) along the study area, Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

For control well the annual mean temperature is 29.9±0.83. There is not much variation in temperature of water till may 2012 (Figure 3.2). After May 2012 the temperature slightly varies.

The hydrogen-ion activity in an aqueous solution is controlled by interrelated chemical reactions that produce or consume hydrogen ions. The dissociation equilibrium for water is applicable to any aqueous solution, but many other equilibrium and no equilibrium reactions that occur in groundwater among solute, solid and gaseous, or other liquid species also involve hydrogen ions. The reaction of dissolved carbon dioxide with water is one of the most important in establishing pH in natural-water systems.

$CO_2(g)+H_2O(l)=H_2CO_3(aq)$

$H_2CO_3(aq)=H^++HCO_3^-$

$HCO_3^-=H^++CO_3^{2-}$

Hydrolysis, precipitation, oxidation-reduction reactions also influence pH.

$CaCO_3(s)+H_2O(l)=Ca^{2+}+ HCO_3^-+OH^-$(calcite hydrolysis)

In shallow aquifers photosynthesis by aquatic organisms takes up dissolved CO_2 during day light and release CO_2 by respiration at night.

In the present study area, the annual mean pH of control well (CW) during year 2012 is 7.8±0.3 and it vary from7.5 to 8.1.The monthly variation of pH is exactly similar for CW anddugwell (DW) strata with slightly lower values in CW. The pH of dug well strata is 7.8±0.4 in January which increases to 8.6±0.1 by March, the hottest month when evaporation is high. So, in March the pH of DW strata crosses the standard limit of 8.5.This makes water alkaline contributed by bicarbonate. After March, pH shows a decreasing tendency till November and slightly increases in December to 7.5±0.3. During monsoon season, almost steady pH is observed, (7.8±0.4in July). The annual mean pH of DW strata during year 2012 is 7.8±0.4 with CI of 7.6-8.1 at 95% significant level. There is not much variation in pH and throughout the year pH is within standard limit of 6.5-8.5 except in March (Figure 3.3). During the monsoon and post monsoon season's slight decrease in pH is observed.

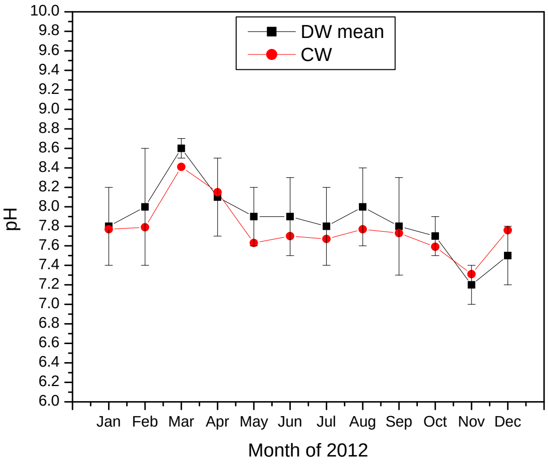

Figure 3.3: Monthly variation of pH of dug well (DW) water sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

3.2.2 Redox Potential (Eh)

The redox potential is a numerical index of the intensity of oxidizing or reducing conditions within a system, with the hydrogen-electrode potential serving as a reference point of zero volts. Positive potentials indicate that the system is relatively oxidizing, and negative potentials indicate that it is relatively reducing. The redox potential is limited in the negative range by the reduction of H_2O to $H_2(g)$ and in the positive range by the oxidation of H_2O to $O_2(g)$. At pH 7 to 8 this range is from about -400mV to +800mV [36]. The effect of oxygen tends to be the dominant control on measurements of redox potential in natural water in contact with air.

The 2012 annual average of Eh of control well in the present study area (Figure: 3.4) is ¯44±14 and it vary from ¯58 to ¯30mV. For shallow wells the Eh value in 2012 January is ¯39±22. By March the environment becomes most reducing with Eh ¯90±6.1, and by July the redox potential become ¯47±22. In November Eh is close to zero, that is the environment become close to oxidising and in December Eh is ¯30±17. The annual mean Eh of DW strata during year 2012 is ¯50±22 with CI of ¯64 -¯36 at 95% significant level. Thus throughout the year the groundwater sustains a stable redox situation with reducing tendency.

Eh relates to ratios of solute activities and give little or no indication of the quantitative capacity of the system to oxidize or reduce material that might be introduced from outside. Other characteristics of the system must be evaluated to apply predictive redox models.

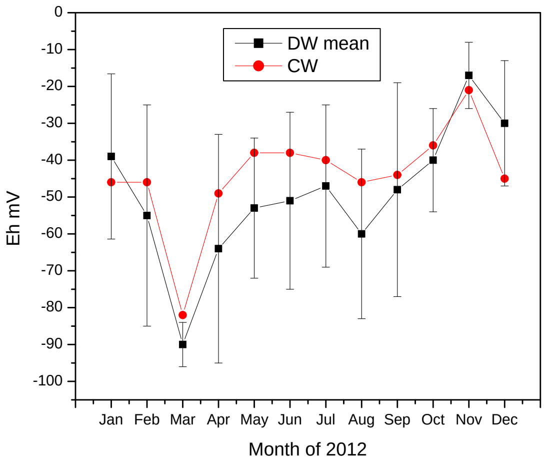

Figure 3.4: Monthly variation of redox potential (Eh) of dug well (DW) water sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

3.2.3 Electrical Conductivity (EC)

Electrical conductance, or conductivity, is the ability of a substance to conduct an electric current. The presence of charged ionic species in solution makes the solution conductive. As ion concentrations increase, conductance of the solution increases; therefore, conductance measurements provide an indication of ion concentration. To conduct current, solute ions actually move through the solution to transfer charges, and the effectiveness of a particular ion in this process depends on its charge, its size, the way it interacts with the solvent and other solvent factors. Natural waters are not simple solutions. They contain a variety of both ionic and undissociated species, and the amounts and proportions of each may range widely.

The annual average conductivity of control well of the study area is 0.34±0.04mS/cm within a range of 0.30-0.38 (Figure: 3.5). So there is not much variation in electrical conductivity of control well over the year. In shallow groundwater sources, the electrical Conductivity is 0.75±1.01 in January, which increases slightly and become 1.14±1.61 in March. In monsoon season EC decreases and it become minimum of 0.75±0.90 in July. After September there is a hike in EC and become 1.96±1.83 in December. Thus EC crosses the standard limit due to sea water intrusion in shallow wells near the sea. The annual mean EC of DW strata during year 2012 is 1.2±1.4 with CI of 0.3-2.1 mS/cm at 95% significant level. The standard limit for EC is 1.5mS/cm. The degree of sea water contamination, defined by sea water- fresh water interface, depends on the height of the fresh water column over the mean sea level. It can be checked by the ratio Cl/HCO_3, which will be 2 or by Ca/Mg ratio, which will be low. Sea water contain magnesium in higher concentration compared to calcium and chloride in very higher amounts compared to bicarbonate.

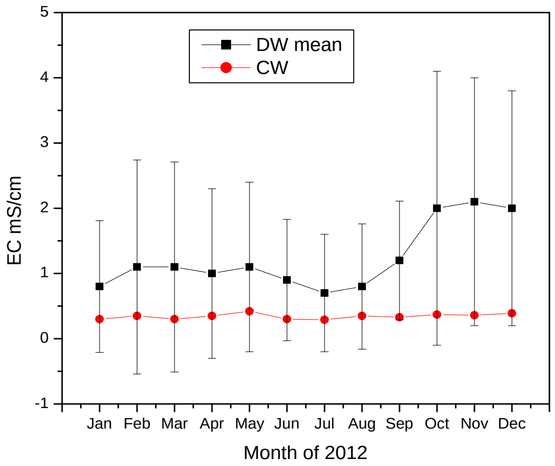

Figure 3.5: Monthly variation of Electrical Conductivity (EC) of dug well (DW) water sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

3.2.4 Total Hardness (TH)

The standards by which water hardness is judged become more rigorous over years, and public water supplies now soften water to less than 100 mg/L of hardness. The World Health Organization suggested an upper limit of 500 mg/L but the American Water Works Association suggested that ideal water should not contain more than 80 mg/L of hardness [37]. Hardness in water used for ordinary domestic purposes does not become particularly objectionable until it reaches a level of 100 mg/L or so. But hardness exceed this level in many places. Waters in contact with limestone or gypsum shows a hardness of 200-300 mg/L or more. Hardness becomes noticeable in all uses at these levels, and becomes increasingly troublesome as the concentration rises. According to IS 2012 permissible limit of TH in the absence of alternate source is 600mg/l. Hardness is contributed by the multivalent cations mainly Ca^{2+}& Mg^{2+}. Other ions include $Fe^{3+}$and Fe^{2+}, Mn^{2+}, Sr^{2+}, Al^{3+} etc. Water as it moves through soil and rock dissolves small amounts of naturally-occurring minerals and carries them into the groundwater supply. Water is a great solvent for calcium and magnesium, so if the minerals are present in the soil around a well, the water obtained from the well will be hard.

TH = Σ multivalent cations ≈Ca^{2+} + Mg^{2+}

The 2012 annual average value of TH (Figure: 3.6) of control well in the present study area is 196±18with a range of178-214mg/l. Thus hardness of control well is comparable to that of DW mean. For shallow wells the TH in 2012 Januaryis192±95 and it shows a variation similar to EC over the year. The higher value observed in March is 263±167, which then decreases slightly and become 219±112 in July. After September a hike in total hardness is observed and in December it is 426±267. The annual mean TH of DW strata during year 2012 is 282±198 with CI of 156-408mg/l at 95% significant level. Towards the end of the year there is sea water mixing in wells near the sea. The value is higher than the BIS standard of 200mg/l and the water become too hard for ordinary domestic purposes.

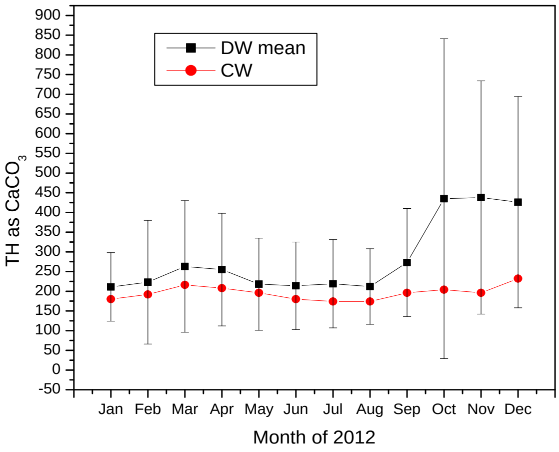

Figure 3.6: Monthly variation of Total Hardness (TH) of dug well (DW) water sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Hardness is a property of water that is not of health concern, but it can be a nuisance. Hard water can cause mineral build-up in plumbing, fixtures, and water heaters, and poor performance of soaps and detergents.

Table 3.2: Groundwater hardness based classification (Vesilind, 2004) [38]

Groundwater hardness based classification		Hardness (mg/l)	Hardness (mg/l) as $CaCO_3$
1.Extremely soft to soft	[ESS]	0 - 0.9	0 - 45
2.Soft to moderately hard	[SMH]	0.9 - 1.8	46 - 90
3.Moderately hard to hard	[MHH]	1.8 - 2.6	91 - 130
4.Hard to very hard	[HVH]	2.6 - 3.4	131 - 170
5.Very hard to excessively hard	[VHEH]	3.4 - 5.0	171 - 250
6.Too hard for ordinary domestic use	[THODU]	> 5.0	> 250

Total hardness (TH) is the sum of two components: Carbonate hardness (CH) known as temporary hardness and noncarbonated hardness known as permanent hardness [ie; TH = CH + NCH], CH being the contribution of CO_3^{2-} and HCO_3^- the so-called scale forming part. NCH is the contribution of all other anions. CH is measured as alkalinity (AL) and in certain occasions it is equal to total hardness (TH). The non carbonate hardness (NCH) is the difference. In circumstances where the alkalinity becomes equal or greater than TH the NCH becomes zero.

3.2.5 Alkalinity (AL)

The property Alkalinity is an important characteristic of natural water which is defined as a capacity function because the property is imparted by several different solute species and is evaluated by acid titration. The principal solutes that constitute alkalinity are imparted to natural water during its passage in liquid form through the hydrologic cycle. The alkalinity value reflects the history of the water, as an imprint left by its interaction in natural environment. Alkalinity also evaluates the potential of the solution for some kinds of water-rock reaction or interaction with other material the water may contact. Most natural waters contain substantial amounts of dissolved carbon dioxide species, which are the principal source of alkalinity and can conveniently be evaluated by acid titrations.

Alkalinity is caused mainly due to –OH, $-CO_3$, $-HCO_3$ ions. The property of alkalinity can be expressed in quantitative terms in various ways. The most common practice is to report it in terms of an equivalent amount of calcium carbonate. The more important noncarbonate contributors to alkalinity include hydroxide, silicate, borate, and organic ligands, especially acetate and propionate. Rarely, other species such as NH_4OH or HS^- may contribute significantly to alkalinity. The contribution of hydroxide to alkalinity can become significant above about pH 10. The alkalinity of natural waters can be assigned entirely to dissolved bicarbonate and carbonate except for waters having pH greater than about 9.5 and some others having unusual chemical composition, especially water associated with petroleum and natural gas or water having much dissolved organic carbon etc.

The annual average of Alkalinity of control well in the present study area is 211±27with CI of 184-238mg/l (Figure 3.7). For shallow wells, the Alkalinity in 2012 January is 209±79, which increases to 205±68 in March, and again increases to 237±105 by April. It then decreases in the monsoon season and in July it is 194±58 and in September alkalinity shows the lowest value of 143±58mg/l. After September alkalinity increases in October, November and in December it is 225±108mg/l. The annual mean Alkalinity of DW strata during year 2012 is 199±80with CI of 148-250mg/l at 95%

significant level. The standard limit of Alkalinity according to BIS is 200mg/l. So there is a slight increased value for Alkalinity in DW & CW strata of the study area. Abnormally, high alkalinity imparts bitter taste to water and makes it unacceptable. Alkalinity in excess of alkaline earth metal is important in determining the suitability of water for irrigation purposes. Alkalinity can react with certain atoms to produce precipitates which can foul pipes and other utilities of water supply system. Alkalinity influence lime and soda ash requirement in water softening by precipitation method. It is an important parameter in pollution control.

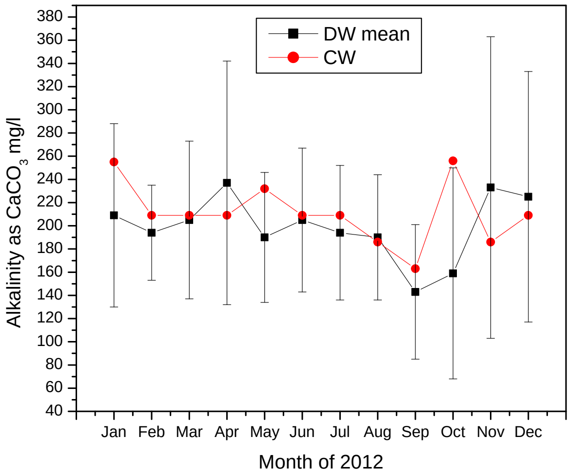

Figure 3.7: Monthly variation of Alkalinity (AL) of dug well (DW) water sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Table: 3.2 can be used to classify water based on Hardness. From the Total Hardness and Alkalinity inferences can be drawn about the Temporary or Permanent Hardness of water.

Table 3.3: Comparison of Total Hardness (TH), Alkalinity (AL), Temporary Hardness (TeH) & Permanent Hardness (PeH) of control well (CW) and dug well (DW) on Arattupuzha coast, Alappuzha, Kerala, India in each month of year 2012.

Year (2012)	**CW**					**DW**				
	TH* mg/l	**Inference**	**AL mg/l**	**TeH mg/l**	**PeH mg/l**	**TH mg/l**	**Inference**	**AL mg/l**	**TeH mg/l**	**PeH mg/l**
Jan	180	VHEH	255	255	0	211	VHEH	209	209	2
Feb	192	VHEH	209	209	0	223	VHEH	194	194	29
Mar	216	VHEH	209	209	7	263	THODU	205	205	58
Apr	208	VHEH	209	209	0	255	THODU	237	237	18
May	196	VHEH	232	232	0	218	VHEH	190	190	28
Jun	180	VHEH	209	209	0	214	VHEH	205	205	9
Jul	174	VHEH	209	209	0	219	VHEH	194	194	25
Aug	174	VHEH	186	186	0	212	VHEH	190	190	22
Sep	196	VHEH	163	163	33	273	THODU	143	143	130
Oct	204	VHEH	256	256	0	435	THODU	159	159	276
Nov	196	VHEH	186	186	10	438	THODU	233	233	205
Dec	232	VHEH	209	209	23	426	THODU	225	225	201
$\bar{x} \pm \sigma$	196±18		211±27	211±27		282±198		199±80	199±80	
μ	196±11		211±17	211±17		282±126		199±51	199±51	
CI	185-207		194-228	194-228		156-408		148-250	148-250	

*as $CaCO_3$

From Table 3.3 it is clear that the water of CW is *very hard to excessively hard* (VHEH) category throughout the year because the hardness is greater than 171mg/l. Also, the hardness is temporary type in majority months. There is slight contribution of permanent hardness in the months March, September, November and December.

In shallow dug wells (DW) in the summer months of March and April and in the months from September to December the water is *too hard for ordinary domestic use* (THODU) because the hardness is greater than 250mg/l. There is the contribution of permanent hardness throughout the year. It shows the presence of Chlorides and sulphates of Calcium and Magnesium. From January to August there is only slight contribution of permanent hardness. But from September to December, permanent hardness is almost equal to temporary hardness. This increased contribution of chlorides and sulphates suggest saline water intrusion.

3.2.6 Calcium (Ca^{2+})

Calcium is the most abundant of the alkaline-earth metals and is a major constituent of many common rock minerals. It is an essential element for plant and animal life forms and is a major component of the solutes in most natural water. Calcium has only one oxidationstate, Ca^{2+}. Its concentration in groundwater is governed by the availability of the more soluble calcium-containing solids and by solution- and gas-phase equilibria that involve carbon dioxide species. Calcium also participates in cation-exchange equilibria at aluminosilicate and other mineral surfaces. Solubility equilibrium models have been used widely in studying the chemical behaviour of calcium.

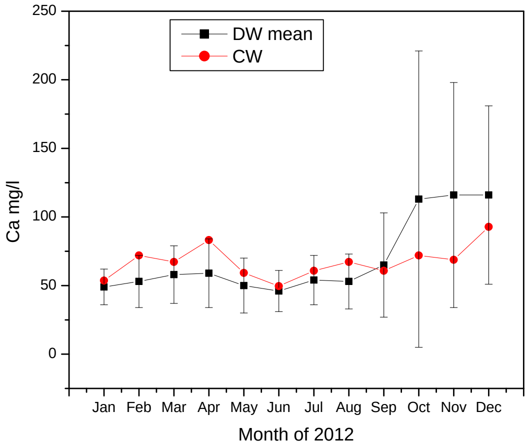

Figure 3.8: Monthly variation of Calcium (Ca) of dug well (DW) water sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The most common forms of calcium in sedimentary rocks are carbonates. The two crystalline forms, calcite and aragonite, both have the formula

$CaCO_3$, and the mineral dolomite can be represented as $CaMg(CO_3)_2$. Limestone consists mostly of calcite with admixtures of magnesium carbonate and other impurities. In sandstone and other detrital rocks, calcium carbonate commonly is present as cement between particles or a partial filling of interstices. Calcium also is present in the form of adsorbed ions on negatively charged mineral surfaces in soils and rocks. Because divalent ions are held more strongly than monovalent ions at surface charge sites, and because calcium is generally the dominant divalent ion in solution, most such sites are occupied by calcium ions in ground-water system.

The 2012 annual average of Calcium of control well in the present study area is 67±12 with a range of 55-79mg/l. For shallow wells the Calcium value in 2012 January is 44±16 which gradually increases and become 58±21 in March and 59±25 in April. It then decreases in June to 45±11 and in July 54.4±18. After September, there is a hike in calcium concentration to 113±108 in October and keeps almost steady value till December with 116±65mg/l. Thus the annual mean of Ca concentration of DW strata during year 2012 is 69±47 with CI of 39-99mg/l at 95% significant level. The standard limit of Ca according to BIS & WHO is 75mg/l. So from October to December some shallow groundwater sources contain calcium in higher than standard limit. It is due to reverse ion exchange occurring in those wells.

3.2.7 Magnesium (Mg^{2+})

Magnesium is an alkaline-earth metal and has only one oxidation state of significance in water chemistry, Mg^{2+}. It is a common element and is essential in plant and animal nutrition. Similar to Ca, it contributes to hardness of water. But its geochemical behaviour is different from Ca. The effect of hydration is much greater for magnesium than for the larger ions of calcium and sodium. Sedimentary forms of magnesium include mainly carbonates. Dolomite has a definite crystal structure in which calcium and magnesium ions are present in equal amounts.

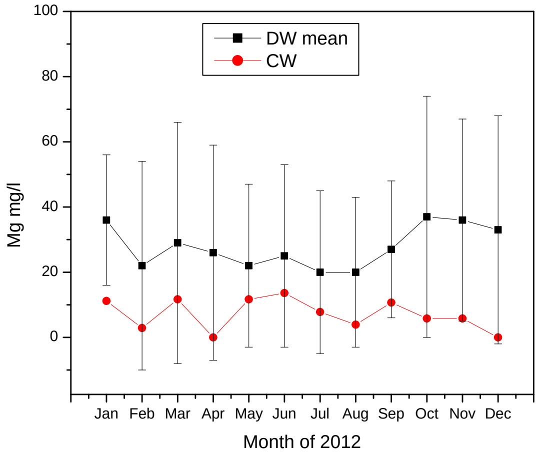

Figure 3.9: Monthly variation of Magnesium (Mg) of dug well (DW) water sources & control well (CW) along the study areaArattupuzha coast, Alappuzha, Kerala, India during year 2012

The 2012 annual average of Mg of control well in the present study area is 7±5 with a range of 2-12mg/l (Figure: 3.9). So the Mg concentration is much lower compared to calcium. For shallow wells, the Mg in 2012 January is 36±20 which decreases in February to 22±32 and slightly increases to 29±37 in March. It again decreases slightly and become 20.3±26 in July and keeps steady in August. Then it increases till December with a mean value of 33.2±35mg/l. Thus the annual mean value Mg concentration of DW strata during year 2012 is 28±29 with CI of 9-47mg/l at 95% significant level. The standard limit of Mg according to BIS &WHO are 30 & 50mg/l respectively. Higher Mg concentration is observed in one station, DW2. In this station, Mg concentration is higher than Ca which is a common observation in sea water. All other stations retained much lesser concentrations. The considerably lower concentration of Mg compared to calcium suggest that minerals rich in Mg like dolomite is not present in the study area.

3.2.8 Sodium (Na)

Sodium is the most abundant member of the alkali metal group of the periodic table. The total sodium is present as minerals in evaporate sediments and in solution in the ocean [39]. When sodium has been brought into solution, it tends to remain in that status. All the alkali metals occur in the +l oxidation state and do not participate in redox processes. Sodium ions are not strongly hydrated. There are no important precipitation reactions, that can maintain low sodium concentrations in water, in the way that carbonate precipitation controls calcium concentrations. Sodium is retained by adsorption on mineral having high cation-exchange capacities such as clays. But the interaction between surface sites and monovalent ions is much weaker than the interactions with divalent ions. Cation exchange processes in freshwater systems tend to extract divalent ions from solution and to replace them with monovalent ions. The feldspars containing sodium and calcium are more susceptible to weathering. Water associated with evaporates formations generally has a very high sodium concentration.

The 2012 annual average of sodium of control well in the present study area is14±3 with a range of 11-17mg/l (Figure 3.10). The control well retains a steady lower sodium concentration throughout the year. For shallow wells the Na in 2012 January is 45.6±38.1, in March 53±39, in July 48±38 mg/l and till July not much variation in sodium concentration. From August it increases and reaches a maximum in October and after that decreases slightly and become 177±163mg/l in December. Thus the annual mean value Na concentration of

DW strata during year 2012 is 107±127with CI of 26-188mg/l at 95% significant level.

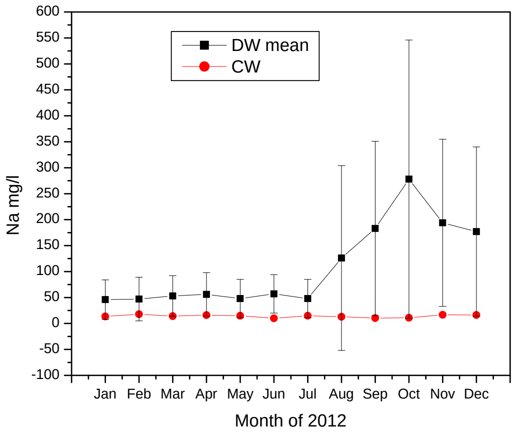

Figure 3.10: Monthly variation of Sodium (Na) of dug well (DW) water sources & control well (CW) along the study areaArattupuzha coast, Alappuzha, Kerala, India during year 2012.

The standard limit of Na according to WHO is 200 mg/l. Like in the case of Mg, the station DW2 retained high Na concentration throughout the year. Other two DW stations showed hike in Na concentration in the post monsoon season which is an indication of sea water contamination. This is confirmed by the high Electrical Conductivity of these stations. Sodium concentration plays an important role in evaluating the groundwater quality for irrigation because sodium causes an increase of the hardness of soil as well as a reduction in permeability.

3.2.9 Potassium (K)

Potassium concentration is much lower than sodium concentration in most natural waters. Potassium is liberated with greater difficulty from silicate minerals and exhibits a strong tendency to be reincorporated into solid weathering products, especially certain clay minerals. Another important factor in the hydrochemical behaviour of potassium is its involvement in the biosphere, especially in vegetation and soil. Potassium is an essential element for both plants and animals. Thus the usual sinks of potassium are plants and clays.

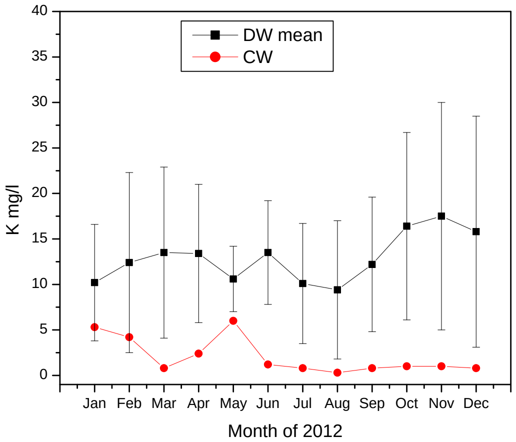

Figure 3.11: Monthly variation of Potassium (K) of dug well (DW) water sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The 2012 annual average of K of control well in the present study area is 2.1±2 with a range of 1.9-4.1mg/l (Figure 3.11). So potassium shows much lower concentration compared to sodium and many sinks are available for potassium. For shallow wells, the K concentration in 2012 January is 10.2±6.4, increases slightly till April with 13±9.4in March, in May slight decrease again increase in June, then decreases in July and August with 10±6.6in July. After August regular increase to16±13mg/lin December. So similar to ionic concentrations of Ca, Mg & Na, potassium also shows increase in post monsoon period. Thus the annual mean K concentration of DW strata during year 2012 is 12.9±5.5 with CI of 7.4-18.4mg/l at 95% significant level. The standard limit of K according to WHO is 12 mg/l.

3.2.10 Bicarbonate (HCO_3^-)

The bicarbonate concentration of natural water generally is held within a moderate range by the effects of carbonate equilibria. The concentration in rainwater commonly is below 10 mg/L and sometimes is much less than 1 .0 mg/L, depending on pH.

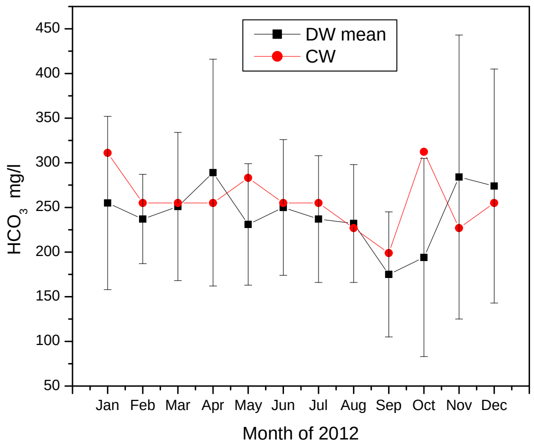

Figure 3.12: Monthly variation of Bicarbonate (HCO_3^-) of dug well (DW) water sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

In the present study area, the 2012 annual average of bicarbonate of control well (CW) is 258±34mg/l with a range of 224-292 mg/l. Thus bicarbonate is the prominent ion present in control well. Since control well has considerable calcium concentration, calcite weathering is the prominent process occurring in control well. For shallow wells the bicarbonate in 2012 January is 255±97, in March 251±83 and increases to 289±127 in April, in July 237±71 and decreases till October with a minimum of 194±111and then increases and shows an average value of 274±131 mg/l in December. Thus, the annual mean bicarbonate concentration of DW strata during year

2012 is 242±98 with CI of 180-304 mg/l at 95% significant level. The standard limit of bicarbonate according to WHO is 500 mg/l.

3.2.11 Chloride (Cl^-)

The most abundant halogen, chlorine (Cl), form compounds with common metallic elements, alkali metals, and alkaline earth metals. These are readily soluble in water. Although, chlorine can occur in various oxidation states ranging from Cl^- to Cl^{7+}, the chloride form is the only one of major significance in water exposed to the atmosphere [40]. More than three-fourths of the total amount of the element present in the Earth's outer crust, atmosphere, and hydrosphere is in solution in the ocean as Cl^- ions. Rainwater, close to the ocean commonly contains from one to several tens of milligrams per litre of chloride, but the concentrations observed generally decrease rapidly in a landward direction.

In the present study area, the 2012 annual average value of Chloride of control well (CW) is 16±7mg/l with a range of 9-23mg/l. So CW has a very low concentration of Chloride. For shallow wells the chloride in 2012 January is147±264 which increases to 326±623in March, then slightly decreases to 205±398in July and keeps almost steady till September. In October, November and December a hike in chloride concentration in shallow wells near the sea which reflected in the mean value and in December it is 436±452mg/l. Thus the annual mean of chloride concentration of DW strata during year 2012 is 311±484 with CI of 3-619mg/l at 95% significant level. So the different sampling dug well stations show a wide variation in chloride concentration. There is one station, DW2, which shows very high chloride concentration throughout the year, may be situated in a saline pocket area as evidence by EC. The sources of chloride are brine, seawater, rainwater and the mineral halite (NaCl). The standard value according to BIS andWHO is 250mg/l. Thus chloride contamination is observed in shallow groundwater sources.

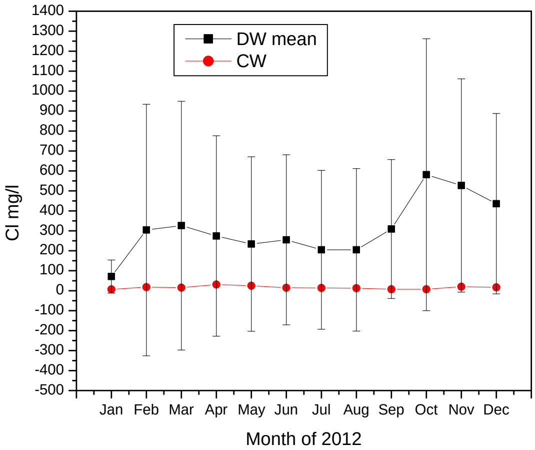

Figure 3.13: Monthly variation of chloride (Cl^-) of dug well (DW) water sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

3.2.12 Total Dissolved Solids (TDS)

The total concentration of dissolved material in water is determined from the weight of the dry residue remaining after evaporation of a definite portion of the sample at 110°C. At 100°C bicarbonate ions are unstable. Half are converted to water and carbon dioxide, and the other half to carbonate ions. Organic matter present is completely removed only if the residue is strongly ignited. Some inorganic constituents such as nitrate and boron are partly volatile [41].

The 2012 annual average of TDS of control well in the present study area is 280±125 with range of 155-405mg/l (Figure 3.14). Thus a moderate TDS is observed. For shallow wells the TDS in 2012 January is 733±574, in

March 926±1410, in July 773±982 and in December it is 1345±1358mg/l. The annual mean TDS of DW strata during year 2012 is 1210±1491with CI of 261-2159mg/l at 95% significant level. The standard limit of TDS according to WHO & BIS is 500mg/l. There is a considerably high value for TDS in DW strata in the study area. Saline water contamination can be considered as the reason for this. DW2 is a station showing salinity throughout the year. Similar to the variation discussed in parameters EC, TH, Na, & Cl there is a hike in TDS of DW strata, after September. This is due to saline intrusion in shallow wells near the sea coast.

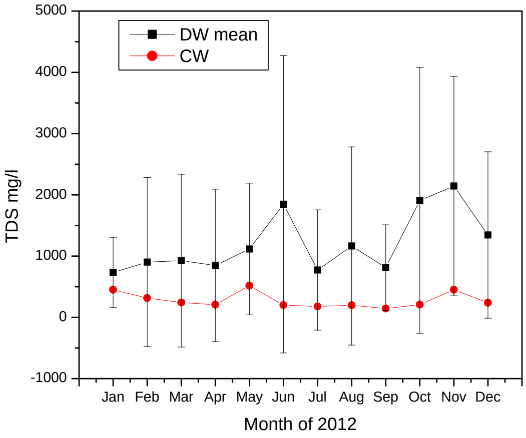

Figure 3.14: Monthly variation of Total Dissolved Solids (TDS) of dug well (DW) water sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

3.2.13 Dissolved Oxygen (DO)

The equilibrium concentration of dissolved oxygen (DO) in water in contact with air is a function of temperature and pressure. The concentration of other solutes also affects its concentration. At 5°C in freshwater the equilibrium DO is 12.75 mg/l. At 30°C the concentration is 7.54 mg/l. Photosynthesizing biota increases the DO whereas organic matter decomposition decreases it [42].

There are abiotic chemical reactions involving dissolved oxygen. Atmospheric oxygen is the principal electron sink for redox processes in the hydrosphere. Peroxide intermediate species are formed during these processes.

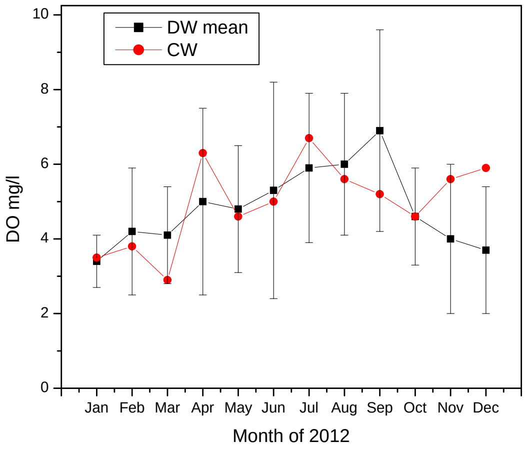

Figure 3.15: Monthly variation of Dissolved Oxygen (DO) of dug well (DW) water sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The 2012 annual average of DO of control well in the present study area is 4.98±1.15 with a range of 3.83-5.13mg/l (Figure 3.15). For shallow wells the DO in 2012 January is 3.4±0.7and in March it is 4.1±1.3mg/l. In Monsoon season as the atmospheric temperature decreases DO shows an increase. When temperature decreases atmospheric pressure increases and more oxygen dissolve making the DO high. In July DO is 6±2.1 and in December it is 3.7±1.7mg/l. The annual mean DO of DW strata during year 2012 is 4.83±1.96 with CI of 3.6-6.1mg/l at 95% significant level.

3.2.14 Biochemical Oxygen Demand (BOD)

Organic debris, or other kinds of material in the water, react with oxygen relatively slowly. The processes are biological, that is a suitable incubation and growth period is required for the organisms involved. As the organisms multiply, the rate at which they use oxygen may exceed the rate at which the dissolved oxygen in the water can be replenished from the atmosphere. So, the dissolved-oxygen concentration will decrease, sometimes drastically. The normal oxygen level of the water is re-established when the processes attain completion. If the oxidizable load is light, the oxygen level will not be depleted much. If considerable oxidizable material is present, the oxygen will be substantially depleted while the digestive processes are going on. Sometimes, a system may be so overloaded by pollutants that oxygen levels fall practically to zero and aerobic organisms are destroyed. To estimate the requirement of given water for oxygen, measurement of biochemical oxygen demand (BOD) is done.

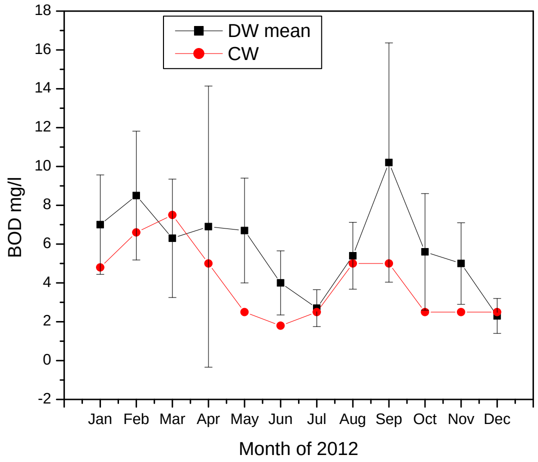

Figure 3.16: Monthly variation of Biochemical Oxygen Demand (BOD) of dug well (DW) water sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The 2012 annual average value of BOD of control well in the present study area is 4.23±1.9 with a range of 2.33-6.13mg/l (Figure 3.16). For shallow wells the BOD value in 2012 January is 7±2.6 which increases in February to 8.5±3.3 and decreases in March to 6.3±3. It again decreases in the subsequent months till July. So rainfall dilutes groundwater and in July it is 2.7±1. After July BOD shows an increase and reaches a maximum value in September and then decreases and become 2.3±1mg/lin December. The annual mean BOD of DW strata during year 2012 is 5.9±3.5with CI of 3.7 -8.1mg/l at 95% significant level. In certain months there is high BOD for selected stations. Then these wells have to be cleaned. So the BOD decreases. Most of the dug wells are contaminated with organic debris.

3.2.15 Sulphate (SO_4^{2-})

The element sulphur (S) exists in oxidation states ranging from +6 to -2. The chemical behaviour of sulphur is related strongly to redox properties of aqueous systems. In the most highly oxidized form, the effective radius of the sulphur ion is only 0.20 angstrom and it forms a stable, four-coordinated structure with oxygen, the sulphate (SO_4^{2-}) anion. Oxidation and reduction processes that involve sulphur species are inclined to be slow unless mediated by microorganisms.

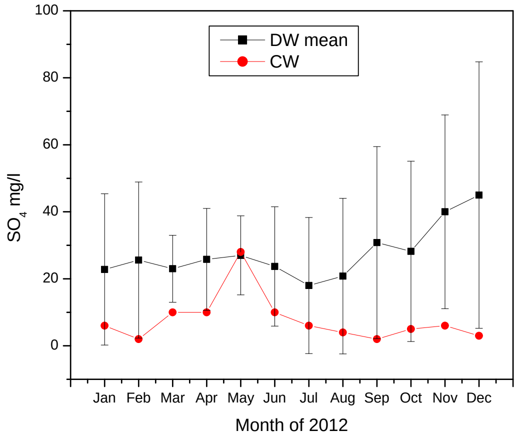

Figure 3.17: Monthly variation of sulphate of dug well (DW) water sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The 2012 annual average of sulphate of control well in the present study area is 4.8±2.5mg/l with range of 2.3-7.3 mg/l. For shallow wells, the sulphate concentration in 2012 January is 23±23 mg/l, in April 26±15 mg/l and remain almost steady till May 2012. It then decreases and become 18±20 mg/l in July and increases till December with 45±40 mg/l. Thus the annual mean of sulphate concentration of DW strata during year 2012 is 27±24 with CI of 12-42mg/l at 95% significant level. The BIS limit for sulphate is 200mg/l. So both CW & DW strata show very small concentration of sulphate.

3.2.16 Nitrate (NO_3^-)

Element nitrogen (N) is present in the atmosphere, hydrosphere, and biosphere at oxidation states covering the full range from N^{3-} to N^{5+}. Most of the Earth's atmosphere consist of nitrogen gas. Processes by which N_2 gas is changed in oxidation state and converted to chemical compounds containing nitrogen are generally called *"nitrogen fixatio*n*"*. Nitrogen in reduced or organic forms is converted by soil bacteria into nitrite and nitrate, which is commonly, termed *"nitrification"*. The nitrogen used by plants is largely in the oxidized form. Nitrate in anaerobic systems can be reduced by other strains of bacteria to nitrous oxide or nitrogen gas, which is called *denitrification*. Nitrogen oxides in the atmosphere undergo various chemical alterations that produce H^+ and finally leave the nitrogen as nitrate. The presence of nitrate (NO_3^-) or ammonium (NH_4^+) might be indicative of pollution but generally the pollution would have occurred at a site or time substantially removed from the sampling point.

In the present study area, nitrate determination conducted in year 2014 shows that control well (CW) has of 0.6mg/l and the DW strata shows an average 2.17±0.59mg/l. Analysis conducted in the year 2015 does not detect nitrate in CW. In the DW strata the average is 1.57±0.67mg/l. So nitrate pollution is not a problem in the present study area since permissible limit for WHO (50mg/l) and BIS (45mg/l) is more than the observed.

3.2.17 Phosphate (PO_4^{3-})

The element phosphorus (P) is fairly abundant in sedimentary rocks but most of its inorganic compounds have low solubility and biota use it as a nutrient. Being the group member of nitrogen, phosphorus can occur in oxidation states ranging from P^{3-} to P^{5+}. Its most common mineral form is calcium phosphate. Domestic and industrial sewage effluents remain as important sources of phosphorus. Reduced forms of phosphorus which are present in certain synthetic organic chemicals (like insecticides) are unstable in aerated water but may persist in reducing environment with significance. Organic phosphate species synthesized by plants and animals constitute a major fraction of the dissolved and particulate phosphorus in many natural waters.

The 2012 annual average of phosphate (PO_4^{3-}) of control well in the present study area is 0.09±0.05mg/l with range of 0.04-0.14mg/l. For shallow wells, the sulphate concentration in 2012 January is 0.15±0.07, in March 0.2±0.16, in July 0.13±0.07 and in December it is 0.23±0.1mg/l. Thus, the annual mean of phosphate concentration of DW strata during year 2012 is 0.19±0.14 with CI of 0.1-0.28mg/l at 95% significant level. Thus a considerable concentration of phosphate is not present in the study area. In all the stations phosphate is not detected.

3.2.18 Iron (Fe)

Although iron (Fe) is the second most abundant metallic element in the earth's outer crust, concentrations present in water generally are small. The chemical behaviour of iron and its solubility in water depend strongly on the oxidation intensity of the system in which it occurs; pH has a strong influence as well [43]. Though Iron is an essential element in the metabolism of animals and plants, if present in water in excessive amounts it forms redoxyhydroxide precipitates that stain laundry and plumbing fixtures and, therefore, is an objectionable impurity in domestic and industrial water supplies. For this reason, iron determinations are commonly included in chemical analyses of water. A recommended upper limit for iron in public water supplies is 0.3 mg/l. High concentrations of dissolved ferrous iron can occur in solution at the sites of either reduction of ferric oxyhydroxides (FeOOH) or oxidation of ferrous sulphides (FeS_2). In the latter process, the sulphur is attacked first and altered to sulphate, releasing the ferrous iron. Iron is present in organic wastes and in plant debris in soils, and the activities in the biosphere may have a strong influence on the occurrence of iron in water. Micro-organisms are commonly involved in processes of oxidation and reduction of iron, and some species may use these reactions as energy sources. Because of the unstable nature of ferrous iron in alkaline groundwater, the iron originally present may have been oxidized and precipitated by the time the analysis is made. To prevent this water for iron estimation is acidified using concentrated HCl at the time of sampling. In the present study area 0.1-0.4mg/l or lesser concentration of iron is found in shallow groundwater sources in certain months of year 2012. The control well (CW) water does not contain Iron. The WHO & BIS standard limit for Iron in water is 0.3mg/l.

3.3 Trace Element Study

Minor and trace constituents are those substances that occur in concentrations less than 1.0mg/l. More than the average abundance of an element in rocks, chemical properties of the element are more important in controlling its concentrations in water. Some supposedly insignificant trace constituents have vital importance to human health, plant nutrition, or other areas of general interest. Human activities have had a particularly strong influence on the occurrence of many of the minor constituents of water [44-46]. Present study area is particularly important for its black sand rich soil which contains trace elements. Trace element study was conducted using ICP-MS method for the elements lithium (Li), rubidium (Rb), caesium (Cs), strontium (Sr), barium (Ba), vanadium (V), chromium (Cr), manganese (Mn), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), silver (Ag), cadmium (Cd), aluminium (Al), gallium (Ga), indium (In), lead (Pb), arsenic (Ar), bismuth (Bi) and selenium (Se). The results are given in Table 3.4.

Compared with sodium and potassium, the other alkali metals-lithium, rubidium, and cesium-are rare. Lithium ions substitute for magnesium in some minerals. The common ion-exchange minerals in soil apparently adsorb lithium less strongly than they do other common elements. Therefore, when lithium is brought into solution by weathering reactions, it should tend to remain in the dissolved state. Lithium can be toxic to plants [40]. Citrus trees may be damaged by irrigation water containing 60 to 100 µg/L of lithium. In the present study area the average concentration of Lithium (Li) in shallow dug wells is 5.63±3.5 µg/l.

Rubidium (Rb) is much more abundant than lithium (Li). Its geochemical behaviour is somewhat like that of potassium (K) and it is generally more strongly held at cation-exchange sites than potassium (K). This characteristic tends to prevent the appearance of much rubidium in solution in natural water. The average concentration of Rubidium (Rb) is 13.15±7.2 µg/l.

Cesium(Cs) is a rarer element and is more strongly adsorbed by clays than either rubidium or lithium and its average concentration in the study area is 0.23±0.12 µg/l.

The chemistry of strontium is similar to that of calcium. It is a fairly common element and its carbonate and sulphate are common in sediments. The strontium-to-calcium ratio in most limestone is less than 1:1,000, although fossils in the limestone tend to be enriched in strontium. Strontianite is considerably less soluble than calcite. In the present study area the average concentration of Strontium in shallow dug wells is 592.82±339.5µg/l.

Barium (Ba) concentration is considerably less in carbonate rocks compared to Strontium (Sr). Barium ions have a larger radius than strontium ions and probably cannot as readily enter the crystal lattices of the carbonates of lighter alkaline-earth metals. The solubility of barium carbonate is about the same as that of calcite. Barium (Ba) is considered an undesirable impurity in drinking water; and its limit according to WHO is 700µg/l. Barium concentration in the present study area is 22.67±9.1 µg/l.

The transition metals commonly have more than one oxidation state that is thermodynamically stable in the presence of water. Several of these elements are likely to be present in water in the form of anionic complexes at neutral pH. In the aqueous geochemistry vanadium (V) forms V^{5+}anionic complexes with oxygen and hydroxide. So a fairly high solubility is possible in oxidizing alkaline environments but it has low solubility in reducing environments. Vanadium (V) is involved in many biochemical processes in nature. Coal and petroleum combustion releases Vanadium (V) element to the natural environment. In dug well (DW) strata the mean V is 2.52±1.32µg/l.

The crustal abundance of chromium (Cr) is similar to that of vanadium. In rock minerals the predominant oxidation state is Cr^{3+}. Dissolved chromium may be present as trivalent cations or as anions in which the oxidation state is Cr^{6+}. Chromite is highly resistant to weathering. Concentrations of chromium in natural waters that have not been affected by waste disposal are commonly less than 10 µg/l. The WHO limit of Cr is 50µg/l. In the present study area shallow dug wells show a mean Cr value of 0.35±0.11µg/l.

Manganese (Mn) can substitute for iron (Fe), magnesium (Mg), or calcium (Ca) in silicate structures. It is an undesirable impurity in water because of its tendency to deposit black oxide stains. It is an essential element for both plant and animal life forms. The WHO limit for Mn is 500µg/l. The concentration of Mn in the DW strata of the present study area is 4.65±3.66µg/l which is much lower than the standard limit.

The concentration of cobalt (Co) in the Earth's outer crust is similar to that of lithium (Li). The element is essential in plant and animal nutrition. Cobalt ions can substitute for part of the iron in ferromagnesian rock minerals and, like iron, cobalt may occur in 2^+ or 3^+ oxidation states. Co precipitation or adsorption of cobalt by oxides of manganese and iron appears to be an important factor in controlling the amounts that can occur in natural water. Cobalt is only a minor constituent of carbonate rocks. Uncontaminated natural water generally contains a few micrograms per litre of cobalt. Present study area can be considered as free of Co. Its concentration in dug well (DW) strata is only 0.1µg/l.

Table 3.4 Trace elemental concentrations shallow groundwater dug well (DW) sampling stations along Arattupuzha coast, Alappuzha, Kerala, India in the year 2012

Trace element	Unit	DW1	DW2	DW 3	DW4	DW5	DW6	$\bar{x} \pm \sigma$	BIS	WHO
Li	µg/l	6.8	11.4	1.8	3.2	3.4	7.2	5.6±3.5		-
Rb	µg/l	22.8	17.3	2.2	16.1	8.7	11.8	13.2±7.2		-
Cs	µg/l	0.1	0.3	ND	0.3	ND	ND	0.23±0.12		-
Sr	µg/l	633.3	459.1	555.7	198.1	493.5	1217.2	593±340		-
Ba	µg/l	14	35.4	15.6	19.4	18.9	32.7	23±9	700	700
V	µg/l	1.3	4.5	0.8	2.7	2.9	2.9	2.52±1.32		-
Cr	µg/l	0.2	0.4	0.3	0.5	0.4	0.3	0.35±0.1	50	50
Mn	µg/l	9.5	8.7	4.7	1.1	2	1.9	4.65±3.66	500	400
Co	µg/l	0.1	0.1	0.1	ND	0.1	0.1	41.68±36.22		-
Ni	µg/l	0.6	1	0.7	0.5	1.5	1.1	0.1±0.0	20	70
Cu	µg/l	2	2	1.4	2.7	4.9	4.7	0.9±0.37	1500	2000
Zn	µg/l	2.6	5.7	6.5	1.8	3.3	7	4.07±2.68	15000	-
Ag	µg/l	0.1	0.7	ND	0.1	0.4	0.2	4.48±2.19		-
Cd	µg/l	0.1	ND	ND	ND	0.1	ND	0.3±0.25	5	-
Al	µg/l	8.5	15.4	19.8	57.8	21.5	27.5	25.1±17.2	200	100
Ga	µg/l	2.7	6.1	3.2	4.2	3.6	5.7	4.3±1.4		-
In	µg/l	ND	ND	ND	ND	ND	ND	ND		-
Pb	µg/l	0.4	0.2	0.5	0.2	1.8	0.4	0.6±0.6	50	10
As	µg/l	1.3	0.2	0.7	1	3.2	1.6	1.3±1.0	50	10
Bi	µg/l	0.1	0.1	ND	0.1	ND	ND	0.1±0.0		-
Se	µg/l	4.2	3.7	4.4	4	4.2	4	4.1±0.2	10	40

Nickel (Ni) is an important industrial metal. Its concentration in most natural freshwater is somewhat greater than that of cobalt. Because of its extensive cultural use, nickel can be contributed to the environment in significant amounts by waste disposal. The WHO limiting value for Ni is 20µg/l. The concentration of Ni in the DW strata of the present study area is 0.9±0.37µg/l which is much lower than the standard limit.

Copper (Cu) is extensively used by modern civilization, and many of its uses result in its dispersal in the environment. It is an essential element in plant and animal metabolism. Copper (Cu) may be dissolved from water pipes and plumbing fixtures, especially by water whose pH is below 7. Copper salts are sometimes purposely added in small amounts to water-supply reservoirs to suppress the growth of algae. Organic and inorganic compounds of copper have been used extensively in agricultural pesticide sprays. The element is therefore likely to be more readily available for solution in surface and groundwater than its low average abundance in rocks might imply. The WHO limit for Cu is 1500µg/l. The concentration of Cu in the DW strata of the present study area is 4.07±2.68µg/l which is much lower than the standard limit.

Zinc (Zn) has about the same abundance in crustal rocks as copper (Cu) or nickel (Ni) and so it is fairly common. It has only one significant oxidation state, Zn^{2+} and tends to be substantially more soluble in most types of natural water than the other two metals. Zinc is essential in plant and animal metabolism, but water is not a significant source of the element in a dietary sense. Zinc (Zn) is widely used in metallurgy. It is a constituent of brass and bronze and is used for galvanizing, in which it is deposited as a coating over iron to inhibit corrosion. Zincalso is used extensively as a white pigment (zinc oxide) in paint and rubber industry. These applications tend to disperse the element widely in the environment. Its availability in water has been greatly enhanced by modern industrial civilization. WHO gave an upper limit of 15000µg/l for Zn. The concentration of Zn in the DW strata of the present study area is only 4.48±2.19µg/l which is much lower than the standard limit.

Silver (Ag) is extensively used by humans, especially in photography. It is a common minor constituent of industrial wastes. In most natural waters its concentration is less than 10µg/l. In 1976 U.S. Environmental Protection Agency suggested an upper limit of 50µg/l for silver. The concentration of Ag in the DW strata of the present study area is 0.3±0.25µg/l which is much lower than the standard limit.

Cadmium (Cd) has many similarities to zinc but cadmium is much less abundant. Cadmium is used for electroplating and for pigments used in paint, printing ink, and plastics. It is used extensively as a stabilizer for PVC plastic and in electrical batteries and fluorescent and video tubes. Many of these uses tend to make the cadmium available to water that comes in contact with buried wastes. Another factor of importance is the tendency for cadmium to enter the atmosphere through vaporization at high temperatures. Cadmium (Cd) may therefore be liberated to the environment in metallurgical processes and in the combustion of fossil fuel. WHO gave an upper limit of 5µg/l for Cd. In the present study Cd concentration of 0.1 µg/l is observed in few wells.

Aluminum (Al) is the third most abundant element in the Earth's outer crust but it rarely occurs in solution in natural water in considerable concentrations. Al occurs in substantial amounts in rock minerals and in clays. In low-pH conditions it may be precipitated as an aluminium hydroxysulphate. In the present study area the pH of water is not very low. Al concentration in DW strata is found to be 25.08±17.24µg/l. WHO gave an upper limit of 200µg/l for Al. Other two elements of the Aluminium group Galium (Ga) and Indium (In) concentrations are also determined. Galium(Ga) shows a mean of 4.25±1.38µg/l whereas, indium (In) is absent in DW strata.

Lead (Pb) is rather widely dispersed in sedimentary rocks but its natural mobility is low owing to the low solubility of lead hydroxy carbonates. Low pH water may dissolve considerable amounts of lead from lead pipe, and may also obtain lead from solder used to join copper pipe and fittings. WHO gave an upper limit of 50µg/l for Pb. But in the study area the Pb concentration in DW strata is only 0.58±0.61.

Arsenic (As) can be toxic to humans, it is considered a highly undesirable impurity in water supplies and an upper concentration limit of 50µg/l is set by WHO. The concentration of As in the DW strata of the present study area is only 1.33±1.03µg/l which is much lower than the standard limit. The concentration of bismuth (Bi) in DW strata is only 0.1 µg/l in certain wells.

Selenium (Se) is chemically similar to sulphur, but it is much less common. Higher selenium (Se) concentrations were found in water that had high dissolved-solids concentrations. WHO gave an upper limit of 10µg/l for Se. In the present study Se concentration of DW strata is found to be 4.08±0.24 µg/l.

3.4 Statistical Analysis

Water quality depends on several parameters, no single reason can be highlighted for its observed deterioration. There exist strong correlations among different parameters as evidence by Pearson matrix. A combined effect of these contributes towards total water quality. A systematic study of correlation and regression coefficients of the water quality parameters helps to assess the overall water quality of a region studied.

Correlation is one of a broad class of statistical relationships involving dependence. In common usage, it most often refers to the extent to which two variables have a linear relationship with each other. There are several correlation coefficients measuring the degree of correlation. The most common of these is the Pearson Correlation coefficient. Correlations are useful because they can indicate a predictive relationship that can be exploited in practice. 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.

The physico-chemical parameters for control well and dug well strata of the study area are analyzed by calculating Pearson's correlation coefficient (r). On studying the Pearson's correlation matrix for CW (Table 3.5), it is clear that no significant correlation is observed between pH and other parameters. It also shows close significant positive association of TH with Ca (r = 0.82), negative correlation of Ca with Mg (r = $^{-}$0.75), slight positive correlation of Na with Cl (r = 0.64).Other noticeable correlations are potassium to sulphate (0.61) and phosphate to BOD (0.64).

Table 3.5: Pearson correlation matrix for control well (CW) strata along Arattupuzha coast, Alappuzha, Kerala, India during year 2012

	pH	**EC**	**TDS**	**TH**	**Ca**	**Mg**	**Na**	**K**	**Fe**	**HCO_3**	**Cl**	**SO_4**	**PO_4**	**DO**	**BOD**
pH	1.00														
EC	-0.33	1.00													
TDS	-0.29	0.21	1.00												
TH	0.37	0.44	-0.27	1.00											
Ca	0.21	0.50	-0.38	0.82	1.00										
Mg	-0.01	-0.46	0.49	-0.50	-0.75	1.00									
Na	0.06	0.32	0.32	0.32	0.54	-0.38	1.00								
K	-0.04	0.27	0.77	-0.25	-0.26	0.46	0.31	1.00							
Fe	-0.12	-0.41	-0.17	-0.27	-0.17	-0.03	0.11	-0.20	1.00						
HCO_3	0.01	0.11	0.41	-0.01	-0.07	0.41	0.00	0.54	-0.02	1.00					
Cl	0.20	0.43	0.24	0.29	0.40	-0.48	0.64	0.25	-0.10	-0.11	1.00				
SO_4	-0.24	0.51	0.56	-0.18	-0.27	0.13	0.05	0.61	-0.04	0.30	0.51	1.00			
PO_4	-0.20	0.23	-0.07	0.10	0.16	-0.17	-0.25	-0.07	-0.12	0.52	-0.33	-0.14	1.00		
DO	-0.35	0.15	-0.42	0.02	0.32	-0.55	0.11	-0.43	0.47	-0.39	0.29	0.11	-0.19	1.00	
BOD	-0.42	0.21	0.23	0.11	0.15	-0.16	-0.01	-0.24	-0.20	0.15	-0.15	-0.20	0.64	-0.07	1.00

Table 3.6: Pearson Correlation matrix for dug well (DW) strata along Arattupuzha coast, Alappuzha, Kerala, India during year 2012

	pH	**EC**	**TDS**	**TH**	**Ca**	**Mg**	**Na**	**K**	**Fe**	**HCO_3**	**Cl**	**SO_4**	**PO_4**	**DO**	**BOD**
pH	1.00														
EC	-0.62	1.00													
TDS	-0.56	0.69	1.00												
TH	-0.62	0.98	0.66	1.00											
Ca	-0.67	0.97	0.64	0.99	1.00										
Mg	-0.46	0.70	0.44	0.73	0.71	1.00									
Na	-0.57	0.81	0.60	0.84	0.84	0.56	1.00								
K	-0.44	0.89	0.73	0.89	0.85	0.68	0.64	1.00							
Fe	-0.34	0.38	0.29	0.42	0.44	0.15	0.28	0.36	1.00						
HCO_3	-0.10	0.08	0.12	0.11	0.11	0.17	-0.35	0.25	0.06	1.00					
Cl	-0.43	0.92	0.71	0.91	0.89	0.52	0.81	0.91	0.34	-0.05	1.00				
SO_4	-0.57	0.78	0.47	0.71	0.69	0.56	0.53	0.69	0.31	0.12	0.60	1.00			
PO_4	0.43	0.04	0.27	0.00	-0.05	-0.10	0.12	0.12	-0.04	-0.25	0.27	-0.21	1.00		
DO	0.12	-0.40	-0.20	-0.35	-0.34	-0.62	0.07	-0.40	-0.16	-0.58	-0.19	-0.26	0.00	1.00	
BOD	-0.51	0.73	0.72	0.74	0.72	0.63	0.75	0.69	-0.03	-0.14	0.78	0.32	0.30	-0.20	1.00

Table 3.6 gives the Pearson's correlation matrix for DW strata. As in the case of CW no significant correlation is observed between pH and other parameters. Analysis of the correlation coefficient suggest that Electrical conductivity of drinking water is an important parameter and it is significantly correlated with TH (r = 0.98), Ca (r = 0.97), Na (r = 0.81), K (r = 0.89) and Cl (r = 0.92) and slightly correlated to TDS (r =0.69), Mg (r = 0.7) and sulphate (r =0.78). Thus EC is correlated to majority parameters. It indicates that EC increases with increase in each of these parameters. TDS show slight positive correlation to TH, Ca, Na, K, Cl and BOD. As in the case of CW strong positive correlation exist between TH and Ca (r = 0.99). Significant correlation is also present between TH and Cl (r = 0.91), Na and Cl (r = 0.81) and K and Cl (r = 0.91).

It may be suggested that drinking water quality can be checked effectively by controlling the conductivity of water. The correlation study and correlation coefficient can help in selecting a few parameters which could be frequently measured to determine the status of water quality regularly. This will help the regulatory bodies to act regulatory measures against deteriorating water quality and taking steps to implement control measures.

3.5 Water Quality Index (WQI)

A number of water quality parameters are discussed in the earlier sections. They are indicators of water quality. This data is used in the development of water quality indices (WQI). WQI has the capability to reduce the bulk of the information into a single value to express the data in a simplified and logical form. Thus WQI give a single value to express water quality of a source. These indices are most effective to communicate the information on water quality trends to the general public or to the policymakers and in water quality management.

Weighted arithmetic water quality index method classified the water quality according to the degree of purity by using the most commonly measured water quality variables (Table 3.7). In the present study the parameters used are pH, EC, TH, Ca, Mg, Na, K, HCO_3, Cl&SO_4.

Table 3.7: Classification of groundwater on the basis of Water Quality Index, WQI (Brown et al. 1972) [47].

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

Table 3.8: Monthly variation of WQI, Water Quality and Grading of Control well & Dug Well strata during year 2012

Year (2012)	**CW**			**DW**			
	WQI	**Water Quality**	**Grading**	**WQI** $\bar{x} \pm \sigma$	**WQI Range**	**Water Quality**	**Grading**
Jan	49	G	B	66±31	35-97	G-VP	B-D
Feb	44	G	B	76±52	24-128	E-UDP	A-E
Mar	55	P	C	99±39	60-138	P-UDP	C-E
Apr	51	G	B	84±35	49-119	G-UDP	B-E
May	45	G	B	68±25	43-93	G-VP	B-D
Jun	33	G	B	69±33	36-102	G-UDP	B-E
Jul	31	G	B	63±32	31-95	G-VP	B-D
Aug	32	G	B	69±37	32-106	G-UDP	B-E
Sep	33	G	B	74±38	36-112	G-UDP	B-E
Oct	30	G	B	90±49	41-139	G-UDP	B-E
Nov	21	E	A	79±48	31-127	G-UDP	B-E
Dec	35	G	B	81±45	36-126	G-UDP	B-E
$\bar{x} \pm \sigma$	38±10			77±39			
μ	38±7			77±25			
CI	31-45	G	B		52-102	P- UDP	C-E

The WQI calculated for CW and DW strata are given in Table 3.8. Along with that the water quality and the grading are also represented. The CW water shows *good* quality in most of the months except in March. In March, the WQI is 55 which come in the *poor* category and C grading. In November WQI is 21which shows *excellent* water quality and A grading. The annual mean value of WQI for CW strata is 38±10 and it vary from 31 to 45. As we see in the parameter wise discussion sections, the water of CW strata keep *good* quality throughout the year.

In DW strata in most of the months, the water quality ranges from *good* (G) to *unfit for drinking purpose* (UDP) category. In January and May the water quality index range is 35-97 and 43-93, which suggest that the quality of water of various shallow wells vary from *good* to *very poor*. In

February WQI range is 24-128. So in some stations, water show *excellent* quality and in others water is *unfit for drinking purpose*. In March, the hottest month in which evaporation is maximum, WQI is 60-138. So all shallow dug well stations have *poor quality* water. In some of them water is *unfit for drinking purpose*. There are some DWs which show high decline in quality based on parameters such as EC, Na, Cl etc. This is the reason for the poor quality water in those wells. For DW strata the 2012 annual mean for WQI is 77±39 and it vary from 52 to 102.Thus in the study area among the shallow groundwater sources only few of them keep good quality throughout the year.

3.6 Sodium – Chloride Ratio (Na/Cl)

The evaluation of the groundwater has been made with respect to the ratio of Na and Cl in the different strata of groundwater analyzed to check what phenomena governs the ratio. In ion exchange process Ca & Mg in water replaces Na in clays. Since Ca & Mg are removed from water this process is also called *natural softening*. In *reverse ion exchange* the opposite change occur and it is observed when highly saline waters come in contact with calcium rich clays. *Ion exchange* is observed if *Na/Na+Cl*> 0.5 and if *Na/Cl* > 1.0.

In the year 2012 the ratios calculated for CW are shown in Table 3.9.From the, less than 0.5 for *Na/Na+Cl*and less than 1.0 for Na/Cl, in the summer months of April and May, it can be inferred that *reverse ion exchange* is occurring. In all other month s*ion exchange* is the major process occurring. The annual mean of *Na/Na+Cl* is 0.6±0.1 and that of Na/Cl is 1.6±0.6.

In August, September and October the *Na/Na+Cl* ratio of dug well strata ranges from 0.5-0.7. Since it is higher than 0.5 only *ion exchange* is occurring in all stations. In all other months the upper limit is higher than

0.5 but the lower limit is less than0.5. So there are stations in which *reverse ion exchange* is prominent. The annual mean value of *Na/Na+Cl* is 0.5±0.2.

Na/Cl ratio is higher than 1.0 in August, but in September and October the lower limit is close to 1.0. So in August only *ion exchange* is the prominent process in all stations. In September and October, *reverse ion exchange* may occur in some stations. In all other months both processes are occurring. Increased concentration of sodium in saline water leads to the exchange of Na with Ca and Mg present in minerals which is called *reverse ion exchange*. Usually Ca & Mg have more chance to occupy active sites of minerals due to their smaller size and higher charge. The annual mean value of Na/Cl is 1.2±0.7.

Table 3.9: Monthly variation of Na/Na+Cl ratio, Na/Cl ratio & probable inference of Control Well of the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012

Year (2012)	$\frac{Na}{Na+Cl}$	$\frac{Na}{Cl}$	**Inference**
Jan	0.75	3.06	Ion exchange
Feb	0.60	1.52	Ion exchange
Mar	0.58	1.40	Ion exchange
Apr	0.45	0.81	Reverse ion exchange
May	0.48	0.93	Reverse ion exchange
Jun	0.51	1.03	Ion exchange
Jul	0.63	1.70	Ion exchange
Aug	0.61	1.57	Ion exchange
Sep	0.69	2.18	Ion exchange
Oct	0.70	2.30	Ion exchange
Nov	0.56	1.29	Ion exchange
Dec	0.59	1.46	Ion exchange
$\bar{x} \pm \sigma$	0.6 ±0.09	1.6 ±0.6	Ion exchange
μ	0.6 ±0.05	1.6 ±0.4	
CI	0.55-0.65	1.2-2.0	

IE-Ion Exchange RIE- Reverse Ion Exchange

Table 3.10: Monthly variation of Na/Na+Cl ratio, Na/Cl ratio & probable inference of DW strata Arattupuzha coast, Alappuzha, Kerala, India during year 2012

Year (2012)	$\frac{Na}{Na+Cl}$	Range	Inference	$\frac{Na}{Cl}$	Range	Inference
Jan	0.5 ±0.2	0.3-0.7	RIE-IE	1.6 ±1.1	0.5-2.7	RIE-IE
Feb	0.5 ±0.2	0.3-0.7	RIE-IE	1.1 ±0.6	0.5-1.7	RIE-IE
Mar	0.4 ±0.2	0.2-0.6	RIE-IE	0.8 ±0.4	0.4-1.2	RIE-IE
Apr	0.4±0.1	0.3-0.5	RIE-IE	0.8±0.3	0.5-1.1	RIE-IE
May	0.4±0.2	0.2-0.6	RIE-IE	0.9±0.5	0.4-1.4	RIE-IE
Jun	0.5±0.2	0.3-0.7	RIE-IE	0.9±0.5	0.4-1.4	RIE-IE
Jul	0.5±0.2	0.3-0.7	RIE-IE	1.2±0.7	0.5-1.9	RIE-IE
Aug	0.6±0.1	0.5-0.7	IE	1.9±0.6	1.3-2.5	IE
Sep	0.6±0.1	0.5-0.7	IE	1.5±0.7	0.8-2.2	RIE-IE
Oct	0.6±0.1	0.5-0.7	IE	1.5±0.8	0.7-2.3	RIE-IE
Nov	0.5±0.2	0.3-0.7	RIE-IE	1.1±0.7	0.4-1.8	RIE-IE
Dec	0.5±0.2	0.3-0.7	RIE-IE	1.3±0.8	0.5-2.1	RIE-IE
$\bar{x}\pm\sigma$	0.5±0.2		RIE-IE	1.2±0.7		RIE-IE
μ	0.5±0.1			1.2±0.4		
CI		0.4-0.6			0.8-1.6	

3.7 Irrigation Quality Studies

Neutral salts, heavy metals and organics and pathogenic organisms are the most harmful for soil, crops and groundwater. Neutral salts may accumulate in soils according to the intensity of irrigation, causing toxic damage to plants and reducing the availability of water for plants through a high osmotic pressure of the soil solution or through changes in soil structure and texture properties. Too high Cl^- contents generally affect tissues and plant leaves. Different crops require different irrigation water qualities. Therefore, testing the irrigation water is prior to contribute to effective management and utilization of the groundwater resources by clarifying relations among many hydrogeological considerations.

3.7.1 Electrical Conductivity (EC), Total Hardness (TH) & Total Dissolved Solids (TDS)

Three major water quality parameters EC, TH, & TDS are important to evaluate the irrigation quality of water(Table3.11).The primary effect of high

EC water on crop productivity was the failure of the plant to compete with ions in the soil solution for water. The higher the EC, the lesser the water available to plants. The soil may show wet, but the useable plant water in the soil solution decreases significantly as EC increases because plants can only transpire "pure" water. The amount of water transpired through a crop was directly related to yield; therefore, irrigation water with high EC reduces yield potential.

Table 3.11: Irrigation quality classification of groundwater on the basis of Electrical Conductivity(EC), Total Hardness(TH) & Total Dissolved Solids(TDS)

EC µS/cm		TH mg/l		TDS mg/l	
<250	Excellent(E)	<75	Soft(S)	<1000	Fresh(F)
250-750	Good(G)	75-150	Moderately hard(MH)	1,000-3,000	Slightly saline(SS)
750-2000	Permissible(P)	150-300	Hard(H)	3,000-10,000	Moderately saline(MS)
2000-3000	Doubtful(D)	>300	Very hard(VH)	10,000-35,000	High saline(HS)
>3000	Unsuitable(U)				

Table 3.12: Monthly variation of Electrical Conductivity (EC), Total Hardness (TH) & Total Dissolved Solids (TDS) of Control well of the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012

Year (2012)	Parameters					
	EC mS/cm	Inference	TH as $CaCO_3$ in mg/l	Inference	TDS mg/l	Inference
Jan	0.3	G	180	H	452	F
Feb	0.35	G	192	H	315	F
Mar	0.3	G	216	H	243	F
Apr	0.35	G	208	H	207	F
May	0.42	G	196	H	518	F
Jun	0.3	G	180	H	200	F
Jul	0.29	G	174	H	179	F
Aug	0.35	G	174	H	92	F
Sep	0.33	G	196	H	144	F
Oct	0.37	G	204	H	208	F
Nov	0.36	G	196	H	451	F
Dec	0.39	G	232	H	93	F
$\bar{x} \pm \sigma$	0.34 ±0.04	G	196±18	H	279 ±125	F
µ	0.34 ±0.03		196±11		279 ±80	
CI	0.31-0.37		185-207		199-359	

G-Good H-Hard F-Fresh

Table 3.13: Monthly variation of Electrical Conductivity (EC), Total Hardness (TH) & Total Dissolved Solids (TDS) of Dug well (DW) strata Arattupuzha coast, Alappuzha, Kerala, India during year 2012

Year (2012)	**Parameters**					
	EC mS/cm	**Inference**	**TH as $CaCO_3$ in mg/l**	**Inference**	**TDS mg/l**	**Inference**
Jan	0.8 ±1.0	G-P	211±87	MH-H	733 ±574	F-SS
Feb	1.1 ±1.6	G-D	223±158	S-VH	903 ±1381	F-SS
Mar	1.1 ±1.6	G-D	263±167	MH-VH	926 ±1410	F-SS
Apr	1.0±1.3	G-D	255±143	MH-VH	848±1245	F-SS
May	1.1±1.3	G-D	218±117	MH-VH	1121±1073	F-SS
Jun	0.8±0.9	G-P	214±111	MH-VH	1573±2274	F-MS
Jul	0.7±0.9	G-P	219±112	MH-VH	773±982	F-SS
Aug	0.8±1	G-P	212±96	MH-VH	1165±1618	F-SS
Sep	1.2±0.9	G-D	273±137	MH-VH	812±699	F-SS
Oct	2±2	G-U	435±406	S-VH	1907±2173	F-MS
Nov	2±2	G-U	438±296	MH-VH	2143±1790	F-MS
Dec	2±2	G-U	426±267	H-VH	1345±1358	F-SS
$\bar{x} \pm \sigma$	1.22±1.4		282±198		1187±1470	
μ	1.22±0.9		282±126		1187±936	
CI	0.3-2.1	G-D	156-408	H-VH	251-2123	F-SS

G-Good P-Permissible D-Doubtful S-Soft H-Hard MH- Moderately hard VH-Very Hard F-Fresh SS-Slightly Saline MS-Moderately Saline U - Unsuitable

The EC, TH and TDS of the CW are obtained from Table 3.14. Control well keeps almost steady EC throughout the year. In all the months the EC is below 750 μS/cm. That is the water is *good* for irrigation.TH of CW water is in the range 150-300mg/l, which shows that the water is *hard*. TDS are much lower than 1000mg/l. So no salinity is observed in CW or throughout the year CW water is in the *fresh* category.

Table 3.15 give the EC, TH and TDS of DW strata. The DWs selected for the present study shows wide variation in many of the parameters. There are some wells which show very low value for these parameters and some other wells which show very high value for the parameters.

Considering electrical conductivity, in January the water quality vary from *good* to *permissible*. In the following summer months the water quality varies from *good* to *doubtful* for irrigation. In those months the upper of EC exceed 2000 µS/cm. So the water of certain wells is exceeding the permissible limit suggested for irrigation. In June, July and August the water quality vary from *good* to *permissible* which suggest a lowering of EC. In October, November and December the upper value become 4000 µS/cm which shows unsuitability of water of those wells for irrigation. The annual mean EC variation of DW strata in the year 2012 is from 300 to 2100 µS/cm, which suggests the risk in using water of certain wells of the study area for irrigation.

Based on total hardness, in January DW show a quality variation from *moderately hard* to *hard*. In February quality vary from *soft* to *very hard* type. In the subsequent months till September water hardness suggest a quality variation of *moderately hard* to *hard*.In October *soft* to *very hard*. In November again *moderately hard* to *very hard* and in December *hard* to *very hard*. In all months in DW strata the mean TH exceed 300mg/l. In October, November and December the upper limit of TH become higher than 600mg/l, which shows *very hard* nature of water.

Considering TDS, in June, October and November the upper limit of TDS crosses 3000mg/l which indicate *moderate salinity* of water. In June station DW2 shows TDS of 6176mg/l. In October and November stations DW2, DW5 & DW6 show TDS higher than 3000mg/l. In all other months TDS variation shows that the water is *fresh* or *slightly saline* in nature.

A further assessment of irrigation quality of the water samples is done by calculating 6 well established parameters using the concentrations of various ions obtained from chemical analysis.

3.7.2 Kelly's ratio (KR)

Kelly devised an equation for the sodium in water. Water having KR less than 1.0 is considered suitable forirrigation. From Table3.15 it is clear that the CW water is suitable for irrigation in all the months based on Kelly's Ratio, because the KR is less than 1.0. The annual mean of KR for CW strata is 0.16±0.03 with a CI of 0.14-0.18 at 95% confidence level. In the case of DW strata Kelly's Ratio calculated is less than 1.0 till July which shows that the water of all shallow groundwater sources are suitable for irrigation. From August to December the upper limit of KR is higher than 1.0 and it is 2.4 in September and October, which shows the *unsuitability* of water for irrigation in some of the stations. The annual mean KR value is 0.8±0.6 with CI of 0.4-1.2.

3.7.3 Magnesium adsorption ratio (MAR)

Magnesium is essential for plant growth, but excess magnesium can have severe toxicity effect on plants. Magnesium in soil reduces the availability of potassium. Leaves of plants develop coppery colour along the marginal veins in the initial stage. Extensive coppery colour develops all over the leaf surface and defoliation of leaf occurs during the final stage of toxicity. The CW water is suitable for irrigation in all the months based on MAR, because MAR is less than 50 in all the months. The annual mean of MAR for CW strata is 15±10 with a CI of 9-21at 95% confidence level. The MAR for DW strata in January is 39±11and the range is below 50 which infers that water of all stations are *suitable* for irrigation. From February to December the range of MAR crosses the suitability limit 50 and hence, all well waters are not suitable for irrigation. Excess Mg present due to salt water intrusion damages the quality.

Table 3.14: Classification of groundwater on the basis of Kelly's ratio (KR), Magnesium Adsorption Ratio (MAR) & Permeability index (PI).

Parameters						
KR[*]		**MAR**[**]		**PI**[***]		
<1	Suitable(S)	<50	Suitable(S)	Class I	>75%	Good for irrigation(G)
>1	Unsuitable(US)	>50	Unsuitable(US)	Class II	25-75%	Good for irrigation(G)
				Class III	<25%	Unsuitable for irrigation(US)

* $KR = Na^{+} / \left(Ca^{2+} + Mg^{2+}\right)$ ** $MAR = Mg^{2+} \times 100 / \left(Ca^{2+} + Mg^{2+}\right)$ ***

$PI = [Na^{+} + \left(HCO_3\right)^{1/2}] \times 100 / [\,Ca^{2+} + Mg^{2+} + Na^{+}]$

Table 3.15: Variation of Irrigation water quality parameters Kelly's ratio (KR), Magnesium Adsorption Ratio (MAR) & Permeability index (PI) of CW strata of the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012

Year (2012)	**Parameters**					
	KR		**MAR**		**PI**	
	$\bar{x} \pm \sigma$	**Water Quality**	**$\bar{x} \pm \sigma$**	**Water Quality**	**$\bar{x} \pm \sigma$**	**Water Quality**
Jan	0.16	S	25.5	S	68	Class II(G)
Feb	0.20	S	6.2	S	61	Class II(G)
Mar	0.14	S	22.2	S	54	Class II(G)
Apr	0.17	S	0.0	S	57	Class II(G)
May	0.17	S	24.4	S	61	Class II(G)
Jun	0.12	S	30.8	S	61	Class II(G)
Jul	0.18	S	17.3	S	62	Class II(G)
Aug	0.15	S	8.7	S	59	Class II(G)
Sep	0.11	S	22.4	S	52	Class II(G)
Oct	0.12	S	11.7	S	60	Class II(G)
Nov	0.19	S	12.2	S	57	Class II(G)
Dec	0.15	S	0.0	S	51	Class II(G)
$\bar{x} \pm \sigma$	0.16±0.03		15±10		59±5	
μ	0.16±0.02		15±6		59±3	
CI	0.14-0.18	S	9-21	S	56-62	Class II(G)

S- Suitable G-Good

Table 3.16: Variation of irrigation water quality parameters; Kelly's ratio (KR), Magnesium Adsorption Ratio (MAR) & Permeability index (PI) of DW strata of the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012

Year 2012	**Parameters**								
	KR			**MAR**			**PI**		
	$\bar{x} \pm \sigma$	**Range**	**Water Quality**	**$\bar{x} \pm \sigma$**	**Range**	**Water Quality**	**$\bar{x} \pm \sigma$**	**Range**	**Water Quality**
Jan	0.5±0.3	0.2-0.8	S	39±11	28-50	S	73±13	60-86	G
Feb	0.5±0.3	0.2-0.8	S	33±22	11-55	S-US	68±15	53-83	G
Mar	0.5±0.3	0.3-0.8	S	37±20	17-57	S-US	62±14	48-76	G
Apr	0.5±0.2	0.3-0.7	S	37±25	12-62	S-US	65±14	51-79	G
May	0.5±0.3	0.2-0.8	S	37±20	17-57	S-US	68±15	53-83	G
Jun	0.5±0.2	0.3-0.7	S	38±19	19-57	S-US	70±12	58-82	G
Jul	0.5±0.3	0.2-0.8	S	31±20	11-51	S-US	68±15	53-83	G
Aug	1.1±1	0.1-2.1	S-US	33±22	11-55	S-US	74±13	61-87	G
Sep	1.4±1	0.4-2.4	S-US	39±18	21-57	S-US	72±17	55-89	G
Oct	1.4±1	0.4-2.4	S-US	33±18	15-51	S-US	70±11	59-81	G
Nov	0.9±0.4	0.5-1.3	S-US	32±17	15-49	S	64±10	54-74	G
Dec	0.8±0.5	0.3-1.3	S-US	28±20	8-48	S	62±17	45-79	G
$\bar{x} \pm \sigma$	0.8±0.6			35±19.6			73±13		
μ	0.8±0.4			35±12.5			68±15		
CI	0.4-1.2		S-US	22.5-47.5		S	62±14		G

S- Suitable US- Unsuitable G-Good

3.7.4 Permeability Index (PI)

Another important parameter to measure the suitability of groundwater for irrigation is the permeability index (PI). The permeability of soil is affected by long-term use of irrigation water and is also influenced by Na^+, Ca^{2+}, Mg^{2+} and HCO^{3-}contents in soil. Based on the permeability index (PI), water suitability classification for irrigation water was developed by Doneen [48]. Permeability Index, for control well is between 25 and 75 in all the months, with an average of 59±5 and CI 56-62. So the water comes under Class II category and good for irrigation in all months. PI calculated for DW strata show greater than 25% in all months, and hence water is good for irrigation based on PI throughout the year.

3.7.5 Sodium Adsorption Ratio (SAR)

SAR is a measure of the suitability of water for use in agricultural irrigation, as determined by the concentrations of solids dissolved in the water. It is also a measure of the sodicity of soil, as determined from analysis of water extracted from the soil.

Table 3.17: Classification of groundwater on the basis of Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC) and Soluble Sodium Percentage (SSP)

Parameters					
$SAR = Na^{+} / [(Ca^{2+} + Mg^{2+}) / 2]^{1/2}$		$RSC = (CO_3^{2-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+})$		$Na\% = Na^{+} \times 100 / (Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})$	
<10	Excellent(E)	<1.25	Good(G)	<20	Excellent(E)
10-18	Good(G)	1.25-2.50	Doubtful(D)	20-40	Good(G)
18-26	Doubtful(D)	>2.5	Unsuitable(US)	40-60	Permissible(P)
>26	Unsuitable(US)			60-80	Doubtful(D)
				>80	Unsuitable(US)

The higher the SAR the less suitable the water is for irrigation. If the SAR is higher than 6-9, the irrigation water will cause permeability problems in shrinking and swelling of clayey soil types. Irrigation using water with high SAR ratio may require soil amendments to prevent long term damage to the soil. When SAR is less than 3 there will not be a problem.

In the present study the SAR of CW strata range from 0.39-0.49 with an average of 0.44.The much lower values suggest the suitability of CW water for irrigation throughout the year (Table: 3.18).

In the case of DW strata the range of SAR is less than 10. In the months of September and October the upper limit comes close to 10. If the concentration of Ca and Mg decreases relative to sodium and the SAR index will be bigger. This will cause an alkalizing effect and increase the pH. So in spite of the higher value for some of the parameters the DW water sources keep an *excellent* quality for irrigation based on SAR throughout the year.

Table 3.18: Variation of Irrigation water quality parameters Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC) and Soluble Sodium Percentage (SSP) of control well (CW) strata of the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012 study area

Year (2012)	**Parameters**					
	$SAR = Na^+ / [(Ca^{2+} + Mg^{2+}) / 2]^{1/2}$		$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$		$Na\% = Na^+ \times 100 / (Ca^{2+} + Mg^{2+} + Na^+ + K^+)$	
	$\bar{x} \pm \sigma$	**Water Quality**	**$\bar{x} \pm \sigma$**	**Water Quality**	**$\bar{x} \pm \sigma$**	**Water Quality**
Jan	0.46	E	1.50	D	16.7	E
Feb	0.44	E	0.34	G	18.7	E
Mar	0.56	E	-0.14	G	12.8	E
Apr	0.42	E	0.02	G	15.5	E
May	0.49	E	0.72	G	17.1	E
Jun	0.47	E	0.57	G	11.4	E
Jul	0.32	E	0.50	G	15.5	E
Aug	0.48	E	0.04	G	13.4	E
Sep	0.41	E	-0.66	G	10.7	E
Oct	0.32	E	1.04	G	10.9	E
Nov	0.33	E	-0.20	G	16.1	E
Dec	0.52	E	-0.46	G	13.6	E
$\bar{x} \pm \sigma$	0.44±0.08		0.27±0.6		14.4±2.6	
μ	0.44±0.05		0.27±0.4		14.4±1.7	
CI	0.39-0.49	E	-0.13– 0.67	G	12.7-16.1	E

E- Excellent G- Good D-doubtful

Higher sodium concentration than calcium leads to the saturation of cation exchange complex with sodium. Alkaline soils are difficult to take into agricultural production. Due to the low infiltration capacity, rain water stagnates on the soil easily and, in dry periods, cultivation is hardly possible without copious irrigated water and good drainage.

Table 3.19: Variation of irrigation water quality parameters Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC) and Soluble Sodium Percentage (SSP) of DW strata of the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012

Year (2012)	**Parameters**								
	$SAR = Na^+ / [(Ca^{2+} + Mg^{2+}) / 2]^{1/2}$			$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$			$Na\% = Na^+ \times 100 / (Ca^{2+} + Mg^{2+} + Na^+ + K^+)$		
	$\bar{x}$ ±σ	**Range**	**Water Quality**	**$\bar{x}$ ±σ**	**Range**	**Water Quality**	**$\bar{x}$ ±σ**	**Range**	**Water Quality**
Jan	1.4±0.9	0.5-2.3	E	0.3±2.1	-1.8-2.4	G-D	35±14	21-49	G-P
Feb	1.3±0.8	0.5-2.1	E	-0.6±3	-3.6-2.4	G-D	34±14	20-48	G-P
Mar	1.4±0.7	0.7-2.1	E	-1.2±3.4	-4.6-2.2	G-D	33±13	20-46	G-P
Apr	1.5±0.7	0.8-2.2	E	-0.4±3.5	-3.9-3.1	G-US	34±12	22-46	G-P
May	1.4±0.7	0.7-2.1	E	-0.6±3	-3.6-2.4	G-D	34±12	22-46	G-P
Jun	1.4±0.8	0.6-2.2	E	-0.06±2.7	-2.8-2.6	G-US	35±13	22-48	G-P
Jul	1.4±0.7	0.7-2.1	E	-0.5±2.7	-3.2-2.2	G-D	34±13	21-47	G-P
Aug	3.4±3.8	-0.4-7.2	E	-0.4±2.1	-2.5-1.7	G-D	46±22	24-68	G-D
Sep	4.6±3.5	1.1-8.1	E	-2.6±2.6	-5.2-0	G	53±23	30-76	G-D
Oct	5.4±4.1	1.3-9.5	E	-5.5±8	-13.5-2.5	G-D	52±23	29-75	G-D
Nov	3.7±2.3	1.4-6.0	E	-4.1±5.5	-9.6-1.4	G-D	45±15	30-60	G-D
Dec	3.3±2.5	0.8-5.8	E	-4±4.5	-8.5-0.5	G	41±21	20-62	G-D
$\bar{x}$ ±σ	2.5±2.2			-0.75±4			40±17		
μ	2.5±1.4			-0.75±2.5			40±11		
CI		1.1-3.9	E		-3.25-1.75	G-D	29-51		G-P

E- Excellent G- Good D-doubtful P- Permissible US- Unsuitable

In USSL diagram, Sodium Adsorption Ratio (SAR) are plotted against Electrical Conductivity (EC) along Y-axis and X-axis respectively to classify water samples [50].

USSL diagram for DW strata illustrates that in most of the months, groundwater fall in the field of C3S1, indicating moderate water quality having *medium to high salinity and low sodium*. So it can be concluded that the groundwater of the study area can be used for irrigation on almost all types of soil with little danger of exchangeable sodium but the salinity level of water is moderate. Water having high salinity will be suitable for plants having good salt tolerance and hence restricted suitability for irrigation.

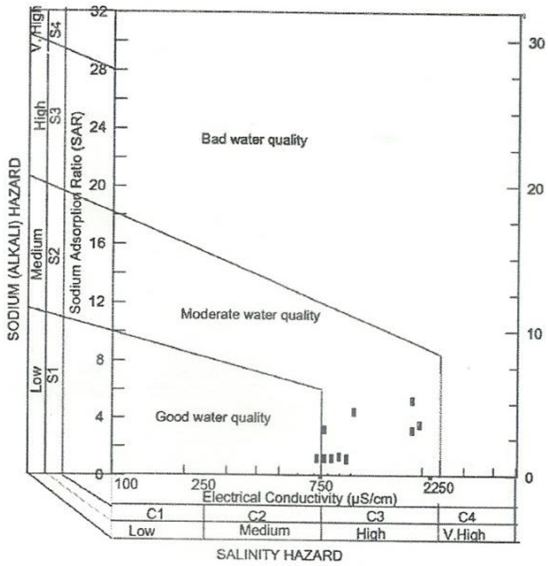

Figure 3.18: USSL Diagram for DW strata showing each month of year 2012

3.7.6 Residual sodium carbonate (RSC)

When the sum of carbonates and bi-carbonates is in excess of calcium and magnesium, there may be a possibility of complete precipitation of calcium carbonate and magnesium carbonate. RSC less than 1.25 are considered safe for irrigation. The RSC for CW strata is less than1.25, which show the good quality of CW water for irrigation in all months except January. In January RSC is 1.5 which indicates doubtful quality of water for irrigation due to higher concentration of bicarbonate. In the case of DW strata, in the months September and December, the upper limit in the range of RSC is lower than 1.25 which suggest that, based on RSC all the dug well stations have good quality water in those months. In April and June the upper limit exceed 2.5 indicating that the water quality ranges from *good* to *unsuitable* category. In all other months the range of RSC suggests a water quality variation of *good to doubtful* for irrigation. The annual mean RSC of year 2012 is -0.75±4.

3.7.7 Sodium percentage (Na%)

The Na% for CW strata is less than 20 in all months which shows the *excellent quality* of CW water for irrigation throughout the year. In the case of DW strata, from January to July the upper limit of Na% is higher than 40% which suggest that the water comes in the *good* to *permissible* category. After that, from August to December the upper limit of Na% becomes higher than 60% which suggest the quality variation of water from *good* to *doubtful* category.

Calculated percent sodium for groundwater in the study area is plotted against electrical conductivity (EC) in Wilcox diagram [51].

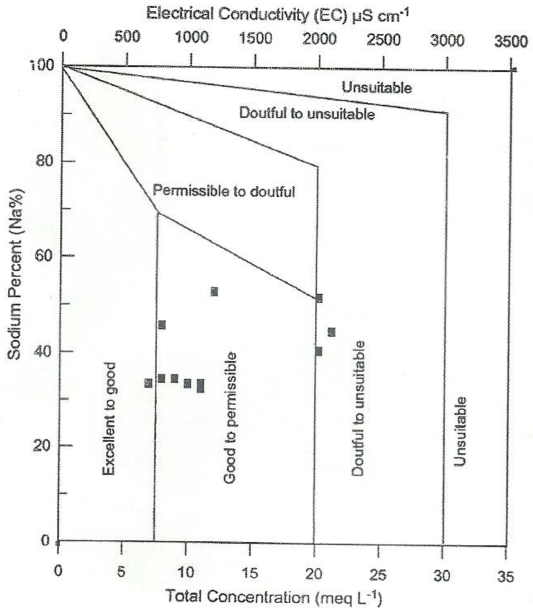

Figure 3.19: Wilcox Diagram for DW strata showing each month of year 2012

From Wilcox Diagram it is confirmed that water of DW strata comes in *Good to Permissible* category in most of the months and in *doubtful to unsuitable category* in the months of October, November and December.

After October, the increase in EC is the reason for the unsuitability of water for irrigation. In July the water is in *excellent* to *good* area because monsoon season decreases the EC to 700µS/cm.

Thus the different irrigation quality parameters consider the major water quality parameters and give inferences about the suitability of water for irrigation.

3.8 Corrosion Study: Saturation Indices

The corrosion of metallic and asbestos-cement distribution system can cause significant threat to health. Selecting the type of steel that will best tolerate the water quality conditions at a specific site requires careful consideration of several key indicators like pH, DO, H_2S, TDS, CO_2, Cl. Using the results of laboratory analyses, these indicators can forecast the potential for corrosion that the groundwater exhibits. Corrosion indices are useful to predict the potential for corrosion or scale-formation of water [52]. They are derived from chemical equilibrium equations for the $CaCO_{3(s)}$ system (Table 3.20).

3.8.1 Aggressiveness Index (AI)

This empirical indicator formula was developed for water's aggressiveness towards the corrosion of asbestos-cement pipes. AI higher than 12 for CW suggests that the water is *non-aggressive* in all months except in February (Table 3.21). In February AI is 11.8, which is less than 12 and so the water shows *moderately aggressive* nature. The annual mean of AI for CW is 12.3±0.3.AI calculated for DW strata suggest that the quality of water ranges from *moderately aggressive* (MA) to *non-aggressive* (NA) in all months (Table 3.22).

3.8.2 Langelier Saturation Index (LSI)

This index predicts the scaling of water based on the calcium carbonate equilibrium. If the actual pH of water is below the calculated pHs, the Langelier Index is negative, indicating that the water will dissolve calcium carbonate, and that it will be *corrosive*, particularly if DO is present. If the actual pH of water is higher than the calculate pHs, the Langlier Index is positive, indicating that incrustants (i.e., scaling) will likely occur. The LSI is temperature sensitive. The LSI becomes more positive as the water temperature increases [52].

In the present study, the LSI varies from -2 to +2 and the corresponding tendency of water are considered. From the LSI of CW strata, it is clear that the water is *slightly scale forming*. In February the value is little lower than 0 ($^{-}$0.04) which shows that water is in the category *slightly corrosive but non scale forming*. In January, September, October and November the LSI is higher than 0.5with the highest 1.13 in October which indicate that the water is in *scale forming but non corrosive* (SFNC) category.

In the case of DW, in January and February the lower limit of LSI is less than 0.0 and the upper limit is higher than 0.5, so the quality of water vary from *slightly corrosive but non scale forming* (SCNSF)to *scale forming but non corrosive* (SFNC). In June LSI vary from 0.1-0.5 and the water of all stations are coming in the category *slightly scale forming and corrosive* (SSFC). In March, April, May, August and December the tendency of water vary from *slightly scale forming and corrosive*(SSFC) to *scale forming but non corrosive*(SFNC). In other months also the variation of quality is from *slightly corrosive but non scale forming* (SCNSF) to *scale forming but non corrosive* (SFNC). The mean of LSI for DW is 0.4±0.4 which suggest the variation in quality from *slightly scale forming and corrosive* (SSFC) to *scale forming but non corrosive* (SFNC). So we can conclude that the Langelier Saturation Index of DW strata in various months of 2012 show a prominence of scale forming character rather than corrosive nature.

Table 3.20: Classification of groundwater on the basis of corrosion indices, Aggressiveness index (AI), Langelier Saturation Index (LSI) & Ryznar Stability index(RSI)

AI*	Tendency of water	LSI**	Tendency of water	RSI***	Tendency of water
< 10.0	Highly aggressive (HA)	$< {}^{-}2$	Intolerable corrosion (IC)	4.0 – 5.0	Heavy scale (HS)
		${}^{-}2$ - ${}^{-}0.5$	Serious corrosion (SC)	5.0 – 6.0	Light scale (LS)
10.0-11.9	Moderately aggressive (MA)	${}^{-}0.5$ - 0	Slightly corrosive but non scale forming (SCNSF)	6.0 – 7.0	Little scale or corrosion (LSC)
		0	Balancedbut pitting (BP)	7.0 – 7.5	Corrosion significant (CS)
> 12.0	Non-aggressive (NA)	0 – 0.5	Slightly scale forming and corrosive (SSFC)	7.5 – 9.0	Heavy corrosion (HC)
		0.5 - 2	Scale forming but non corrosive (SFNC)		

* AI = pH + log (AH)   ** LSI = pH - pHs   *** RSI = 2pHs – pH

Table 3.21: Variation of corrosion indices, Aggressiveness index(AI), Langelier Saturation Index(LSI) &Ryznar Stability index(RSI) of CW strata of the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Year (2012)	Parameters & Tendency of water					
	AI	Tendency of water	LSI	Tendency of water	RSI	Tendency of water
Jan	12.4	NA	0.66	SFNC	6.4	LSC
Feb	11.8	MA	-0.04	SCNSF	7.4	CS
Mar	12.3	NA	0.40	SSFC	6.8	LSC
Apr	12.1	NA	0.30	SSFC	7.1	CS
May	12.3	NA	0.46	SSFC	6.9	LSC
Jun	12.2	NA	0.33	SSFC	7.0	LSC
Jul	12.1	NA	0.26	SSFC	7.2	CS
Aug	12.2	NA	0.31	SSFC	7.0	LSC
Sep	12.8	NA	0.97	SFNC	6.2	LSC
Oct	13.0	NA	1.13	SFNC	6.2	LSC
Nov	12.4	NA	0.52	SFNC	6.7	LSC
Dec	12.3	NA	0.47	SSFC	6.8	LSC
$\bar{x} \pm \sigma$	12.3±0.3		0.48±0.3		6.8±0.4	
μ	12.3±0.2		0.48±0.2		6.8±0.2	
CI	12.1-12.5	NA	0.28-0.68	SSFC -SFNC	6.6-7.0	LSC

NA- Non-aggressive MA- Moderately aggressive SFNC- Scale forming but non corrosive SCNSF- Slightly corrosive but non scale forming SSFC- Slightly scale forming and corrosive LSC- Little scale or corrosion CS- Corrosion significant

Table 3.22: Variation of corrosion indices, Aggressiveness index(AI), Langelier Saturation Index(LSI) &Ryznar Stability index (RSI) of DW strata of the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012

Year (2012)	Parameters & Tendency of water					
	AI	Tendency of water	LSI	Tendency of water	RSI	Tendency of water
Jan	12.1±0.5	MA-NA	0.25±0.5	SCNSF- SFNC	7.3±0.7	LSC- HC
Feb	12.3±0.7	MA-NA	0.5±0.6	SCNSF- SFNC	7.0±0.8	LSC- HC
Mar	13±0.3	MA-NA	1.1±0.3	SSFC- SFNC	6.3±0.6	LS-LSC
Apr	12.6±0.4	MA-NA	0.7±0.4	SSFC- SFNC	6.7±0.6	LSC- CS
May	12.2±0.3	MA-NA	0.3±0.3	SSFC- SFNC	7.2±0.5	LSC- HC
Jun	12.2±0.3	MA-NA	0.3±0.2	SSFC	7.3±0.2	CS
Jul	12.2±0.4	MA-NA	0.3±0.4	SCNSF- SFNC	7.2±0.6	LSC- HC
Aug	12.4±0.3	MA-NA	0.5±0.3	SSFC- SFNC	7.0±0.5	LSC- CS
Sep	12.1±0.6	MA-NA	0.2±0.6	SCNSF- SFNC	7.4±0.9	LSC- HC
Oct	12.1±0.5	MA-NA	0.2±0.5	SCNSF- SFNC	7.3±1.0	LSC- HC
Nov	11.9±0.5	MA-NA	0.004±0.4	SCNSF- SSFC	7.2±0.8	LSC- HC
Dec	12.2±0.3	MA-NA	0.3±0.3	SSFC- SFNC	6.9±0.7	LSC- HC
$\bar{x} \pm \sigma$	12.2±0.4	MA-NA	0.4±0.4	SSFC- SFNC	7.1±0.7	LSC- CS
μ	12.2±0.3		0.4±0.3		7.1±0.4	
CI	11.9-12.5		0.1-0.7		6.7-7.5	

NA- Non-aggressive MA- Moderately aggressive SFNC- Scale forming but non corrosive SCNSF- Slightly corrosive but non scale forming SSFC- Slightly scale forming and corrosive LSC- Little scale or corrosion CS- Corrosion significant HC-Heavy corrosion

3.8.3 Ryznar Stability index (RSI)

RSI range of 4.0-9.0 and the corresponding tendency of water are given in Table 3.22. CW strata in most of the months come between 6 and 7 which indicate the water has *little scale or corrosion* (LSC) nature. In the months February, April and July the RSI is in the range 7.0-7.5 which shows *corrosion significant* (CS) nature of water. RSI of DW strata suggest that in most of the months water tendency vary from *little scale or corrosion* to *heavy corrosion* (LSC-HC). In March the lower mean suggest *light scale* forming nature. In June RSI of all stations suggest that the water is having *corrosion significant* nature. Understanding the corrosion and scaling potential of groundwater is important in determining the industrial use of water.

3.9 Piper plots and water quality studies

The composition of dominant ions can be displayed graphically by several methods. A more useful summation used in this study is the Hill-Piper Trilinear diagram [53]. It is used to infer hydrogeochemical facies. On this diagram, the relative concentrations of the major ions in percent meq/L are plotted on cation and anion triangles. The cation and anion fields are combined to show a single point in a diamond shaped field, from which inference is drawn on the basis of hydrogeochemical facies concept.

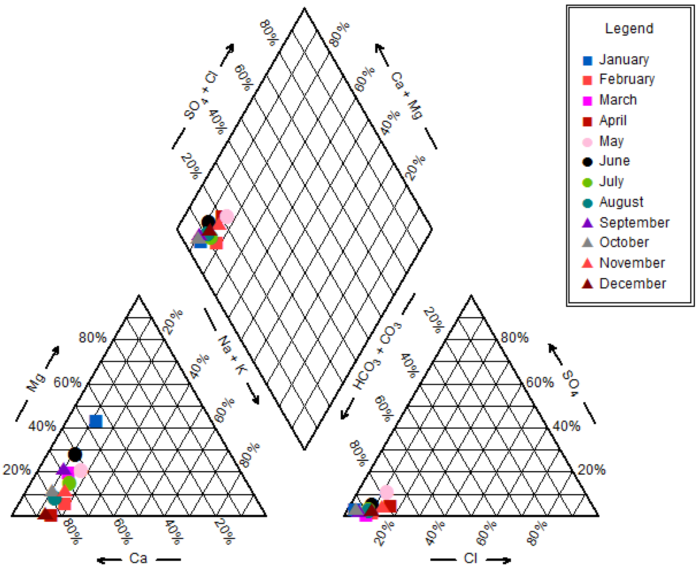

Figure 3.20: Hill-Piper-Trilinear Diagram for control well (CW) strata showing each month of year 2012

Piper trilinear plot prepared with the hydrochemical results of groundwater collected from CW during each month of year 2012 clearly illustrates that the water is Ca–Mg–HCO_3 type. All the points cluster in the region of *Temporary Hardness* (Figure 3.20). That is the water is rich in cations Ca and Mg and anion HCO_3. The rock type of the area is mainly calcite type [54]. Considering the cation triangle, in January 45% Ca, 42%

Mg & 13% Na+K are observed. In all other months a definite calcium apex is observed in the cation triangle. In the anion triangle all the data points cluster in the bicarbonate apex.

A thorough study of shallow groundwater sources in different months is done using Hill- Piper Trilinear diagrams.

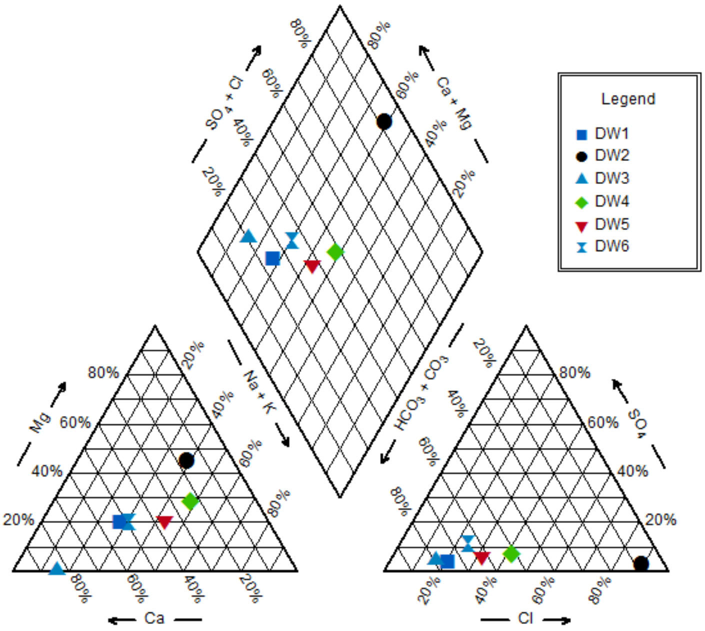

Figure 3.21: Hill Piper Trilinear Diagram showing dug well (DW) water sources in April 2012

Piper plot for DW water sources in April 2012, which represent a month in the summer season, indicates that majority stations lie in the region of *Temporary Hardness* (Figure 3.21). DW2 lies in the *Permanent Hardness*. In cation triangle the point corresponding to DW2 shows the prominence of Mg (44% Mg, 38% Ca & 18% Na+K). In the anion triangle the point is near the Cl apex (90% Cl and less than 10% HCO_3& SO_4^{2-}). So there is the presence of Chloride of Magnesium. Thus in the diamond area the point corresponding to DW2 is in border of saline area. DW1, DW4, DW5 & DW6 are close together.

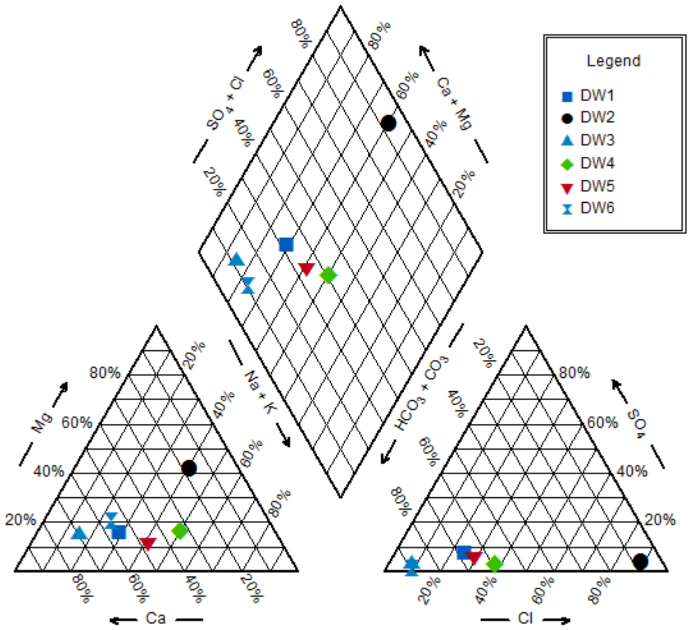

Figure 3.22: Hill Piper Trilinear Diagram showing DW water sources in July 2012

Considering DW4 which is close to saline region, from the cation triangle 30% Mg, 48% Na+K & 22% Ca are observed whereas from anion triangle 52% HCO_3, 40%Cl & 8% SO_4^{2-} are observed. The higher concentration of Na+K and comparatively higher concentration of Cl is the reason for the shift in the point to the saline region. In the case of DW3, from the cation triangle 82% Ca, 15% Na+K & negligible concentration of Mg are observed whereas from anion triangle 80% HCO_3, less than 20%Cl & less than 10% SO_4^{2-} are observed. So DW3, which is the control well, clearly shows Ca- HCO_3 type water and no salinity is observed in the water. In July 2012, which represent a month in the monsoon season, there is not much change in the positions of points in the Hill-Piper Trilinear plot except slight change in the cation triangle (Figure 3.22).

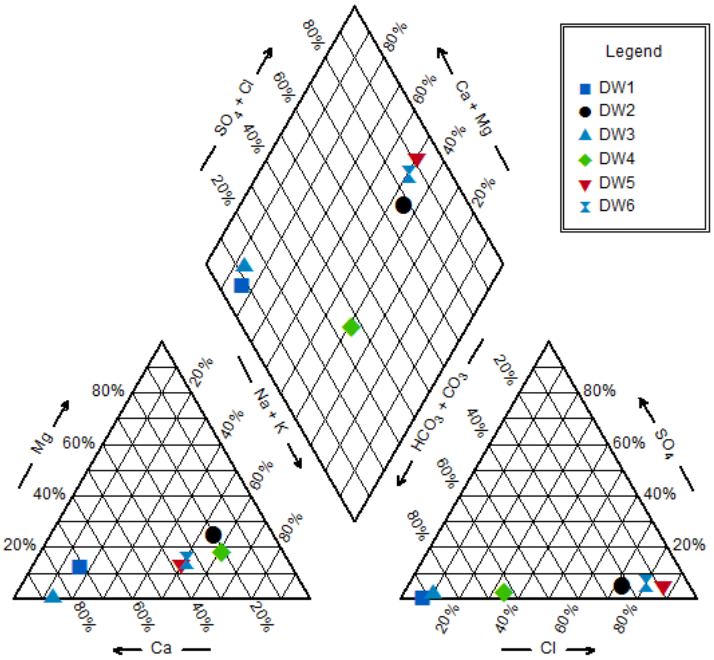

Figure 3.23: Hill Piper Trilinear Diagram showing DW water sources in December 2012

In DW3 there is slight increase in Mg concentration (70% Ca, 15% Mg & 15% Na+K). All stations except DW2 come in the Temporary Hardness area. DW4 in the border line of saline area. DW2 in the permanent hardness area but close to the border line separating permanent hardness area and saline area.

Piper plot of December 2012 (Figure 3.23) shows considerable variation. Points corresponding to all stations except DW3 show marked shift in position. So towards the end of the year stations DW2, DW5, DW6 exhibit distinct saline behaviour. In the anion triangle the points corresponding to these stations are close to the chloride apex. In the cation triangle also the increase in the concentration of Na+K is evident. So as we discussed in the session of parameters, after September there is salinity in some of the DW stations. DW4 shows a slight shift towards the alkali carbonate side. In the diamond area it comes in the *no dominant zone*, from cation triangle 60% Na+K, 22% Ca &18% Mg and from anion triangle 60% HCO_3, 35% Cl & 5% SO_4^{2-} are observed. So the station shows *sodium bicarbonate type* water. Since the chloride concentration is low, the source of sodium is not saline water. Points corresponding to DW1and DW3are close together in both triangles and in the diamond area, showing Ca- HCO_3 type water.

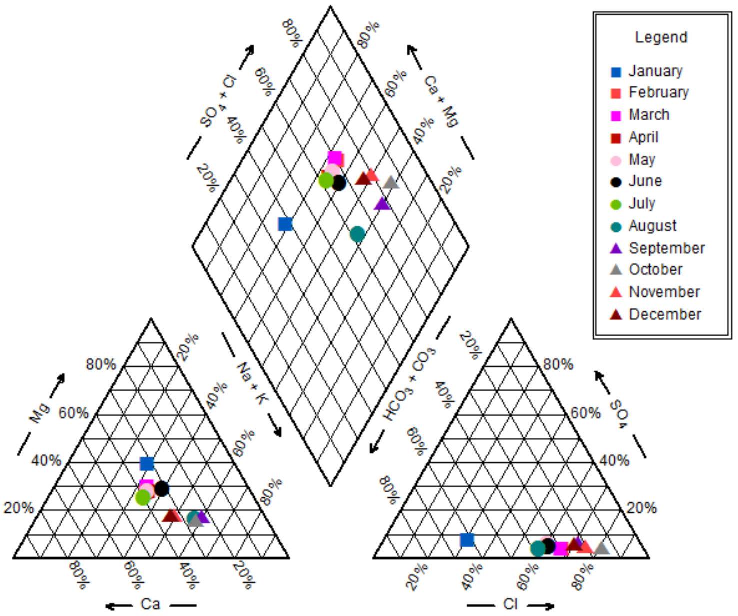

Figure 3.24: Hill Piper Trilinear Diagram showing monthly water type of DW strata in year 2012

Hill-Piper Trilinear plot prepared with the hydrochemical results of groundwater collected from DWs during each month of year 2012 identify a mixed nature of different hydrochemical facies mainly (i) Ca–Mg–HCO_3 (Temporay Hardness), (ii) Ca-Mg-Cl-SO_4 (Permanent Hardness) and (iii) Na– K–Cl(Saline). Few groundwater samples of the coastal area show Na-K-Cl facies during the post monsoon period. The results from the diamond area suggest that mixed cation-HCO_3 is the dominant hydrochemical facies for the surveyed groundwaters. Occasional shift to salinity can also be observed from the monthly plots. The principal water type depicts rock–water interaction involving the dissolution of carbonates by weathered zone above the underlying rocks. There is a tendency in the groundwater towards carbonate mineral saturation by dissolving calcite in the soil and bedrock in the recharge area. Saline water intrusion also damages the water quality.

3.10 Gibb’s Plot

Identifying and understanding the hydro geochemical processes are essential to evaluate the causes for changes in groundwater quality for planning groundwater protection. Gibbs plots are used to identify the mechanisms that control the groundwater chemistry of the study area [55]. A number of factors influence water chemistry. Gibbs proposed that rock weathering, atmospheric precipitation, evaporation and crystallisation control the chemistry of water.

The Gibb’s plot of anion ratio for DW strata (Figure 3.25) shows that most of the data points plot in the rock dominance zone except a few in the evaporation dominance zone which indicate that interaction between aquifer material and water is the major process controlling the groundwater chemistry of this area. Towards the end of the year 2012,(from September to December), the anion ratio become greater than 0.5, which shows the increase in the concentration of chloride. TDS values are higher than 1000mg/l which indicate salinity. The points corresponding to these data are present in the evaporation dominance area.

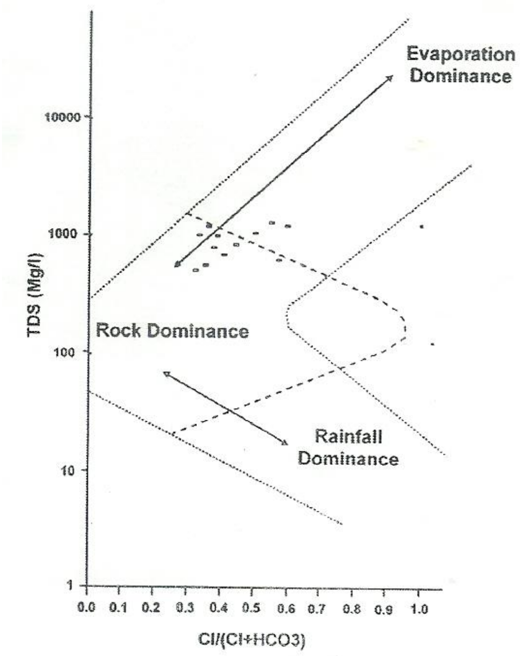

Figure 3.25: Gibb's plot of anion ratio against TDS for Dug Well strata during each month of year 2012

Similar behaviour is obtained in cation ratio plot (Figure 3.26). The data points equally distribute in the *rock dominance* and *evaporation dominance area*. The higher concentration of sodium after September leads to higher cation ratio and the data points are present in the evaporation dominance area. No point comes in the rainfall dominance area.

Thus from Gibb's plots for anion ratio and cation ratio of shallow groundwater sources, the major processes occurring in these stations are rock weathering and evaporation.

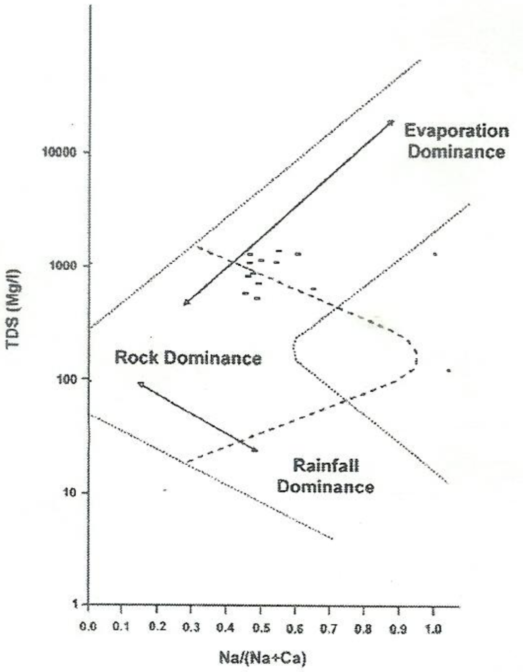

Figure 3.26: Gibb's plot of cation ratio against TDS for Dug Well strata during each month of year 2012

3.11 Total Carbon analysis

TOC analysis is widely used for water quality control

- Total Carbon (TC) – all the carbon in the sample, including both inorganic and organic carbon
- Total Inorganic Carbon (TIC) – often referred to as inorganic carbon (IC) include carbonates, bicarbonates and dissolved carbon dioxide (CO_2).
- Total Organic Carbon (TOC) – material derived from decaying vegetation, bacterial growth, and metabolic activities of living organisms or chemicals.

A total organic carbon analyzer determines the amount of carbon in a water [56]. By acidifying the sample and flushing with nitrogen the sample removes inorganic carbon, leaving only organic carbon sources for measurement. TOC analyzers measure the CO_2 formed when organic carbon is oxidized. Non-volatile organic carbon (OC) levels of uncontaminated groundwater are generally 0.1-4mg/l. Inorganic carbon may exceed 100-200mg/l depending on pH, temperature and partial pressure of CO_2.

The carbon analysis of shallow groundwater sources reveal that, major contribution is of inorganic origin and organic carbon is mostly negligible in some samples. Only one station (DW4) shows a considerable contribution of organic carbon, 6.14mg/l. The mean TC of DW strata is 34±14, TIC is 34±14 and TOC is 1.7±2.3.

Table 3.23: Total carbon (TC), total inorganic carbon (TIC) & total organic carbon (TOC) of various shallow groundwater sources of the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012

Station	TCmg/l	TICmg/l	TOCmg/l
DW1	40.00	39.74	0.26
DW2	48.83	46.99	1.85
DW3	20.56	19.50	1.06
DW4	14.53	8.39	6.14
DW5	48.83	48.79	0.04
DW6	32.41	31.80	0.61
$(\bar{x})\pm SD(\sigma)$	34±14	34±14	1.7±2.3

TOC measurements are superior to laborious manual determinations of chemical (COD) or biological (BOD) oxygen demand as their methodologies are biased by the presence of reducing agents, refractory compounds or toxic materials. TOC determinations are frequently required by regulatory agencies for compliance monitoring

3.12 Designated Best Use

In India, Central Pollution Control Board (CPCB), Ministry of Environment and Forest, Government of India has identified water quality requirements in terms of a few chemical characteristics, known as primary water quality criteria. Central Pollution Control Board classified the water into fiveclasses i.e.; from A to E on the basis of their designated best use (DBU) (Table 3.24). The classification has been made in such a manner that with the degradation in quality, the water quality requirement becomes progressively lower from A to E. The study area is designated with a specific use mostly domestic and irrigation which demands higher/purest quality is decided based on designated-best-use. This system of classification of fresh and saline waters are also adopted by BIS to meet the essential requirement of the people [57-59].

In 2012 December biological analysis of shallow groundwater samples revealed the presence of total coliform and E.coli in different stations. Other parameters of 2012 December are used to infer the class of water of various shallow groundwater sources based on CPCB (Table3.25). In all stations pH is between 6.5-8.5. Biological analysis shows that 3 stations have total coliforms MPN/100ml 1100 or more. The possibility of different stations to come in A, B, C, or D class is evaluated and it is found that DW3& DW4 comes in class C. To come in class A, DO should be 6 or more. To come in class B total coliforms MPN/100ml should be ≤ 500 and DO should be ≥ 5. So the selected dug well water sources are not coming in either class A or class B.

Table 3.24: 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**

Table 3.25: Classification of dug well stations based on designated best use by CPCB

Station	**Total coliforms MPN/100ml**	**E. Coli**	**pH**	**DO mg/l**	**BOD mg/l**	**Class**
DW1	23	Present	7.4	4.6	2.5	-
DW2	>1100	Present	7.5	1	2.5	-
DW3	1100	Present	7.8	5.9	2.5	Class C
DW4	75	Absent	7.9	4.4	1.3	Class C
DW5	290	Absent	7.3	3.6	3.8	-
DW6	>1100	present	7.1	2.5	1.3	-

Biological examination is done for determining the causes of objectionable tastes and odours in water and controlling remedial treatments, in helping to interpret the results of various chemical analyses, and in explaining the causes of clogging in distribution pipes and filters.

3.13 Overall Water Quality of the Region

This chapter of the thesis elaborately discusses the monthly variation of groundwater quality of shallow groundwater sources along the study area in the year 2012. The mean values of various physico-chemical characteristics of shallow groundwater sources of the study area are compared with the IS and WHO standards in Table 3.26. The mean values during each month are compared with IS 10500: 2012 & WHO standards in Table 3.27.

As per BIS (IS 10500: 2012) drinking water is water intended for human consumption for drinking and cooking purposes from any source. It includes water (treated or untreated) supplied by any means for human consumption. Drinking water shall comply with the requirements such as organoleptic and physical parameters, general parameters concerning substances undesirable in excessive amounts, parameters concerning toxic substances and parameters concerning radioactive substances. Analysis of pesticide residues shall be conducted by a recognized laboratory using internationally established test method meeting the residue limits. Drinking water shall also comply with bacteriological requirements, virological requirements and biological requirements.

Table 3.26: Physico-chemical characteristics of shallow ground water sources of the study area

Sl. No	Parameter	Mean $(\bar{x})$±SD(σ)	True Value(μ)	Confidence Interval(CI)	Drinking water standard as per IS 10500 : 2012		WHO 2011	
					Acceptable	Permissible	Most desirable	Max. allowable
1	Temperature °C	29.9±1.1	29.9±0.7	29.2-30.6	-	-	-	
2	pH	7.8±0.4	7.8±0.2	7.6-8.1	6.5-8.5	No relaxation	6.5-8.5	No relaxation
3	EC (mS/cm)	1.2±1.4	1.2±0.9	0.3-2.1	-	-	1.5	-
4	Eh mV	-50±22	-50±14	-64--36	-	-	-	-
5	DO (mg/l)	4.83± 1.96	4.83± 1.24	3.6-6.1	-	-	-	-
6	BOD (mg/l)	5.9± 3.5	5.9± 2.2	3.7 -8.1	-	-	-	-
7	TA(mg/l)as$CaCO_3$	199± 80	199± 51	148-250	200	600	-	-
8	TH(mg/l)as $CaCO_3$	282± 198	282± 126	156-408	300	600	100	500
9	TDS(mg/l)	1210± 1491	1210±949	261-2159	500	2000	500	1500
10	Ca (mg/l)	69± 47	69± 30	39-99	75	200	75	200
11	Mg (mg/l)	28± 29	28± 19	9--47	30	100	50	150
12	Na (mg/l)	107± 127	107± 81	26-188	-	-	-	200
13	K (mg/l)	12.9± 8.7	12.9± 5.5	7.4-18.4	-	-	-	12
14	Fe (mg/l)	0.08±0.14	0.08±0.14	0-0.22	0.3	No relaxation	0.1	-
15	HCO_3^- (mg/l)	242± 98	242± 62	180-304	-	-	-	-
16	Cl^- (mg/l)	311± 484	311± 308	3-619	250	1000	250	600
17	SO_4^{2-} (mg/l)	27± 24	27± 15	12--42	200	400	250	400
18	PO_4^{3-} (mg/l)	0.19±0.14	0.19±0.09	0.1-0.28	-	-	-	-
19	NO_3^- (mg/l)	1.6±0.7	1.6±0.7	0.9-2.3	45	No relaxation	50	-
Trace Elements								
20	Li (μg/l)	5.6±3.5	5.6±3.6	2-9.2	-	-	-	
21	Rb(μg/l)	13.2±7.2	13.2±7.4	5.8-20.6	-	-	-	
22	Cs (μg/l)	0.23±0.12	0.23±0.12	0.11-0.35	-	-	-	
23	Sr (μg/l)	593±340	593±346	247-939	-	-	-	
24	Ba(μg/l)	23±9	23±9	14-32	700	No relaxation	700	No relaxation
25	V (μg/l)	2.52±1.32	2.52±1.34	1.18-3.86	-	-	-	
26	Cr (μg/l)	0.35±0.1	0.35±0.1	0.25-0.45	50	No relaxation	50	No relaxation
27	Mn (μg/l)	4.65±3.66	4.65±3.74	0.91-8.39	100	300	400	No relaxation
28	Co (μg/l)	0.1±0.0	0.1±0.0	0.1	-	-	-	
29	Ni (μg/l)	0.9±0.37	0.9±0.38	0.52-1.28	20	No relaxation	70	No relaxation
30	Cu (μg/l)	4.07±2.68	4.07±2.73	1.34-6.3	50	1500	2000	No relaxation
31	Zn (μg/l)	4.48±2.19	4.48±2.24	2.24-6.72	500	15000	-	-
32	Ag (μg/l)	0.3±0.25	0.3±0.26	0.04-0.56	100	No relaxation	-	-
33	Cd (μg/l)	0.1±0.0	0.1±0.0	0.1	3	No relaxation	-	-
34	Al (μg/l)	25.1±17.2	25.1±17.6	7.5-42.7	30	200	100	No relaxation
35	Ga (μg/l)	4.3±1.4	4.3±1.4	2.9-5.7	-	-	-	-
36	In (μg/l)	ND	ND	ND	-	-	-	-
37	Pb (μg/l)	0.6±0.6	0.6±0.6	0-1.2	10	No relaxation	10	No relaxation
38	As (μg/l)	1.3±1.0	1.3±1.0	0.3-2.3	10	50	10	50
39	Bi (μg/l)	0.1±0.0	0.1±0.0	0.1	-	-	-	-
40	Se (μg/l)	4.1±0.2	4.1±0.2	3.9-4.3	10	No relaxation	40	No relaxation

Table 3.27: Physico-chemical characteristics of shallow ground water sources of the study area during each month of year 2012

Strata	Data	pH	Eh	EC mS/cm	TH mg/l	Alkalinity mg/l	TDS mg/l	DO mg/l	BOD mg/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Fe mg/l	HCO_3 mg/l	Cl mg/l	SO_4 mg/l	PO_4 mg/l
	$\bar{x}\pm\sigma$	7.8±0.3	-44±14	0.34±0.04	196± 18	211± 27	280± 125	4.98± 1.15	4.23± 1.9	67± 12	7± 5	14±3	2.1± 2	ND	258± 34	16± 7	4.8± 2.5	0.09± 0.05
CW2012	Range	7.5-8.1	-58- -30	0.3-0.38	178-214	184-238	155-405	3.83-5.13	2.33-6.13	55-79	2-12	11-17	1.9-4.1		224-292	9--23	2.3-7.3	0.04-0.14
DW2012	$\bar{x}\pm\sigma$	7.8± 0.4	-39± 22	0.75± 1.01	211± 87	209± 79	733± 574	3.4± 0.7	7± 2.6	44± 16	36±20	45.6± 38.1	10.2± 6.4	ND	255± 97	147± 264	23± 23	0.15±0.07
January	Range	7.4-8.2	-61- -17	0-1.76	124-298	130-288	159-1307	2.7-4.1	4.4-9.6	28-60	16-56	7.5-83.7	3.8-16.6		158-352	0-411	0-46	0.08-0.22
DW2012	$\bar{x}\pm\sigma$	8.0± 0.6	-55± 30	1.08± 1.64	223± 158	194± 41	903± 1381	4.2± 1.7	8.5± 3.3	53± 19	22± 32	47± 41	12± 10	0.4	237± 50	304± 630	26± 23	0.1± 0.06
February	Range	7.4-8.6	-85- -25	0-2.72	65-381	153-235	0- 2284	2.5-5.9	5.2-11.8	34-72	0-54	6--88	2--22		187-287	0-934	3--49	0.04-0.16
DW2012	$\bar{x}\pm\sigma$	8.6± 0.1	-90± 6.1	1.14± 1.61	263± 167	205± 68	926± 1410	4.1± 1.3	6.3± 3.1	58± 21	29± 37	53± 39	13±9.4	ND	251±83	326±623	23±10	0.2±0.16
March	Range	8.4-8.7	-96- -85	0-2.75	96-430	137-273	0- 2336	2.8-5.4	3.2-9.4	37-79	0-66	14-92	3.6-22.4		168-334	0-949	13-33	0.04-0.36
DW2012	$\bar{x}\pm\sigma$	8.1±0.4	-64±31	1.01±1.29	255±143	237±105	848±1245	5.0±2.5	6.9±7.2	59±25	26.4±33	55.6±42.3	13±7.6	ND	289±127	274±502	26±15	0.27±0.23
April	Range	7.7-8.5	-95- -33	0-2.3	112-398	132-342	0-2093	2.5-7.5	0-14.1	34-84	0-59.4	13.3-97.9	5.4-20.6		162-416	0-776	11--41	0.04-0.50
DW2012	$\bar{x}\pm\sigma$	7.9±0.3	-53±19	1.06±1.32	218±117	190±56	1121±1073	4.8±1.7	6.7±2.7	50.4±20	22.4±25	48±37	11±3.6	ND	231±68	234±437	31±15	0.4±0.28
May	Range	7.6-8.2	-72- -34	0-2.38	101-335	134-246	48-2194	3.1-6.5	4.0-9.4	30.4-70.4	0-47.4	11--85	7.4-14.6		163-299	0-671	16-46	0.12-0.68
DW2012	$\bar{x}\pm\sigma$	7.9±0.4	-51±24.4	0.89±0.93	214±111	205±62	1847±2429	5.3±2.9	4.0±1.7	45.4±11	25±28	57±37	14±6	0.3±0.1	250±76	255±426	24±**18**	0.19±0.13
June	Range	7.5-8.3	-75- -27	0-1.82	103-325	143-267	0-4272	2.4-8.2	2.3-5.7	34.4-56.4	0-53	20-94	8--20	0.2-0.4	174-326	0-681	6--42	0.06-0.32
DW2012	$\bar{x}\pm\sigma$	7.8±0.4	-47±22	0.75±0.9	219±112	194±58	773±982	6±2.1	2.7±1	54.4±18	20.3±26	48±38	10±6.6	0.2±0.1	237±71.1	205±398	18±20	0.13±0.07
July	Range	7.4-8.2	-69- -25	0-1.65	107-331	136-252	0-1755	3.9-8.1	1.7-3.7	36.4-72.4	0-46.3	10--78	3.4-16.6	0.1-0.3	166-308	0-603	0-38	0.06-0.2
DW2012	$\bar{x}\pm\sigma$	8.0±0.4	-60±23	0.83±0.96	212±96	190±54	1165±1618	6.0±1.9	5.4±1.7	53±20	20±23	126±178	9.4±7.6	ND	232±66	205±407	21±23	0.13±0.1
August	Range	7.6-8.4	-83- -37	0-1.79	116-308	136-244	0-2783	4.1-7.9	3.7-7.1	33-73	0-43	0-304	1.8-17.0		166-298	0-612	0-44	0.03-0.23
DW2012	$\bar{x}\pm\sigma$	7.8±0.5	-48±29	1.16±0.9	273±137	143±58	812±699	6.9±2.7	10.2±6.2	65±38	27±22	183±163	12±7.4	ND	175±70	309±348	31±29	0.14±0.11
September	Range	7.3-8.3	-77- -19	0.26-2.06	136-410	85-201	113-1511	4.2-9.6	4-16.4	27-103	5--49	20-346	4.6-19.4		105-245	0-657	2--60	0.03-0.25
DW2012	$\bar{x}\pm\sigma$	7.7±0.2	-40±14	2±2.1	435±406	159±91	1907±2173	4.6±1.3	5.6±2.93	113±108	37±37	278±268	16±10	0.1	194±111	581±681	28±27	0.17±0.04
October	Range	7.5-7.9	-54- -26	0.1-4.1	29-841	68-250	0-4080	3.3-5.9	2.7-8.5	5-221	0-74	10-544	6--26	0.1	83-305	0-1262	0-55	0.13-0.21
DW2012	$\bar{x}\pm\sigma$	7.2±0.2	-17±9.4	2.11±1.91	438±296	233±130	2143±1790	4.0±2	5.0±2.1	116±82	36±31	194±161	18±12	ND	284±159	527±534	40±29	0.25±0.07
November	Range	7-7.4	-26.4- -7.6	0.2-4.02	142-734	103-363	353-3933	2--6	2.9-7.1	34-198	5--67	33-355	6--30	ND	125-443	0-1061	11--69	0.18-0.32
DW2012	$\bar{x}\pm\sigma$	7.5±0.3	-30±17	1.96±1.83	426±267	225±108	1345±1358	3.7±1.7	2.3±1	116±65	33.2±35	177±163	16±13	ND	274±131	436±452	45±40	0.23±0.1
December	Range	7.2-7.8	-47- -15	0.13-3.79	159-693	117-333	0-2703	2-5.4	1.3-3.3	51-181	0-68.2	14-340	3--29	ND	143-405	0-888	5--85	0.13-0.33
DW2012	$\bar{x}\pm\sigma$	7.8±0.4	-50±22	1.2±1.4	282± 198	199± 80	1210± 1491	4.83± 1.96	5.9± 3.5	69± 47	28± 29	107± 127	12.9± 8.7	0.08±0.14	242± 98	311± 484	27± 24	0.19±0.14
Overall	μ	7.8±0.2	-50±14	1.2±0.9	282± 126	199± 51	1210±949	4.83± 1.24	5.9± 2.2	69± 30	28± 19	107± 81	12.9± 5.5	0.08±0.14	242± 62	311± 308	27± 15	0.19±0.09
	CI	7.6-8.1	-64-36	0.3-2.1	156-408	148-250	261-2159	3.6-6.1	3.7 -8.1	39-99	9--47	26-188	7.4-18.4	0-0.22	180-304	3-619	12--42	0.1-0.28
BIS2012		6.5-8.5		-	200	200	500			75	30	-	-	0.3	-	250	200	
WHO2011		6.5-8.5		1.5	-		500			75	50	200	12	0.3	500	250	250	

Results of ANOVA tests conducted to check the various hypotheses, suggested in the chapter 1, give the following results:

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

Table 3.28: ANOVA table for the comparison of water quality parameters between different months of CW stratum in 2012.

Source	ss	df	ms	F	p-value
Total	1835915.48	191			
Months	9324.33	11	847.6663	0.078	p>0.05
Parameters	44601.66	15	2973.4437	0.275	p>0.05
Residual	1781989.5	165	10799.9364		

Inferences

1) There is no significant difference between months and between parameters (p>0.05)

b) *Whether there is any significant difference between the values of various parameters of dug well strata in April 2012*

Table 3.29: ANOVA table for the comparison of water quality parameters between different dug well stations in April 2012

Source	ss	df	ms	F	p-value
Total	13606877.68	95			
Dug wells	2479919.3	5	495983.8590	5.525	p<0.001
Parameters	4393572.31	15	252904.8206	3.263	p<0.001
Residual	6733386.07	75	89778.4810		

Inferences

1) There is significant difference in mean parametric values between dug wells (p<0.001). DW 2 is having significantly higher mean parameter value compared to others (p<0.001).

2) Parameters also exhibited a significant difference between them (p<0.001). TDS is the highest among all the parameters reported in all the dug wells.

c) *Whether there is any significant difference between the values of various parameters of dug well strata in July 2012*

Table 3.30: ANOVA table for the comparison of water quality parameters between different dug well stations in July 2012

Source	**ss**	**df**	**ms**	**F**	**p-value**
Total	9246740.56	95			
Dug wells	611595.92	5	122319.1846	1.798	p>0.05
Parameters	3531904.31	15	235460.2875	3.46	p<0.001
Residual	5103240.33	75	68043.2044		

Inferences

1) Between dug wells there is no significant difference in the mean values of the parameters ($p>0.05$)

2) The parameters differ significantly ($p<0.001$). Among all the parameters, TDS is significantly very high compared to all others.

d) Whether there is any significant difference between the values of various parameters of dug well strata in December 2012

Table 3.31: ANOVA table for the comparison of water quality parameters between different dug well stations in December 2012

Source	**ss**	**df**	**ms**	**F**	**p-value**
Total	21566164.96	95			
Dug wells	886983.03	5	177396.6069	1.336	p>0.05
Parameters	10719740.69	15	714649.3790	5.382	p<0.001
Residual	9959441.25	75	132792.5500		

Inferences

1) Among dug wells the difference in the mean values of the parameters is not significant ($p>0.05$)

2) Variation in the mean values of the parameters is highly significant ($p<0.001$). The mean occurrence of the parameters Cl, TDS, Na and HCO_3 are significantly higher than the rest ($p<0.001$). Among the four, TDS is the highest.

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

Table 3.32: ANOVA table for the comparison of mean values of various parameters of dug well strata in each month of year 2012

Source	ss	df	ms	F	p-value
Total	20174779.73	191			
Months	180311.18	11	170937.383	16.636	$p<0.001$
Parameters	16599101.43	15	1106606.7623	107.699	$p<0.001$
Residual	1695367.11	165	10274.9522		

Inferences

1) There is significant difference between months ($p<0.001$). The mean value of the parameters are significantly higher during the month of June, October, November and December.

2) The mean value of the parameters also exhibit significant difference between them ($p<0.001$). TDS, TH, Na, HCO_3 and Cl are significantly higher than rest of the parameters, the highest among them is TDS.

f) *Whether there is any significant difference between mean values of various parameters of dug well (DW) and control well (CW) strata in each month of year 2012*

Table 3.33: ANOVA table for the comparison of water quality parameters between CW and DW for the different months of year 2012.

Source	ss	df	ms	F	P-value
Total	22816292.49	383			
Bet. CW & DW	1590010.12	1	1590010.1200	70.120	$P<0.001$
Bet. Months	215287.75	11	19571.6136	0.863	$P> 0.05$
Bet. Parameters	12938489.44	15	862565.9627	38.039	$P<0.001$
Residuals	8072505.18	356	22675.5763		

Inference

1) There is significant difference in the mean value of the parameters between CW and DW ($P<0.001$). Mean values of the parameter in DW are significantly higher than that of CW.

2) Between months variation is not significant at 5% level of significance ($P > 0.05$)

3) Mean values of the parameters differ significantly ($P<0.001$). Parameters TDS, TH, Cl and HCO_3 are significantly higher compared to others. The highest among them is TDS ($P< 0.001$).

g) *Whether there is any significant difference between mean values of water quality index of dug well (DW) strata in each month of year 2012.*

Table 3.34: ANOVA table for the comparison of Water Quality Index for DW strata in various months of 2012.

Source	SS	df	ms	F	P-value
Total	96774.00	71			
Months	7681.67	11	698.335	1.944	P> 0.05
Dugwell	69336.33	5	13867.266	338.606	P< 0.001
Residual	19756	55	359.20		

Inference

1) There is no significant difference in WQI for the 12 months of the year 2012 ($P> 0.05$)
2) There is highly significant difference between the dug wells ($P < 0.001$). WQI is significantly higher in DW2 compared to others.

h) Whether there is any significant difference between water quality index of control well (CW) and dug well (DW) strata in year 2012.

Table 3.35: ANOVA table for the comparison of water quality index for control well and Dug well strata for the year 2012.

	Control Well	Dugwell	t	df	P-value
Mean	38.29	76.58	8.988	22	P<0.001

Inference

There is significant difference in the mean WQI between control well and Dug well ($P<0.001$). The mean WQI of Dug well is significantly higher than that of control well in 2012, almost double.

3.14 Conclusion

In some of the DW stations groundwater quality parameters exceed the permissible standard limit. The annual mean values of important water quality parameters are; pH 7.8±0.4, Eh $^{-}$50±22mV, EC 1.2±1.4mS/cm, TH 282±198mg/l, Alkalinity 199±80mg/l, TDS 1210±1491mg/l, DO 4.8±2.0mg/l, BOD 5.9±3.5mg/l, Ca 69±47mg/l, Mg 28±29mg/l, Na 107±127mg/l, K 13±8.7mg/l, Fe 0.08±0.14mg/l, HCO_3 242±98mg/l, Cl 311±484mg/l, SO_4 27±24mg/l, PO_4 0.19±0.14mg/l. Trace elements analysed are not present in harmful levels. The prominent water quality parameters evaluated will be most useful to compute the overall variability of the water quality of the region over the year to come as a baseline data.

Pearson's Correlation matrix study suggest that, in Dug well(DW) strata electrical conductivity of water is an important parameter and it is significantly correlated with TH, Ca, Na, K and Cl. So water quality can be checked effectively by controlling the conductivity of water. WQI calculation reveals that there are some DWs which show high decline in quality as revealed by its mean of 77±39. From Sodium – Chloride ratio calculations, it is inferred that occasionally reverse ion exchange occur in DW strata.

Irrigation quality study using 6 parameters suggest the unsuitability due to salinity in some shallow wells. USSL diagram show the moderate water quality of DW and Wilcox diagram also suggest mainly Good to Permissible category for DW strata.

Saturation Indices calculation suggest slightly scale forming nature of shallow wells.

The results of Piper plot study suggest that Mixed Cation-HCO_3 is the dominant hydro chemical facies for the region's groundwater. In shallow dug wells the mixed nature of different hydro chemical facies mainly (i) Ca–Mg–HCO_3 (Temporay Hardness), (ii) Ca-Mg-Cl-SO_4 (Permanent Hardness) and (iii) Na– K–Cl (Saline) are observed.

The results of two factor and three factor ANOVA tests reveal that, for control well (CW) there is no significant difference in various parameters between months. That is the CW keep good quality throughout the year. From the ANOVA tests for comparing various parameters of various dug well stations, in the months April there is significant difference in mean parametric values between dug wells. DW 2 is having significantly higher mean parameter value compared to others, in July and December among dug wells the difference in the mean values of the parameters is not significant. Comparison of mean values of various parameters of dug well strata in each month of year 2012 suggest that there is significant difference between months. The mean value of the parameters are significantly higher during the month of June, October, November and December. Comparison of water quality parameters between CW and DW for the different months of year 2012 using three factor ANOVA test suggest that there is significant difference in the various parameters between CW and DW. Mean parameters in DW are significantly higher than that of CW. Mean WQI of various months of year 2012 for DW strata do not differ significantly. Among different stations WQI is significantly higher in DW2 compared to others. Comparison of water quality index for control well and dug well strata for the year 2012 suggest that the mean WQI of dug well is significantly higher than that of control well in 2012, almost double.

Systematic assessment of groundwater quality along the coastal area provide useful data for the formulation of viable policy for the management of groundwater sources of the coastal zone.

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Chapter 4

HYDROGEOCHEMISTRY OF DEEP GROUNDWATER SOURCES OF ARATTUPUZHA COAST, ALAPPUZHA, KERALA, INDIA

Contents

4.1 Introduction

Hydrology is the science of water on Earth, their occurrence, distribution, circulation, chemical and physical properties and reaction with the environment, including the relation to living things. The domain of hydrology embraces the full life history of water and the study is closely related to geology/ earth science. The study of water quality mainly includes the various aspects of chemistry of water. Thus, hydrogeochemistry include hydrology, geology and chemistry. Groundwater quality has become an important area of water science discussed in recent times as a key resource for development. The three major factors that determine the composition of groundwater are atmospheric inputs, interaction of water with soil and rock and anthropogenic activities [1-6]. Study presented in this chapter, is carried out in much closer temporal and spatial intervals to study the hydrochemistry of deep groundwaters. In each month of year 2012, through field trip water were collected from selected stations and analysed. Continuous monitoring of groundwater quality parameters help to generate a database for future reference. GIS maps make the study of variation of different water quality parameters along the study area easier [7-13].

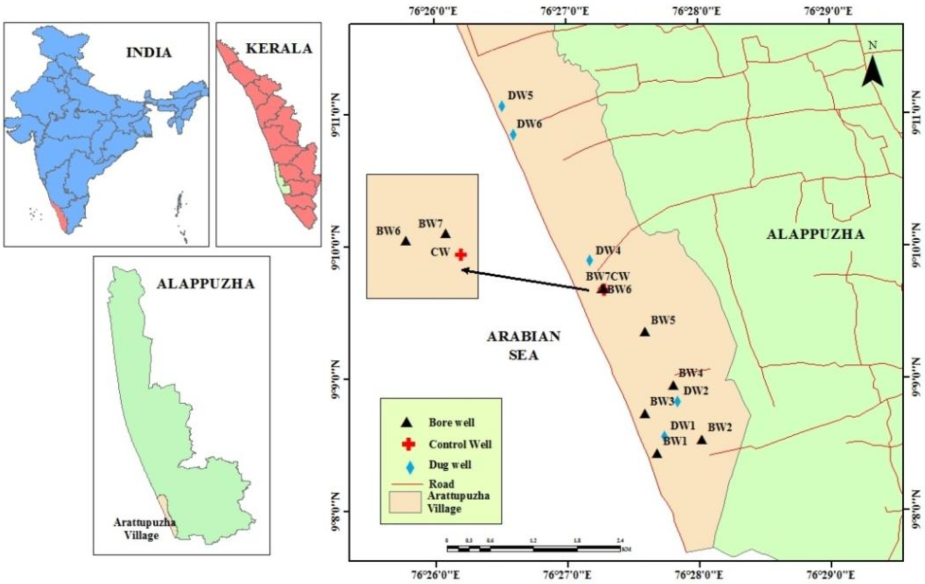


Figure 4.1: Groundwater sampling locations in 26th December 2004 Indian Ocean Tsunami affected coastal areas of Arattupuzha village, Alappuzha, Kerala, India for the year 2012.

The present study area is a narrow strip of coastal land in the southern end of Alappuzha district (Figure 4.1). This chapter discusses the hydrogeochemistry of deep groundwater sources along Arattupuzha coast by collecting and analysing samples from 7 bore well stations in each month of year 2012. The sampling stations and their locations are given in Table 4.1

Table 4.1: Sampling stations along Arattupuzha coast, Alappuzha, Kerala, India for studying deep groundwaters in year (2012)

Sl.No.	Station	Description	Remarks	Location
1	BW1	Thara – house owner	Bore well BW1	09° 08' 26 N, 76° 27'41E
2	BW2	Valiyazheekal pump - jetty	Bore well BW2	09° 08' 32 N, 76° 28'01E
3	BW3	Prown shed	Bore well BW3	09° 08' 43 N, 76° 27'35E
4	BW4	Yuvasakthi	Bore well BW4	09° 08' 56 N, 76° 27'48E
5	BW5	Baiju –house owner	Bore well BW5	09° 09' 21 N, 6° 27'35E
6	BW6	Kuriappassery –pipe water	Bore well BW6	09° 09' 40 N, 76° 27'15E
7	BW7	Kuriappassery pump house	Bore well BW7	09° 09' 40 N, 76° 27'16E

4.2 Water Quality Parameters

The work presented in the following section of the thesis comprises the major results and discussions on the water quality parameters of the deep groundwater sources of the study area. For a comparison the control well (CW) data is also plotted in the graphs. The quality standards for drinking water specified by the Bureau of Indian Standards, IS 2012 and World Health Organization (WHO 2011) have been used. The spatial analysis of various physico-chemical parameters is carried out using the Arc GIS 10 software. In order to interpolate the data spatially and to estimate values between measurements, an inverse distance weighed (IDW) algorithm is used. GIS maps showing the variation of different parameters in representative months (January, March, July & December 2012) are also discussed along with each parameter.

4.2.1 pH

The pH of unpolluted natural waters occur within a narrow range and major deviations from that range, caused by natural or anthropogenic sources, may have very strong impact on the aquatic ecosystems [14]. Physical, chemical and biological processes associated with water supply and sanitary engineering activities are strongly pH dependent. Temperature has a strong effect on *hydrogen-ion behaviour*. The 2012 annual mean temperature of water samples of deep aquifers is 31.1±1.5°C. There is not much variation in temperature of water over the year (Figure 4.2). The limit of pH for drinking water is specified as 6.5–8.5 (WHO 2011; IS 2012). The pH of BW strata in January 2012 is 7.3±0.2, it increases to 8.7±0.2 by March 2012, then decreases and remain almost steady till the end of the year. In July pH is 7.4±0.2 and in December 2012 also it is 7.4±0.2. The 2012 annual mean $(\bar{x} \pm \sigma)$ pH of BW strata in the study area varies from 7.35 to 7.65 (Figure 4.3), which clearly shows that the groundwater in the study area is slightly alkaline in nature. The 2012 annual mean pH of DW strata in the study area is 7.8±0.4 at 95% significant level. So in BW strata there is a slight decrease in pH. On comparing with DW strata, BWs are slightly less alkaline.

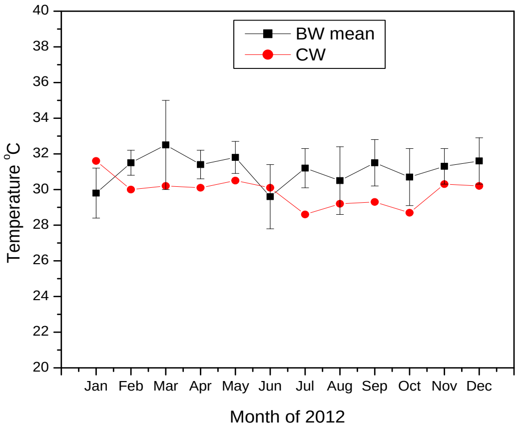


Figure 4.2: Monthly variation of Temperature of deep groundwater bore well (BW) sources & control well (CW) along the study area, Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

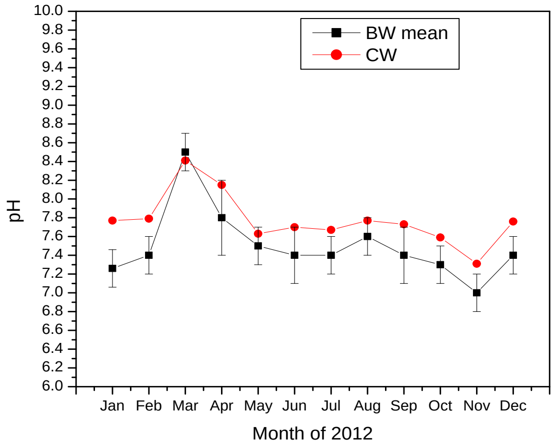
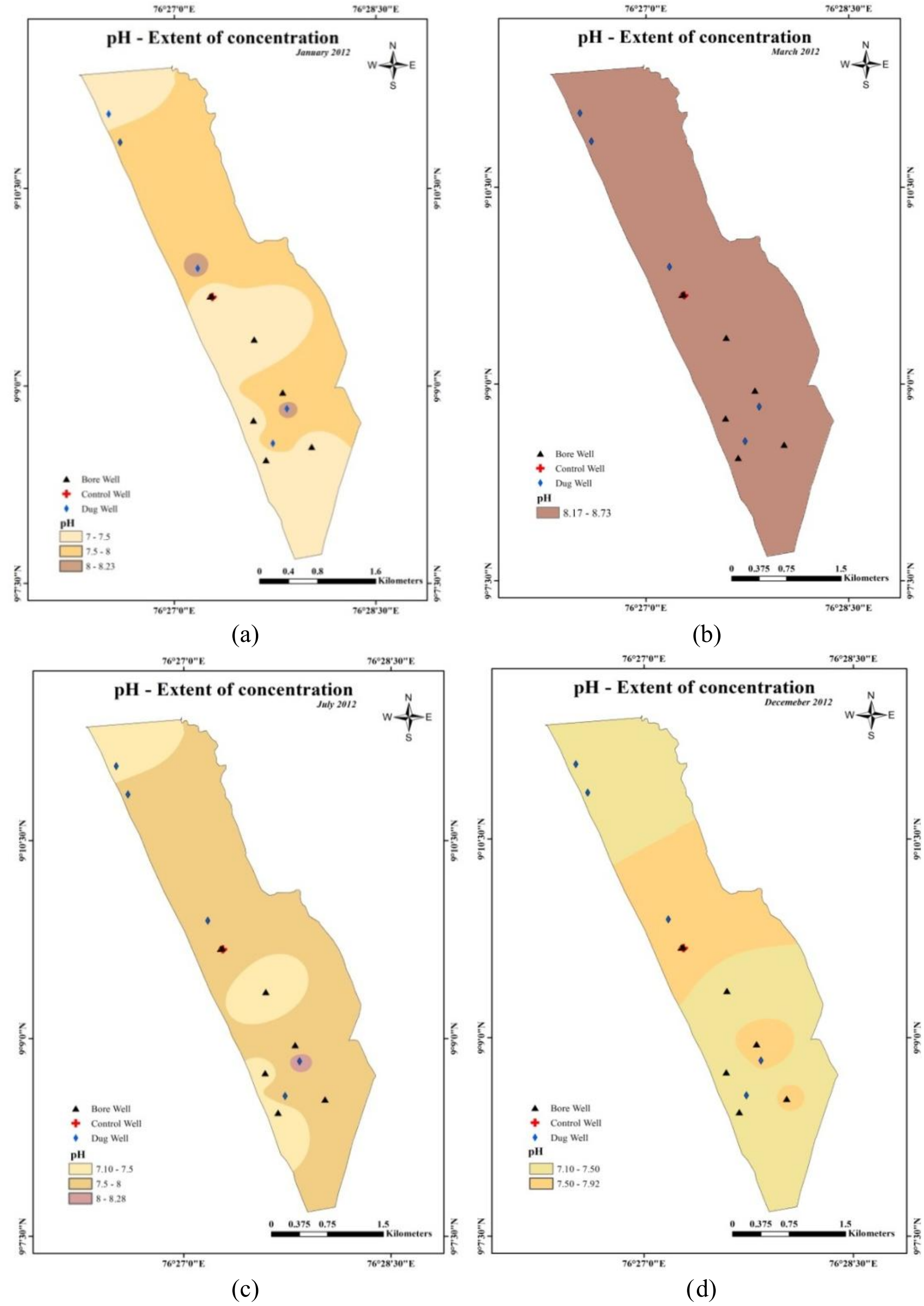


Figure 4.3: Monthly variation of pH of deep groundwater bore well (BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The spatial and temporal variation of pH is done using geographical information system (GIS) for a better understanding of the quality variation. GIS maps of four months (January, March, July & December 2012) representing pre monsoon, monsoon and post monsoon are represented (Figure 4.4).

In January 2012 pH range 7-7.5 in northern, southern ends and 7.5-8 range in central area are observed. During March 2012, pH shows a distinct alkaline range of 8.2-8.7 throughout the study area. By July, in majority area pH range is 7.5-7.8. There are pockets showing nearly neutral pH in the range 7.1-7.5 and a small area where pH maintains the alkaline range of 8-8.3. By the end of the year, in December 2012, again variation in pH distribution in the study area is observed. At the central region as well as in 2 pockets in the southern end pH range of 7.5-7.9 is observed. In the rest of the study area pH range is 7.1-7.5.



(a) (b)

(c) (d)

Figure 4.4: Spatial distribution map for pH of the study area Arattupuzha coast, Alappuzha, Kerala, India during a) January b) March c) July and d) December of year 2012.

4.2.2 Redox Potential (Eh)

The 2012 annual mean Eh of BW strata in the study area is $^{-}$27.95±22.2 (Figure 4.5), which clearly shows that the deep groundwater in the study area is reducing in nature.

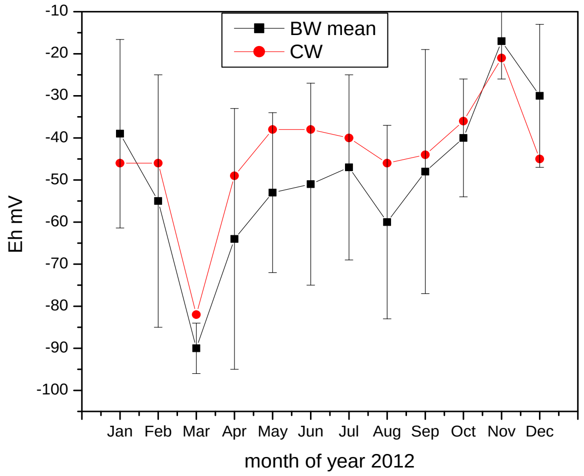


Figure 4.5: Monthly Variation of Eh of deep groundwater bore well (BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Eh decreases from January to March 2012 and the environment is most reducing in March 2012 with mean ($\bar{x} \pm \sigma$) Eh -60±63. In the subsequent months, it increases and remains almost steady.

In July 2012 Eh is -24±10 and in November 2012 it become close to oxidising range with a mean of -1±11. In December 2012 again the environment become more reducing with Eh -27±12. The 2012 annual mean Eh of DW strata in the study area is -50±22 at 95% significant level. So in DW strata the redox environment is slightly more reducing than the BW strata.

4.2.3 Electrical Conductivity (EC)

Electrical conductivity of water is a measure of capacity to convey electric current. The most desirable limit of EC in drinking water is prescribed as 1,500 µmhos/cm. Electrical conductivity may be an approximate index of the total content of dissolved substance in water. It depends upon temperature, concentration and types of ions present. In January 2012, mean ($\overline{x} \pm \sigma$) EC of BW strata is 0.26±0.08mS/cm, which increases in February 2012 to 0.35± 0.09, then decreases, again increases in May 2012 to 0.42±0.04 and then decreases. In 2012 the EC of the BW strata is varying from 0.28 to 0.38 mS/cm with an average of 0.33mS/cm. The annual mean ($\overline{x} \pm \sigma$) EC of DW strata during year 2012 is1.2±1.4 with CI of 0.3-2.1 mS/cm at 95% significant level. Thus, compared to DW EC is lower in BW strata and it maintained almost steady value throughout the year. So the deep aquifers are protected from sea water intrusion and anthropogenic influences. In shallow wells, there is high variation of EC and it exceed standard limit in certain locations.

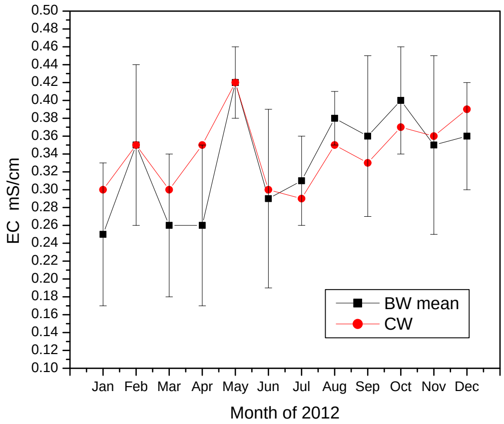
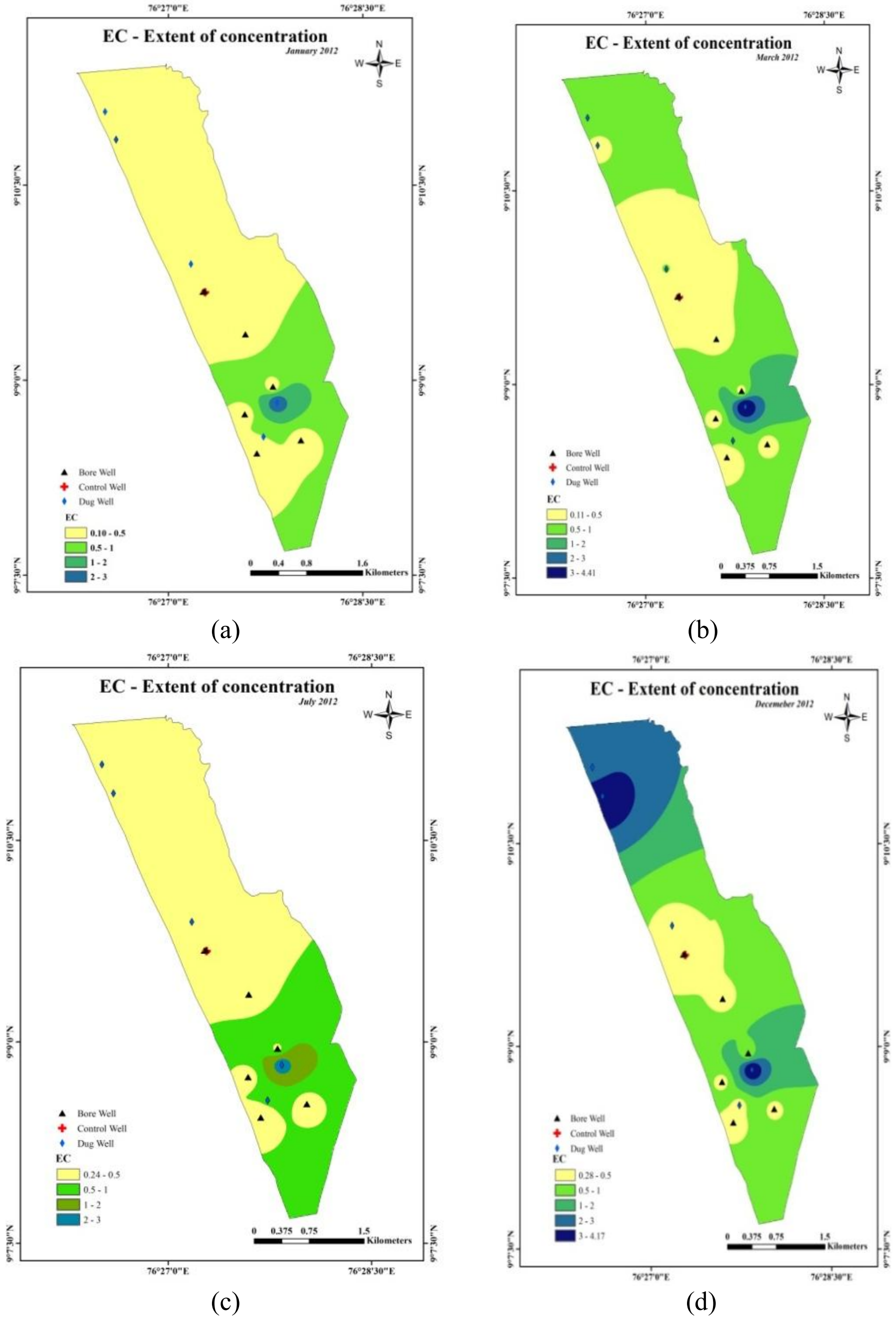


Figure 4.6: Monthly variation of EC of deep groundwater bore well (BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The spatial variation map for EC of the study area is presented in Figure 4.7.



(a) (b)

(c) (d)

Figure 4.7: Spatial distribution map for EC of the study area Arattupuzha coast, Alappuzha, Kerala, India during a) January b) March c) July and d) December of year 2012.

GIS plot of electrical conductivity in January 2012 shows EC range of 0.1-0.5mS/cm in major area and 0.5-1.0 range in lower part with a small pocket area of very high EC of 2-3mS/cm. In March 2012 it shows a central area of lower EC in the range 0.11-0.5mS/cm. There are some pockets of lower EC in the southern area. There is a small pocket of very high EC, higher than 2mS/cm, which suggests saline water. In all other area, an EC range of 0.5 -1mS/cm is observed. In July 2012, an overall lowering of EC is observed. Major area shows EC range of 0.24-0.5mS/cm. In the lower part EC range is 0.5-1mS/cm with one pocket of high EC, greater than 2mS/cm. In December 2012, considerable variation of EC is clear from the GIS map. In the northern end EC is higher than 2mS/cm. Small portion in the central area and small pockets in southern area shows EC in the range 0.28-0.5mS/cm. In the rest of the area EC vary from 0.5-1 & 1-2mS/cm.

4.2.4 Total Hardness (TH)

The mean ($\bar{x} \pm \sigma$) total hardness, TH of deep BW strata is 165±33mg/l in January 2012, which increases to 178±31in February 2012, then decreases reaches the lowest 129±54 in June 2012, then increases and become 147±48 in December 2012. The total hardness (TH) of BW strata is varying from 142 to 194 mg/l in the year 2012 (Figure 4.8). So TH of BW strata of the study area is lower than CW and it lies within the maximum permissible limit prescribed by BIS. Thus Total Hardness keeps almost steady value throughout the year and compared to DW strata hardness is lower in BW strata.

The hardness of the water is mainly due to the presence of alkaline earths such as calcium (Ca^{2+}) and magnesium (Mg^{2+}). According to the classification in Table 3.2, in most of the months of year 2012, the water of BW strata lies either in the *hard to very hard* [HVH] category or in the *very* *hard to excessively hard* [VHEH] category. TH is lowest in June 2012 and the water is in *moderately hard to hard* [MHH] category.

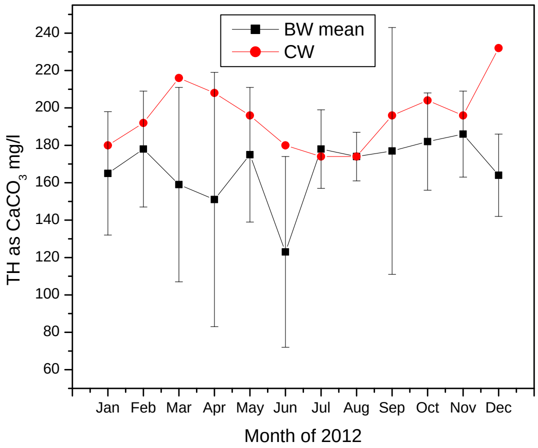
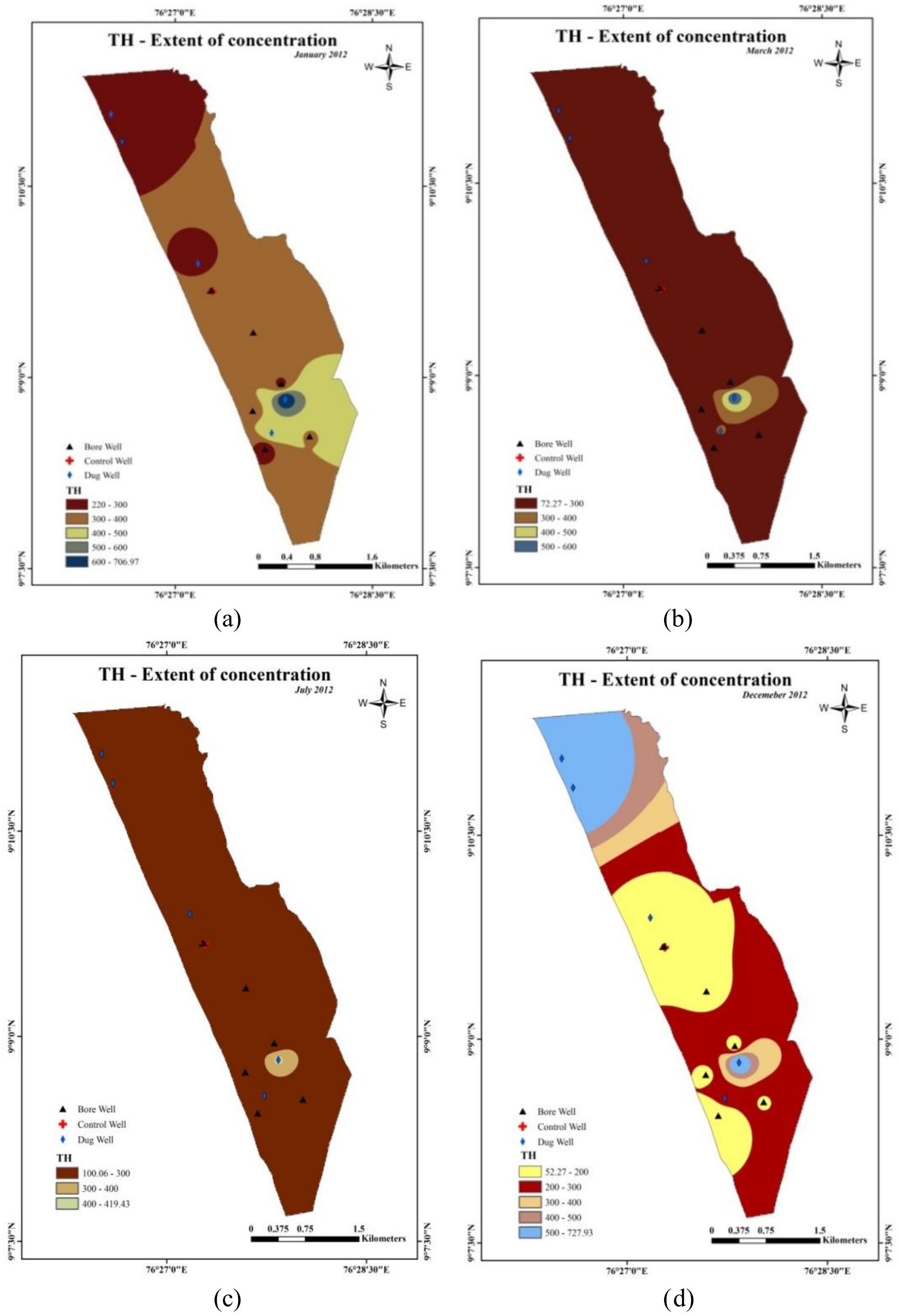


Figure 4.8: Monthly variation of TH of deep groundwater bore well(BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The spatial variation map for TH of the study area is presented in Figure 4.9. In January 2012 major area shows TH range 300-400mg/l and small areas of very high hardness up to 600mg/l are seen. In March 2012, throughout the study area TH range is 72-300mg/l except in a small pocket near the southeast side with TH higher than 500mg/l. In July 2012, not much change in TH distribution is visible. In majority area, TH range is 100-300mg/l and in the small pocket it is higher than 400mg/l. By December 2012, prominent variation in TH distribution is observed. TH higher than 500mg/l is observed in uppermost region and in the small pocket area. In the central area and small pocket areas in south show lower TH range of 52-200mg/l. In rest of the region moderate TH of 200-300mg/l is observed.



(a) (b)

(c) (d)

Figure 4.9: Spatial distribution map for TH of the study area Arattupuzha coast, Alappuzha, Kerala, India during a) January b) March c) July and d) December of year 2012.

4.2.5 Alkalinity (AL)

In BW strata the mean ($\bar{x} \pm \sigma$) alkalinity in January 2012 is 255±38mg/l, which exceed standard limit. It decreases and reaches 155±84mg/l in April, then increases in May 2012, again show decreasing tendency and reaches a minimum of 146.4±58.1mg/l in October 2012 and then slightly increases. The annual mean alkalinity of BW strata during year 2012 is 198±45mg/l with CI of 170-226mg/l at 95% significant level (Figure 4.10). The standard limit of alkalinity according to BIS is 200mg/l.

In addition to carbonate alkalinity other common natural components that can contribute to alkalinity include borate, hydroxide, phosphate, silicate, nitrate, dissolved ammonia, the conjugate bases of some organic acids and sulphide. Alkalinity is important because it buffers pH changes that occur naturally during photosynthetic cycles, water exchanges, etc

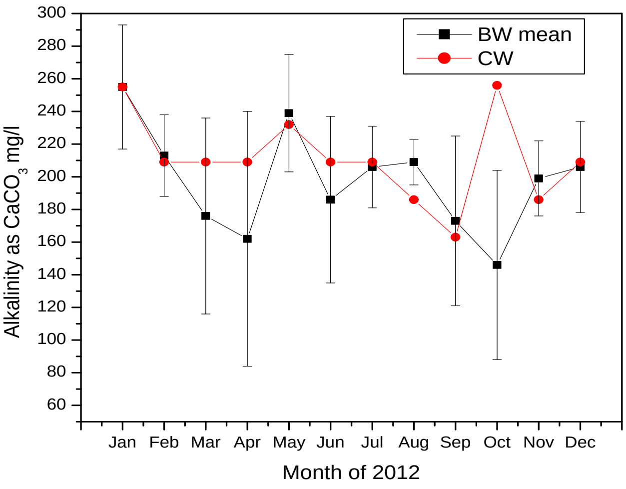
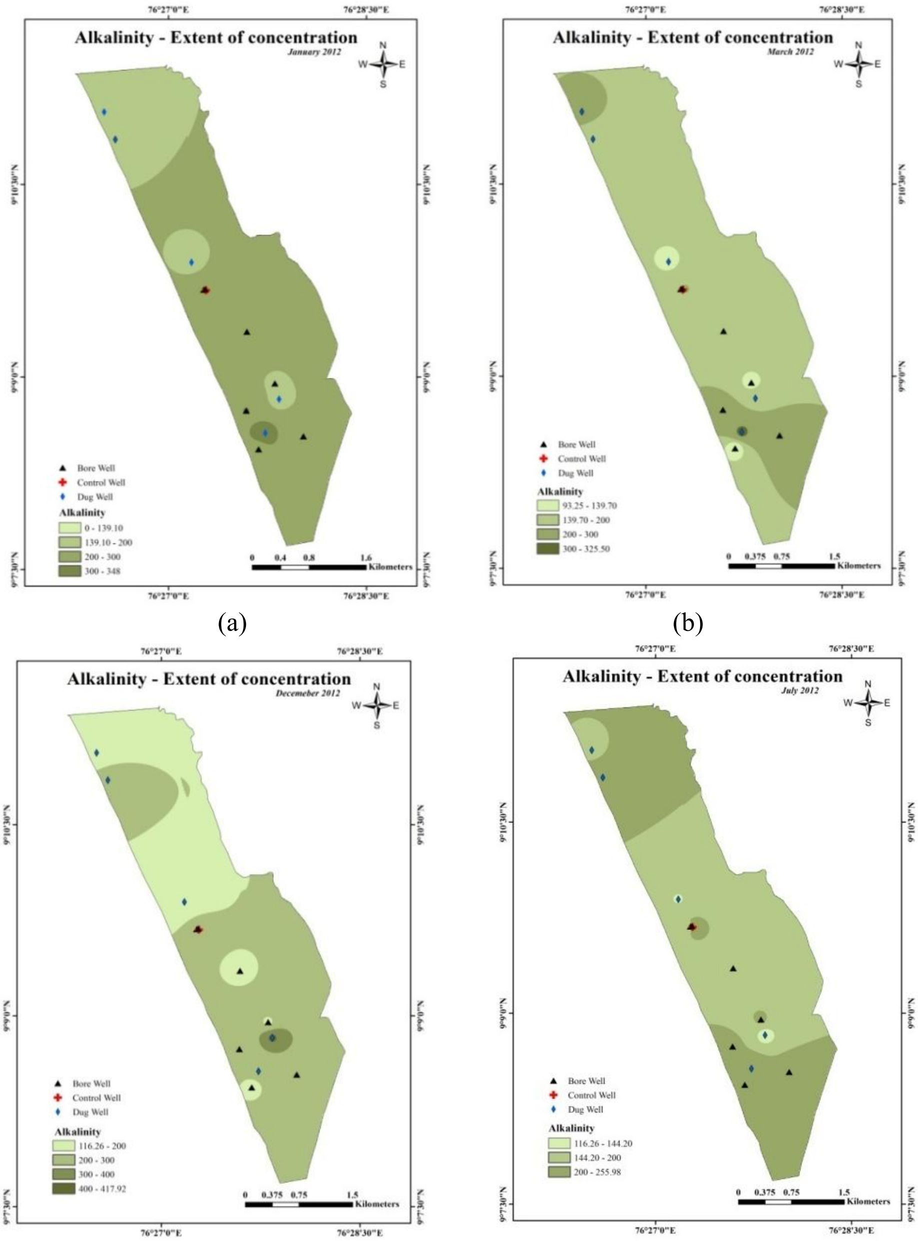


Figure 4.10: Monthly Variation of Alkalinity of deep groundwater bore well(BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The spatial variation map for Alkalinity of the study area is presented in Figure 4.11.



(a) (b)

(c) (d)

Figure 4.11: Spatial distribution map for Alkalinity of the study area Arattupuzha coast, Alappuzha, Kerala, India during a) January b) March c) July and d) December of year 2012.

In January 2012 alkalinity of major area vary from 140-300mg/l with small pockets of lower and higher alkalinity. In March 2012 major area having lower than 300mg/l alkalinity. In July 2012 upper and lower parts having higher alkalinity and central area of lower alkalinity are observed. In December 2012 upper half show very low alkalinity compared to lower area. From the data of total hardness and alkalinity inferences can be drawn about the *temporary or permanent hardness of water*. An excess of total alkalinity over total hardness indicate the presence of bicarbonate of sodium. In case the waters showing the existence of free $NaHCO_3$ it may be presumed that the waters might not have been contaminated with sea water.

Table 4.2: Comparison of Total Hardness (TH), Alkalinity (AL), Temporary Hardness (TeH) & Permanent Hardness (PeH) of Control well (CW) and Bore well (BW) in each month of year 2012 along the study area Arattupuzha coast, Alappuzha, Kerala, India

Year (2012)	**CW**					**BW**				
	TH mg/l	**Inference**	**AL mg/l**	**TeH mg/l**	**PeH mg/l**	**TH mg/l**	**Inference**	**AL mg/l**	**TeH mg/l**	**PeH mg/l**
Jan12	180	VHEH	255	255	0	165	HVH	255	255	0
Feb12	192	VHEH	209	209	0	178	VHEH	213	213	0
Mar12	216	VHEH	209	209	7	159	HVH	176	176	0
Apr12	208	VHEH	209	209	0	151	HVH	162	162	0
May12	196	VHEH	232	232	0	175	VHEH	239	239	0
Jun12	180	VHEH	209	209	0	123	MHH	186	186	0
Jul12	174	VHEH	209	209	0	178	VHEH	206	206	0
Aug12	174	VHEH	186	186	0	174	VHEH	209	209	0
Sep12	196	VHEH	163	163	33	177	VHEH	173	173	4
Oct12	204	VHEH	256	256	0	182	VHEH	146	146	36
Nov12	196	VHEH	186	186	10	186	VHEH	199	199	0
Dec12	232	VHEH	209	209	23	164	HVH	206	206	0
$\bar{X} \pm \sigma$	196± 18		211± 27	211± 27		168±41		198±45	198±45	
μ	196± 11		211± 17	211± 17		168±26		198±28	198±28	
CI	185-207		194-228	194-228		142-194		170-226	170-226	

From Table 4.2 it is clear that except in October 2012 considerable permanent hardness is not observed in BW strata. In September 2012, 4mg/l and in October 2012, 36mg/l permanent hardness is observed. In control well also slight contribution of permanent hardness is observed in the post monsoon season.

4.2.6 Calcium (Ca^{2+})

The mean ($\overline{x} \pm \sigma$) Ca concentration of BW strata during January 2012 is 43±9.3mg/l, decreases slightly to 37±24 mg/l in April 2012, shows slight increase in May 2012, again decreases in June 2012 to 31±13 mg/l, then increase in July 2012, and a decreasing tendency is observed after that and the Ca concentration become 42.1±13.1mg/l in December 2012. The annual mean ($\overline{x} \pm \sigma$) Ca of BW strata during year 2012 are 43±11 mg/l with CI of 36-50 mg/l at 95% significant level (Figure 4.12).

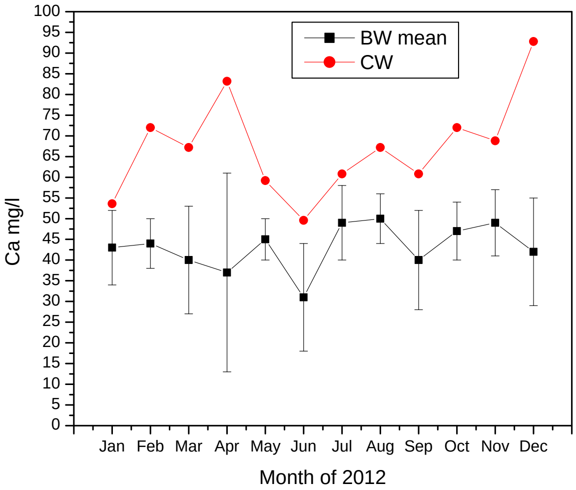
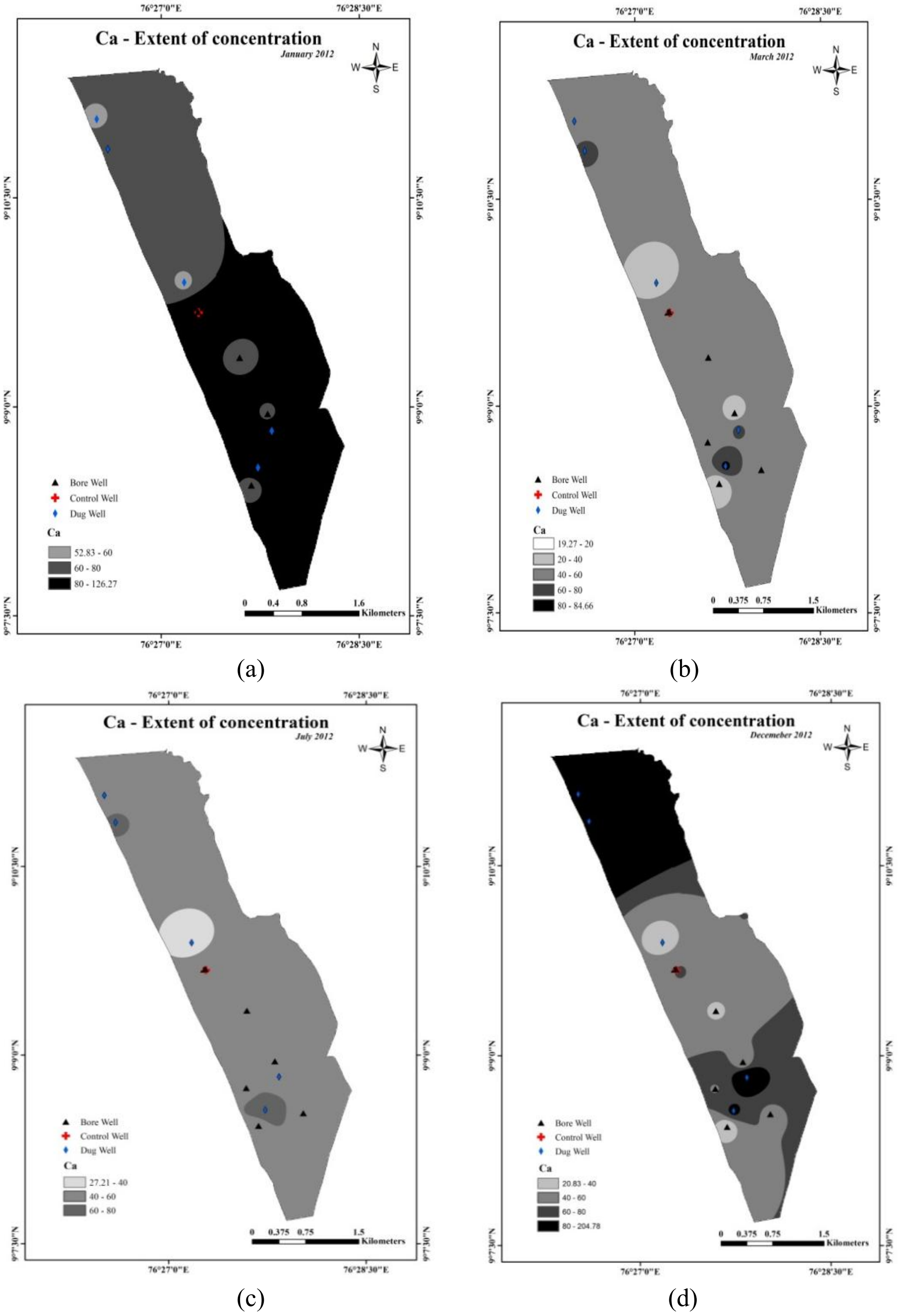


Figure 4.12: Monthly Variation of Calcium of deep groundwater bore well(BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The standard limit of Ca according to BIS &WHO is 75mg/l. BW strata have lower calcium than control well. Equilibria involving carbonates such as the calcite dissolution-precipitation and dissolved carbon dioxide species equilibria are the major factors limiting the solubility of calcium in most natural water. The concentrations of calcium ions common in waters where carbonate rocks occur. Water percolating through the soil and the unsaturated zone above the water table is exposed to air, visibly pore spaces of soil is greatly enriched with carbon dioxide. Partial pressures of carbon dioxide in soil air are commonly l0-100 times more than in the atmosphere. The carbon dioxide originates from plant respiration and decay of dead plant material. This CO_2 is expected to play greatest role in natural environment that promote the growth of and support dense vegetation.

The spatial variation map for Ca of the study area is presented in Figure 4.13. In January 2012 lower part of below 60mg/l calcium concentration and upper and pocket areas of higher than 60mg/l are observed. In March 2012, calcium concentration 40-60mg/l is observed in major portion of study area. There are small pocket areas of lower concentration of 20-40mg/l range and higher concentration of above 80mg/l. In July 2012, not much variation in the distribution of calcium is seen. In major part of the study area its range is 40-60mg/l. At the central area a small pocket of lower calcium of 20-40mg/l range and at the upper and lower ends small pockets of higher calcium of 60-80mg/l range. In December 2012 large variation is observed. Upper end and a small pocket near lower part exhibit high calcium concentration, greater than 80mg/l. Central and lower most areas show 40-60mg/l range. Small pockets of lower calcium 20-40mg/l is also seen. Remaining part of the region show 60-80mg/l of calcium.



(a) (b)

(c) (d)

Figure 4.13: Spatial distribution map for Ca of the study area Arattupuzha coast, Alappuzha, Kerala, India during a) January b) March c) July and d) December of year 2012.

4.2.7 Magnesium (Mg^{2+})

The annual mean ($\bar{x} \pm \sigma$) Mg of BW strata during year 2012 is 16±6mg/l with CI of 12-20mg/l at 95% significant level (Figure 4.14). The standard limit of Mg according to BIS &WHO are 30 & 50mg/l respectively. Monthly variation suggests that, Mg of BW strata doesn’t show high range. Slight increase is observed in May and September 2012. But deep groundwater show high Mg than control well.

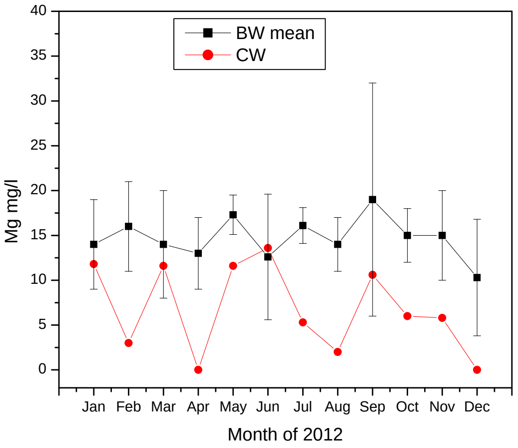
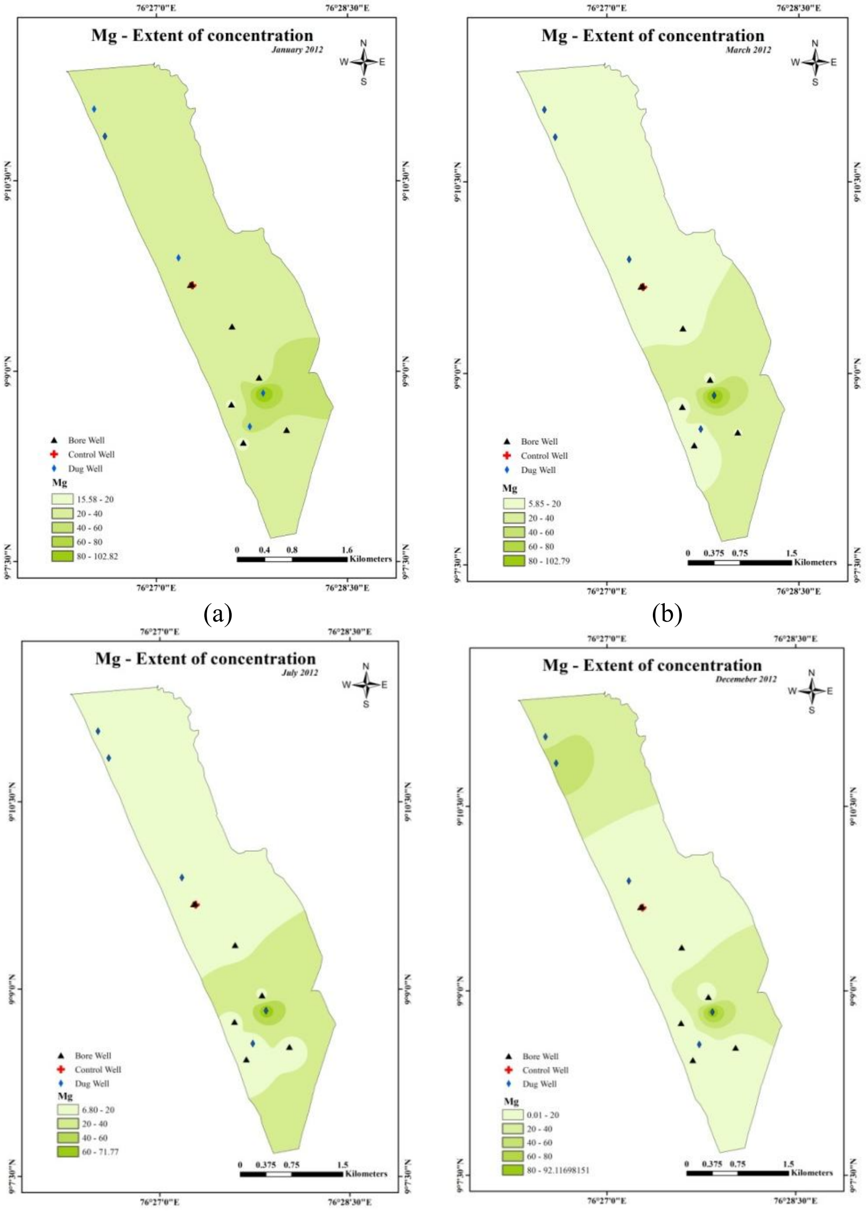


Figure 4.14: Monthly variation of Magnesium of deep groundwater bore well (BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The spatial variation map for Mg of the study area is presented in Figure 4.15. In January 2012 Magnesium below 40mg/l is observed in most of the study area with a small pocket area of higher concentration. In March 2012, major area has a Mg range of 5-20mg/l. A small pocket area of high Mg is observed at lower part. The remaining lower most region shows a magnesium range of 20-40mg/l. In 2012 July also similar distribution is observed. In December 2012 distinct change in Mg distribution is observed. Upper area show high Mg concentration in the range 20-40mg/l. Remaining major area show less than 20 and pocket areas in the upper and lower parts show very high Mg of above 80mg/l.



(a) (b)

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Figure 4.15: Spatial distribution map for Mg of the study area, Arattupuzha coast, Alappuzha, Kerala, India during a) January b) March c) July and d) December of year 2012.

Carbonate equilibria involving magnesium are more complicated than those governing calcium activities. There are several different forms of magnesium carbonates and hydroxycarbonates and many of them not dissolve reversibly. Magnesite, $MgCO_3$, from solubility products, seems to be about twice as soluble as calcite. However, the hydrated species, $MgCO_3.3H_2O$, and $MgCO_3.5H_2O$ are considerably more soluble than magnesite. The basic carbonate hydromagnesite, $Mg_4(CO_3)_3(OH)_2.3H_2O$, may be the least soluble species under some conditions. Magnesite is not usually precipitated directly from solution, and a considerable *degree of super saturation* with respect to all magnesium carbonate species may be required before precipitation can occur. The *cation-exchange behavior* of magnesium is similar to that of calcium. Both ions are strongly adsorbed by clay minerals and other surfaces having exchange sites.

4.2.8 Sodium (Na^+)

The annual mean ($\bar{x} \pm \sigma$) Na of BW strata during year 2012 is 19±6mg/l with CI of 15-23mg/l at 95% significant level (Figure 4.16). The standard limit of Na according to WHO is 200mg/l. So in BW strata Na is very low. Considering monthly variation, in January 2012, mean ($\bar{x} \pm \sigma$) Na 18±4.5mg/l, decreases to 13.4±7.2mg/l in May 2012, then increases to 23.8±5.8mg/l in August 2012 and after that slight decrease and become 23.3±7.2mg/l in December 2012. The intake of high level of Na^+ causes increased blood pressure, arteriosclerosis, oedema and hyperosmolarity. Groundwater with high Na content is not suitable for agricultural use as it tends to deteriorate the soil. The sodium of dilute waters in which dissolved solids concentrations are below 1,000mg/l is generally in the form of the Na^+ ion. In more concentrated solutions, however, a variety of complex ions and ion pairs is possible.

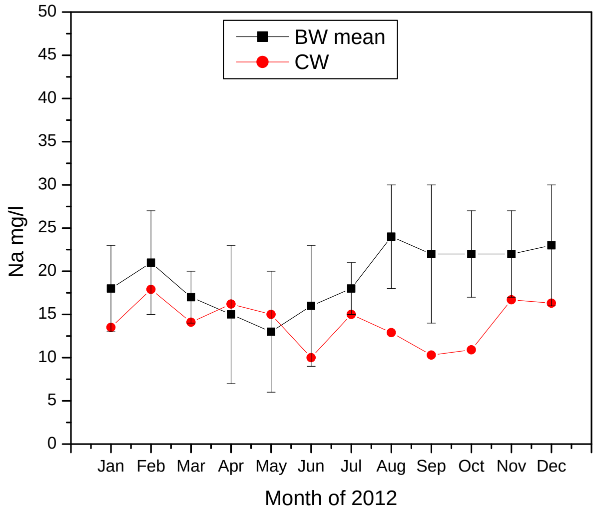
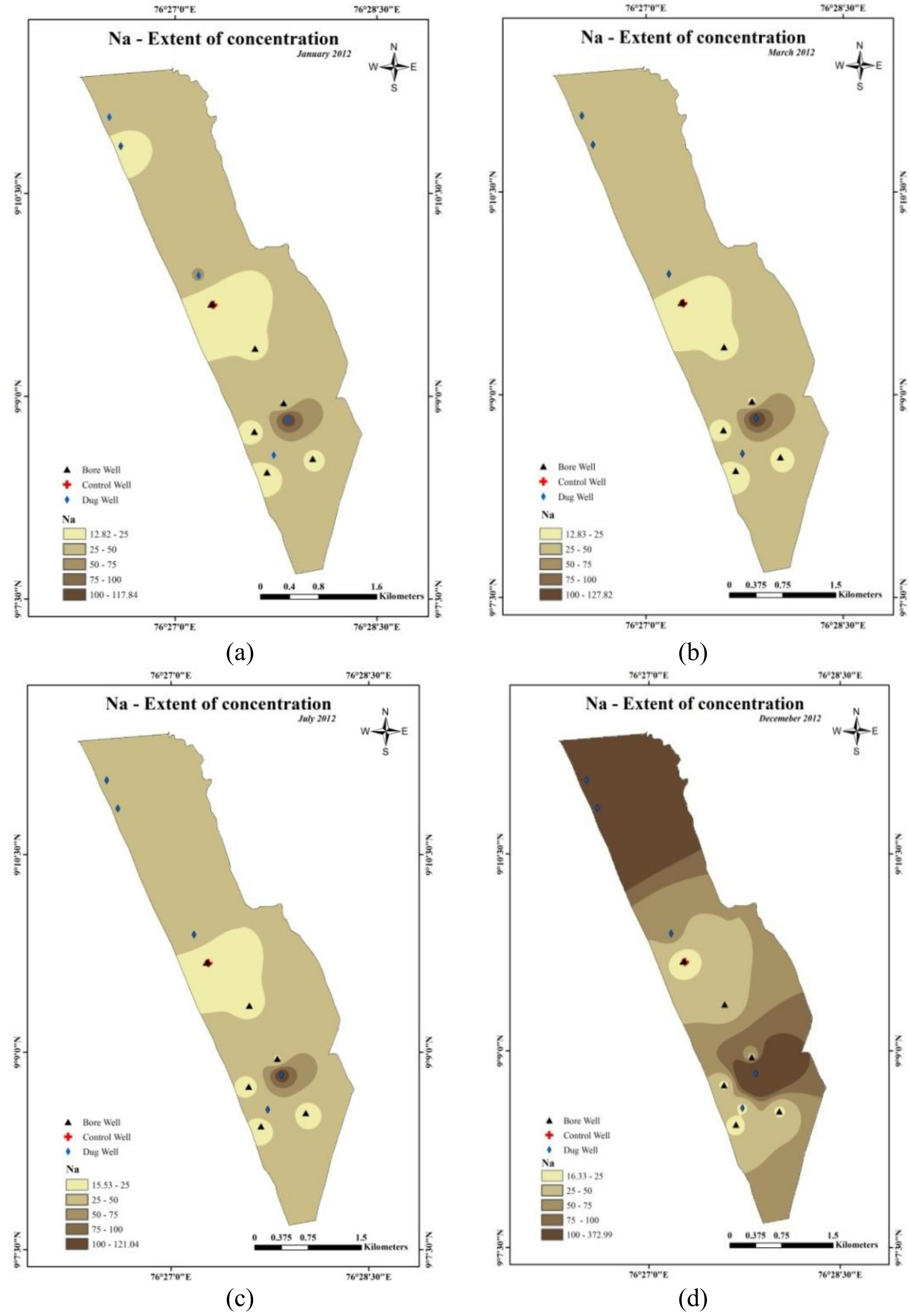


Figure 4.16: Monthly variation of Sodium of deep groundwater bore well(BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Considering the sources of sodium, in resistate sediments, sodium may be present in unaltered mineral grains, as an impurity in the cementing material. Otherwise as crystals of readily soluble sodium salts deposited with the sediments or left in them by saline water entered at a later time. In hydrolyzate sediments, the particles normally are very small, and the circulation of water through the material is impaired. Thus, the water trapped in the sediment when it was laid down may be retained with its solute load for long periods. The hydrolyzates include a large proportion of clay minerals having large *cation exchange capacities*.

The spatial variation map for Na of the study area is presented in Figure 4.17. In January 2012 major area has sodium in the range 25-50mg/l with small pockets of lower and one pocket area of higher concentration. In March 2012, major part of the area shows sodium concentration in the range 25-50mg/l.



(a) (b)

(c) (d)

Figure 4.17: Spatial distribution map for Na of the study area Arattupuzha coast, Alappuzha, Kerala, India during a) January b) March c) July and d) December of year 2012.

Small pocket areas of lower sodium (<25mg/l) are also seen. There is one pocket area of much higher sodium (>100mg/l) near the southern end. In July almost similar distribution of sodium is observed. In December 2012, large variation in the distribution occurs. In the uppermost area (near to the sea shore) and in the pocket area at the bottom part, much higher sodium (>100mg/l) is observed. Small pockets of lower sodium (<25mg/l) are also present.

Where sands and clays are interbedded, water and sodium may be retained longer in the less permeable strata during leaching and flushing by freshwater circulation. When such interbedded sections are penetrated by wells, water will be drawn mainly from more permeable sections at first. Long-continued withdrawals and water-table declines can be expected to alter water-circulation patterns, and saline solutions can be induced to move from the clay and shale layers. When this occurs on a large scale, a substantial increase in sodium concentration of the pumped water will occur. Pumping of groundwater, which alters *hydraulic gradients*, can induce lateral movement of seawater into freshwater coastal aquifers. When compacted, clays may preferentially adsorb sodium, but when dispersed in water, they may preferentially adsorb calcium.

4.2.9 Potassium (K)

Potassium is a naturally occurring element, but its concentration remains quite lower compared with Ca^{2+}, Mg^{2+} and Na^{+}. The annual mean K concentration of BW strata during year 2012 is 6±1.4mg/lwith CI of 5.1-6.9mg/l at 95% significant level. The standard limit of K according to WHO is 12mg/l.

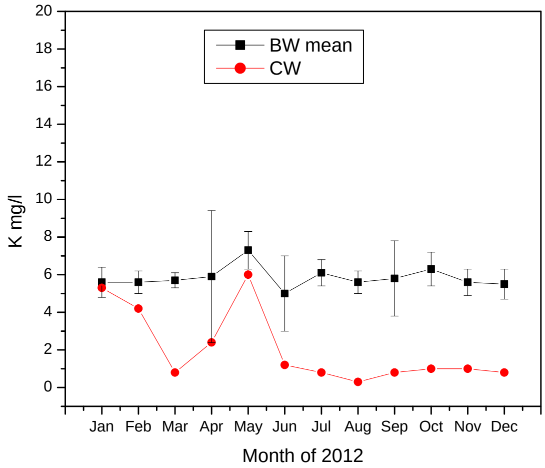
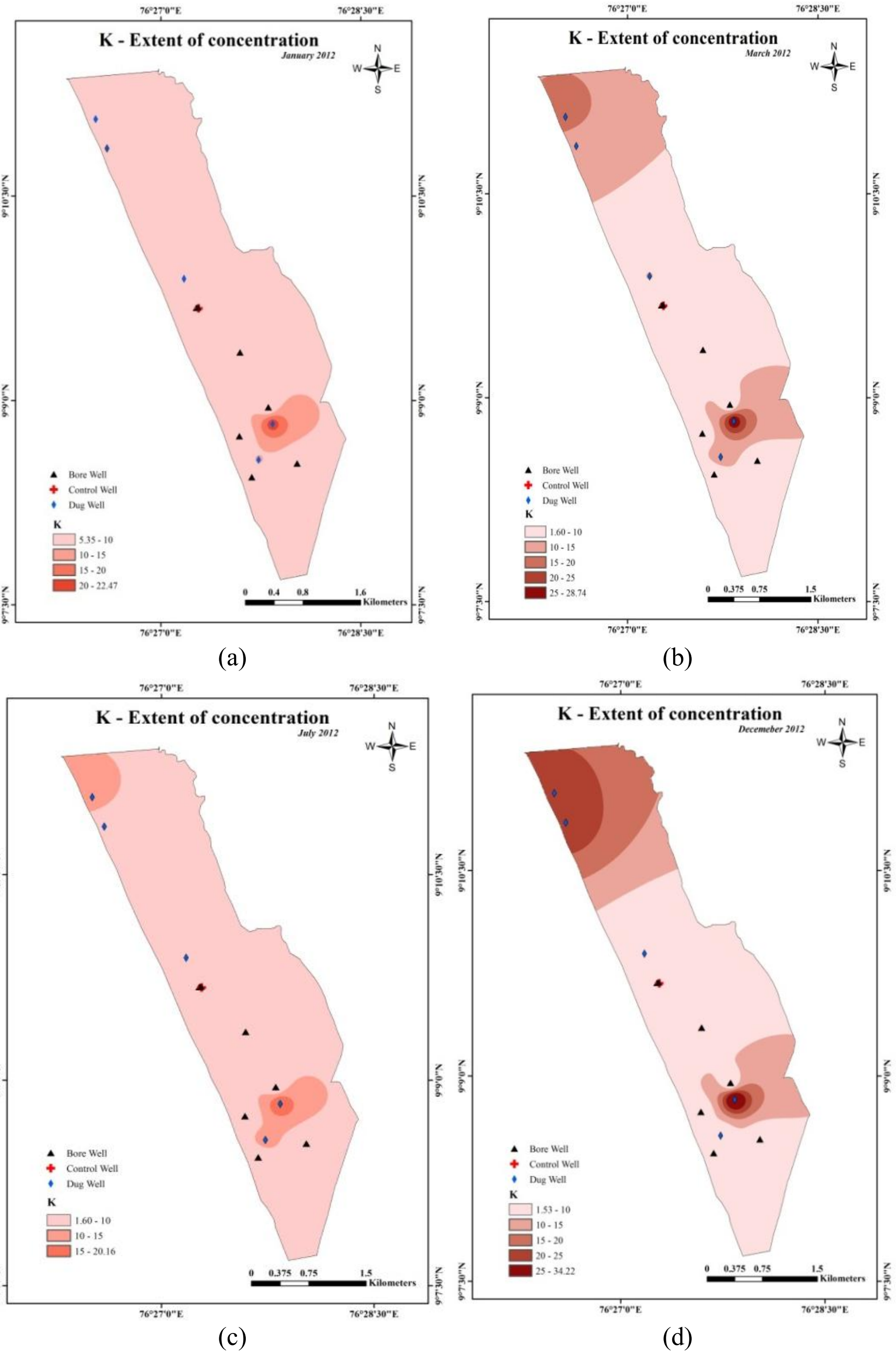


Figure 4.18: Monthly variation of Potassium of deep groundwater bore well (BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

From monthly pattern, almost uniform concentration of potassium is observed throughout the year with slight increase in May (7.7±0.2mg/l). Compared to control well (CW), bore well (BW) strata has higher potassium.

The spatial variation map for K of the study area is presented in Figure 4.19. In March 2012, lower than 10mg/l in major area. In uppermost area and pocket area in lower part are having higher concentration in the range 15-20mg/l. Near DW2 is having higher potassium than 25mg/l is observed. In July 2012, there is lowering of potassium concentration. Major part is having K less than 10mg/l. In December 2012, there is slight increase in the sodium concentration near the upper regions of the study area.



(a) (b)

(c) (d)

Figure 4.19: Spatial distribution map for K of the study area Arattupuzha coast, Alappuzha, Kerala, India during a) January b) March c) July and d) December of year 2012.

4.2.10 Bicarbonate (HCO_3^-)

The mean ($\bar{x} \pm \sigma$) bicarbonate concentration of BW strata in 2012 January is 312 ±46.3mg/l, which decreases to 189±102 in April 2012, again increase in May 2012 to 289±42mg/l, then decrease to 179±71mg/l in October 2012 and then increase to 251.2±34.5mg/l in December 2012. The annual mean bicarbonate concentration of BW strata during year 2012 is 241±58mg/l with CI of 204-278mg/l at 95% significant level.

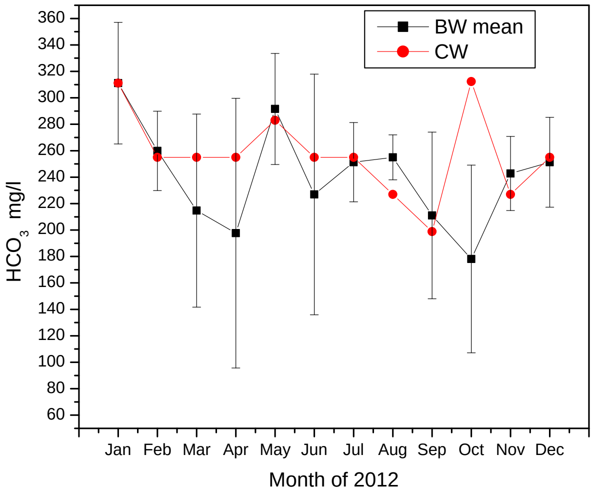
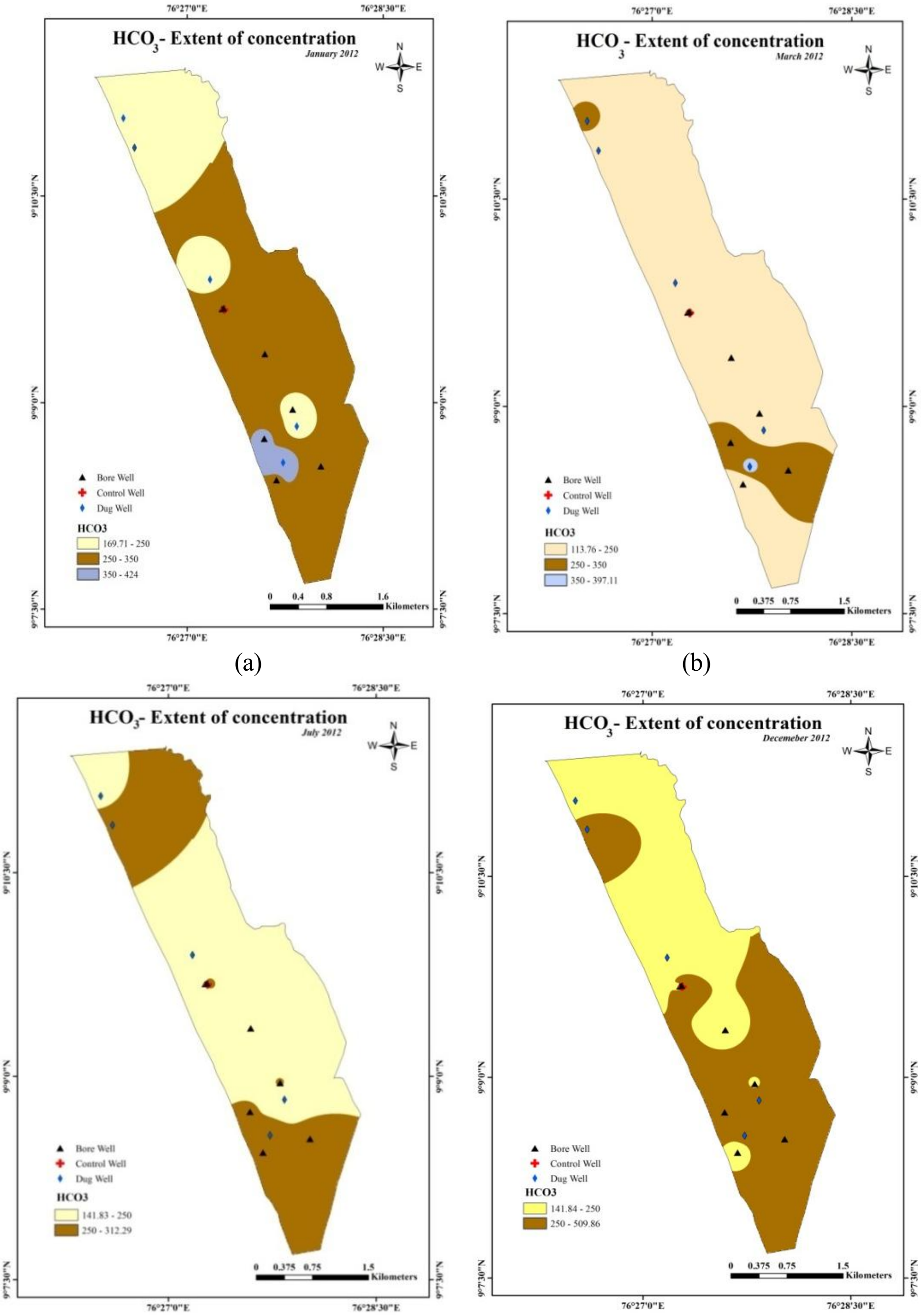


Figure 4.20: Monthly variation of Bicarbonate of deep groundwater bore well(BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The standard limit of bicarbonate according to WHO is 500mg/l. Thus in BW strata the only prominent ion having comparable concentration to DW strata is bicarbonate. The higher concentration of HCO_3^- in the water points to the dominance of mineral dissolution. In deep aquifers rock weathering is the source of major constituents in water [15, 16].



(a) (b)

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Figure 4.21: Spatial distribution map for HCO_3 of the study area Arattupuzha coast, Alappuzha, Kerala, India during a) January b) March c) July and d) December of year 2012.

The spatial variation map for HCO_3^- of the study area is presented in Figure 4.21. In January 2012 major area shows bicarbonate in the range 250-350mg/l with uppermost part and small pockets of lower than 250 and a small pocket of higher than 350mg/l. In March 2012, major area has lower than 250mg/l bicarbonate. Small pocket areas in the upper and lower part showing higher than 250mg/l bicarbonate. There is a spot in lower part having higher than 350mg/l bicarbonate. In July 2012, there are lower and upper areas higher than 250mg/l bicarbonate and central area of lower bicarbonate (140-250mg/l). In December 2012 area of higher bicarbonate (250-500mg/l) increases.

4.2.11 Chloride (Cl^-)

Chloride concentration of BW strata doesn't show much variation in each month of year 2012. Highest Cl^- is observed in February 2012 with 24±26.3mg/l. The annual mean of chloride concentration of BW strata during year 2012 is 16±13 with Cl^- of 8-24mg/l at 95% significant level. The standard limit of Cl^- ion concentration according to BIS and WHO is 250mg/l.

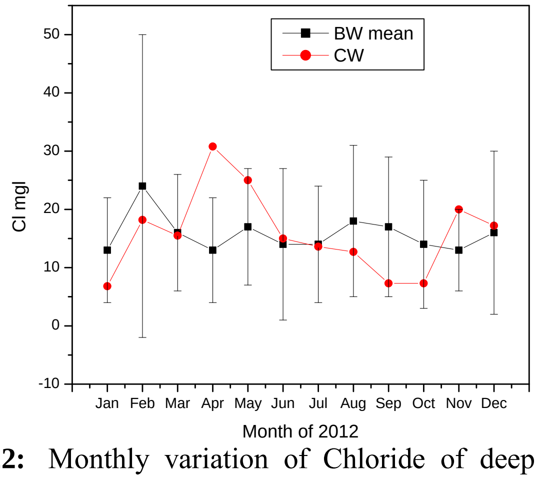
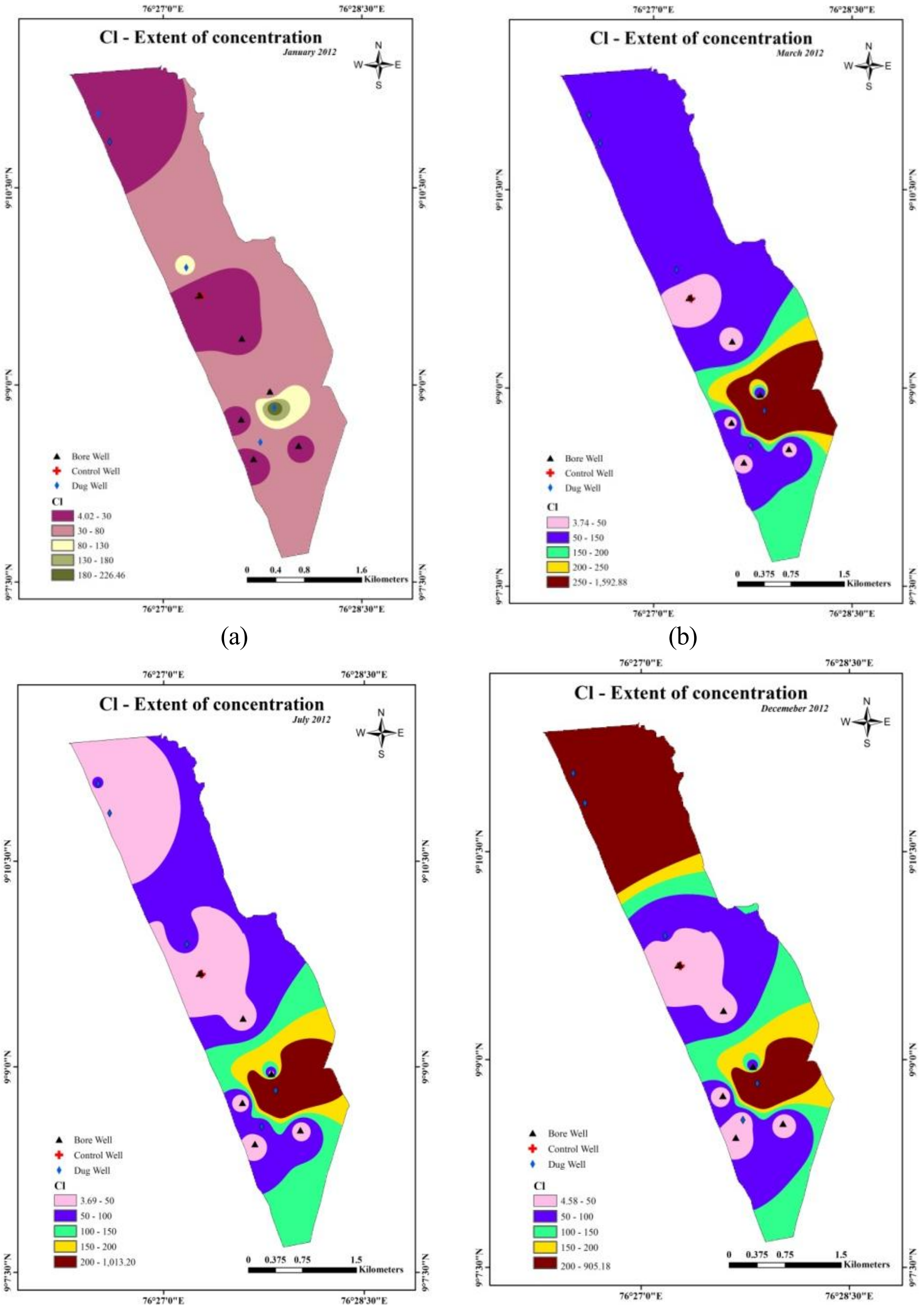


Figure 4.22: Monthly variation of Chloride of deep groundwater bore well(BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.



(a) (b)

(c) (d)

Figure 4.23: Spatial distribution map for Cl of the study area Arattupuzha coast, Alappuzha, Kerala, India during a) January b) March c) July and d) December of year 2012.

The spatial variation map for Cl of the study area is presented in Figure 4.23. In January 2012 major area shows 30-80mg/l range, upper, central and pocket areas of lower than 30 and 2 pockets of higher than 80mg/l are also observed. In march 2012, major area has chloride in the range 50-150mg/l. There is a lower pocket area of higher than 250mg/l. In July 2012, lowering of concentration is visible in some areas. In December 2012, upper area and a small pocket area near lower part exhibit higher than 200mg/l chloride.

Sedimentary rocks, particularly the evaporates is an important source of chloride. Chloride may be present in resistates as the result of inclusion of connate brine and in cementing material and is to be expected in any incompletely leached deposit laid down in the sea or in a closed drainage basin. When porous rocks are submerged by the sea at any time after their formation, they become impregnated with soluble salts, in which chloride plays a major role. Fine-grained marine shale might retain some of this chloride for very long periods. Leaching of evaporites and return of connate water to circulating groundwater are important routes by which marine chloride is returned to the sea. Rainwater close to the ocean commonly contains from one to several tens of milligrams per liter of chloride, but the concentrations observed generally decrease rapidly in a landward direction.

4.2.12 Total Dissolved Solids (TDS)

Dissolved-solids are widely used in evaluating water quality and are a convenient means of comparing waters with one another. Some waters which are high in magnesium, chloride and nitrate give residues that are partly decomposed or volatilized at the drying temperature. The variation of TDS of BW strata is similar to that of control well. It decreases from

January 2012 (533±119mg/l) to March 2012 (193±57mg/l), increases in May 2012 (500±73mg/l), again decreases till September 2012 (164±54mg/l), increases in November 2012 and decreases in December 2012 to 113±38mg/l. The annual mean ($\bar{x} \pm \sigma$) TDS of BW strata during year 2012 is 299±86mg/l with CI of 245-353mg/l at 95% significant level. The standard limit of TDS according to WHO & BIS is 500mg/l.

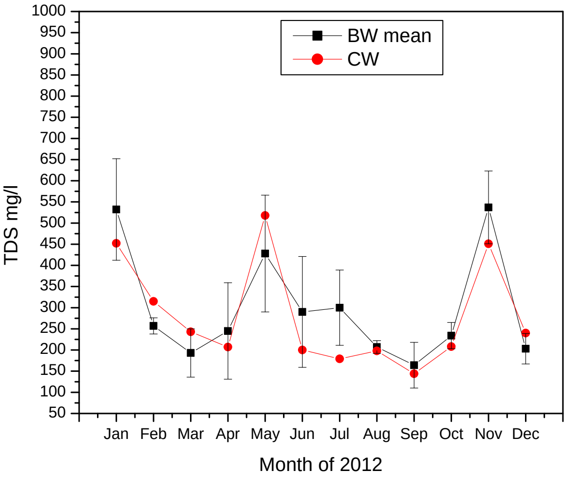
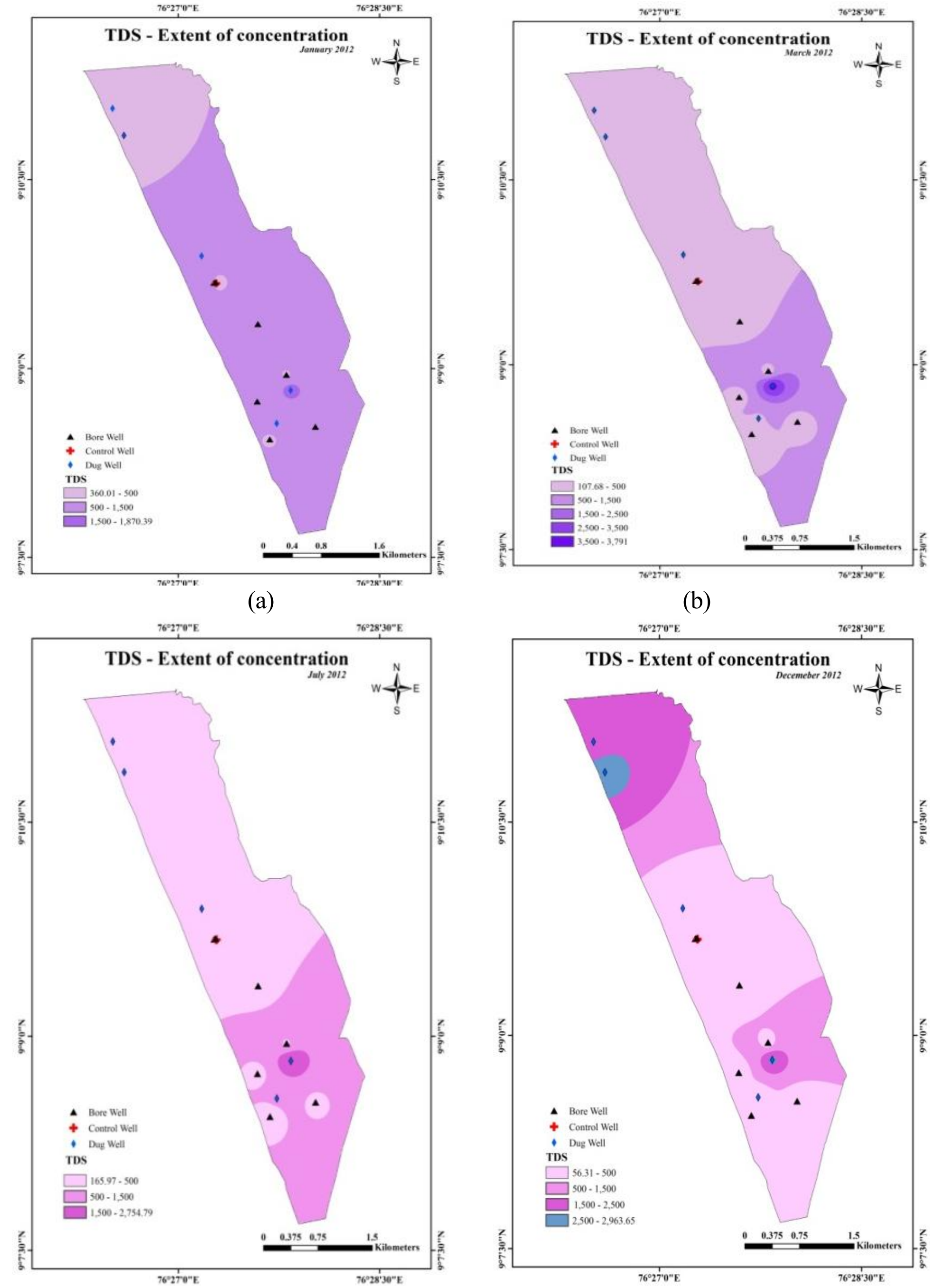


Figure 4.24: Monthly variation of Total Dissolved Solids (TDS) of deep groundwater bore well(BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The spatial variation map for TDS of the study area is presented in Figure 4.25. In January 2012 TDS distribution is almost uniform in the range 500-1500mg/l with upper end and pockets of lower than 500 and one pocket of higher than 1500mg/l. In March 2012, upper area TDS range is 100-500mg/l. There is a small pocket of unusually high TDS (>3000mg/l). In July, overall lowering of TDS occurs. In December again increase in TDS is prominent.



(a) (b)

(c) (d)

Figure 4.25: Spatial distribution map for TDS of the study area Arattupuzha coast, Alappuzha, Kerala, India during a) January b) March c) July and d) December of year 2012.

4.2.13 Dissolved Oxygen (DO)

In January 2012 the DO of BW strata is 3.1±1.3mg/l. It shows an increasing tendency and becomes 5.4±1.1mg/l in December. The annual mean ($\overline{x} \pm \sigma$) DO of BW strata during year 2012 is 4.7±1.6 with CI of 3.7-5.7 mg/l at 95% significant level. Deep aquifers have lower DO compared to shallow aquifers. Oxygen is supplied to groundwater through recharge and by movement of air through unsaturated material above the water table. This oxygen reacts with oxidizable material encountered along the flow path of the water. Water containing measurable amounts of dissolved oxygen may penetrate long distances into the system if little reactive material is available. The principal reacting species are organic materials and reduced inorganic minerals such as pyrite and siderite. As time passes, the oxidizable material in the aquifer will be removed or altered for long distances from the point of recharge.

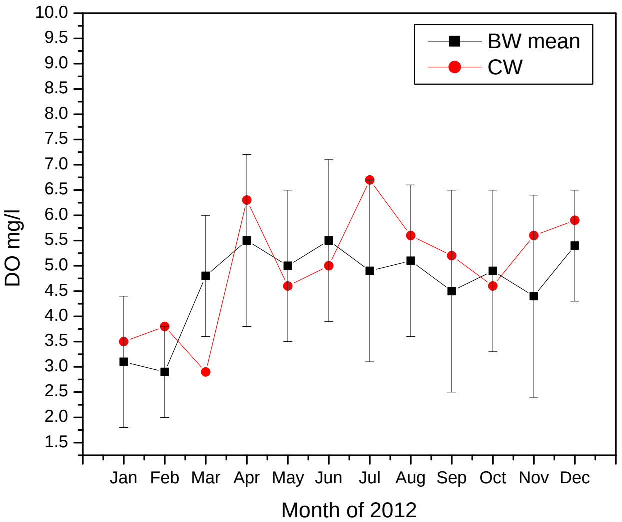
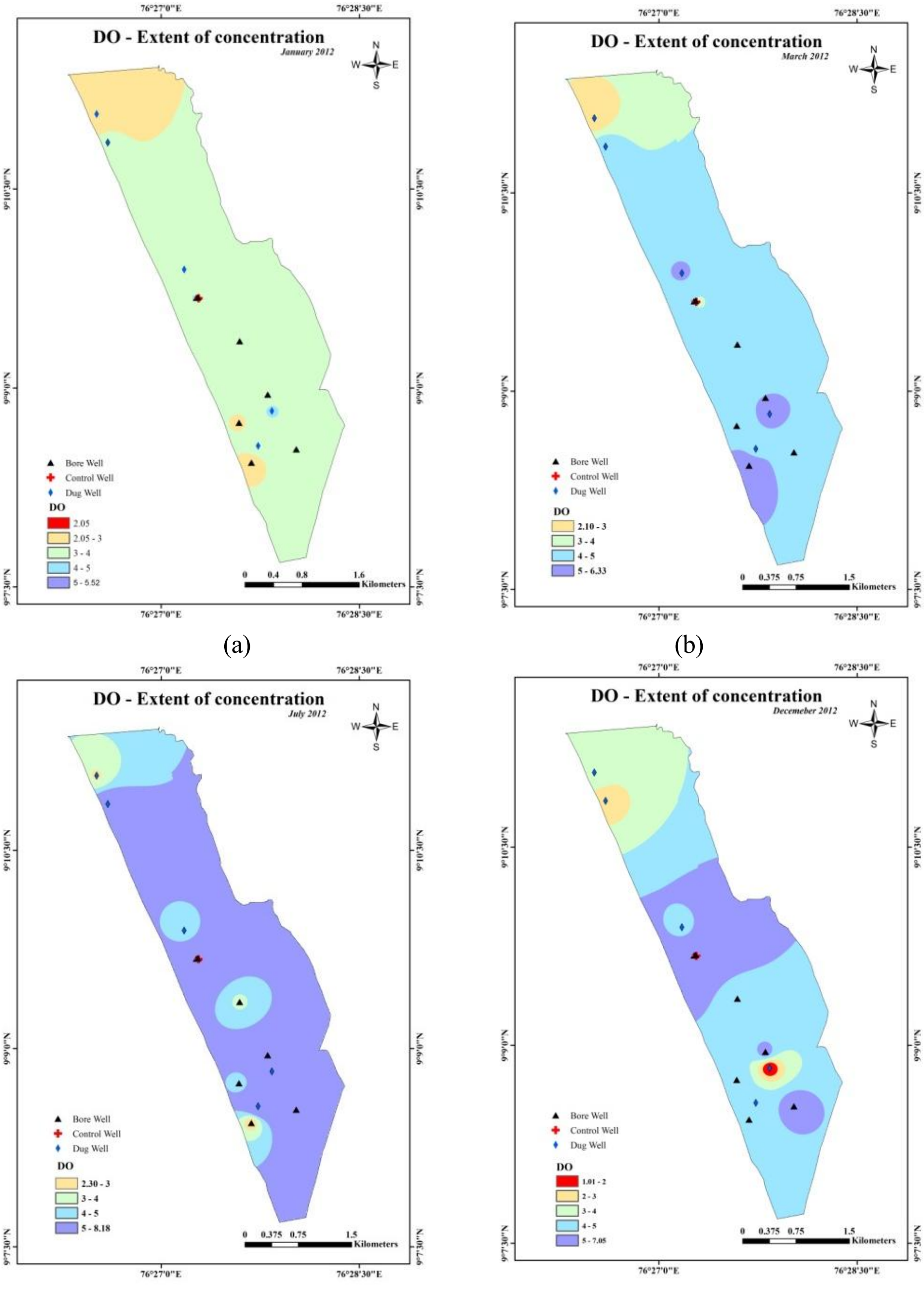


Figure 4.26: Monthly variation of Dissolved Oxygen (DO) of deep groundwater bore well(BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.



(a) (b)

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Figure 4.27: Spatial distribution map for DO of the study area Arattupuzha coast, Alappuzha, Kerala, India during a) January b) March c) July and d) December of year 2012.

The spatial variation map for DO of the study area is presented in Figure 4.27. In January 2012 DO of major area is in the range 3-4mg/l with small pockets of lower DO. In March 2012, major area has DO in the range 4-5mg/l. There are small pockets of higher than 5mg/l. In the uppermost end there is less than 3mg/l DO level. In July 2012 an overall increase in DO is observed. In December 201 considerably lower DO in the small pocket area near the lower part is observed.

4.2.14 Biochemical Oxygen Demand (BOD)

To evaluate the organic pollution load in a quantitative way measurement of biochemical oxygen demand (BOD) is done. The BOD determination is commonly made by diluting portion of a sample with oxygenated water and measuring the residual dissolved oxygen after an incubation period of 5 days at 20°C. The determination has biological significant, has no particularly direct geochemical importance, but it is extensively applied in pollution studies. BOD is not a measure of some specific pollutant, but rather a measure of the amount of oxygen required by aerobic bacteria and other microorganisms to stabilize decomposable organic matter.

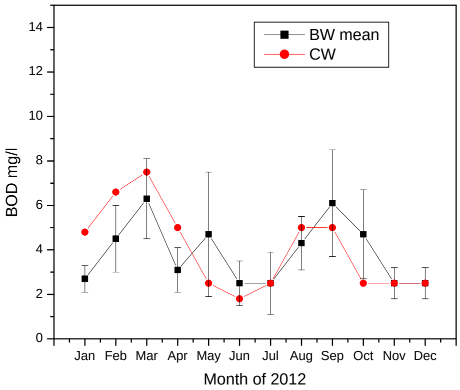
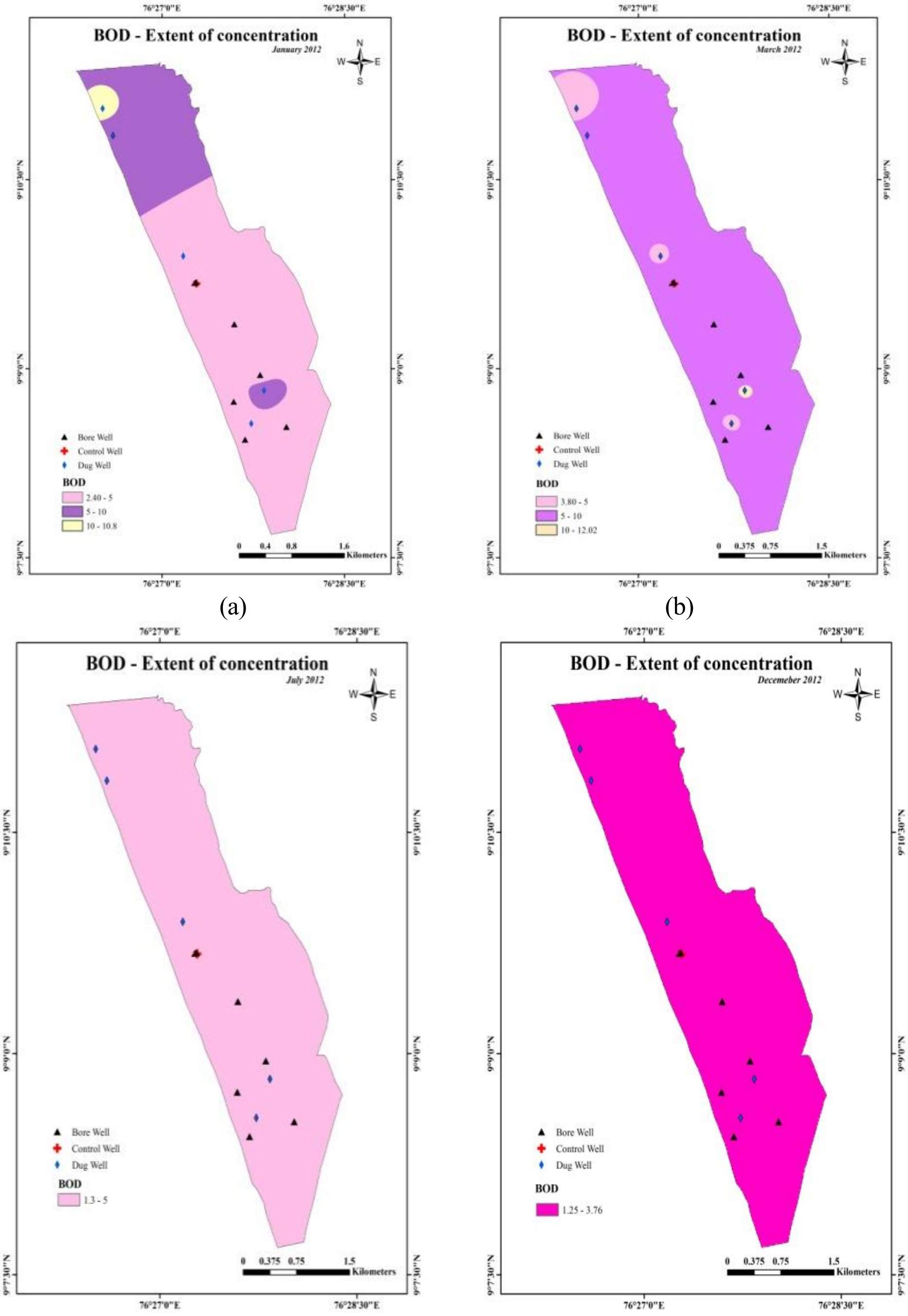


Figure 4.28: Monthly variation of Biochemical Oxygen Demand (BOD) of deep groundwater bore well(BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.



(a) (b)

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Figure 4.29: Spatial distribution map for BOD of the study area Arattupuzha coast, Alappuzha, Kerala, India during a) January b) March c) July and d) December of year 2012.

BOD of BW strata increases from January 2012 (2.7±0.6mg/l) to March 2012 (7.7±3.0mg/l), decreases in April (3.0±1.0mg/l), increase in May (5±3.6mg/l), again decline in June 2012 and hike to 6.1±2.4mg/l in September 2012. The annual mean ($\overline{x} \pm \sigma$) BOD of BW strata during year 2012 is 3.8±1.7 with CI of 2.7-4.9 mg/l at 95% significant level.

The spatial variation map for BOD of the study area is presented in Figure 4.29. In January 2012 major area has BOD in the range 2-5mg/l. Upper and lower pockets are of 5-10 range and one upper pocket area of higher than 10mg/l. In March 2012 almost uniform distribution of BOD in the range 5-10 mg/l is observed. In July and December 2012 uniform distribution in the range 1.3-5mg/l and 1.25-3.76mg/l are observed

4.2.15 Sulphate (SO_4^{2-})

In the BW strata sulphate is detected only in the months February, April and October 2012. Its average is only 2.5±0.5mg/l. So minerals containing sulphate are rare in the rocks of present study area. Pyrite crystals occurring in many sedimentary rocks constitute a source of both ferrous iron and sulphate in groundwater. Effects of pyrite oxidation on groundwaters is sometimes more subtle, as the iron so released may be precipitated or lost by *cation exchange* and the sulphate may be lost by reduction as the water moves through the aquifer.

4.2.16 Nitrate (NO_3^-)

Influence on the nitrogen cycle includes production and use of synthetic fertilizers such as ammonia and other nitrogen compounds. Ammonium cations are strongly adsorbed on mineral surfaces. Anionic species such as nitrate are readily transported in water and are stable over a considerable range of conditions. The nitrite and organic species are unstable in aerated water and are generally considered to be indicators of pollution through disposal of sewage or organic waste. The full impact of leached fertilizer nitrogen on groundwater is slow to develop in many areas because transport of solutes through the unsaturated zone between the land surface and the water table is slow. In some soil profiles, a substantial fraction of the transported nitrate was lost by *denitrification*. Presence of nitrate in groundwater may be due to pollution from barnyards, septic tanks, nitrogen fertilizers etc.

In the present study area nitrate determination conducted in year 2014 shows that BW strata has an average value of 1.7±0.9mg/l. Analysis conducted in the year 2015 shows that the nitrate concentration of BW strata is 1.12±0.44mg/l. The WHO & BIS standard limit for nitrate in water is 50mg/l. So nitrate pollution is not a problem in the present study area with respect to the condition of deep groundwater.

4.2.17 Phosphate (PO_4^{3-})

Domestic and industrial sewage effluents remain as important sources of phosphorus in water. In the BW strata phosphate is detected only in the months February, July and October. Its average value is only 0.1mg/l.

4.2.18 Iron (Fe)

The annual mean Iron concentration of BW strata during year 2012 is 1.5±0.8 with CI of 1.0-2.0 mg/l at 95% significant level. Iron is not present in the control well. The WHO & BIS standard limit for Iron in water is 0.3mg/l. Lateritic soil present in the study area at depth is the reason for the higher iron concentration in BW strata [17].

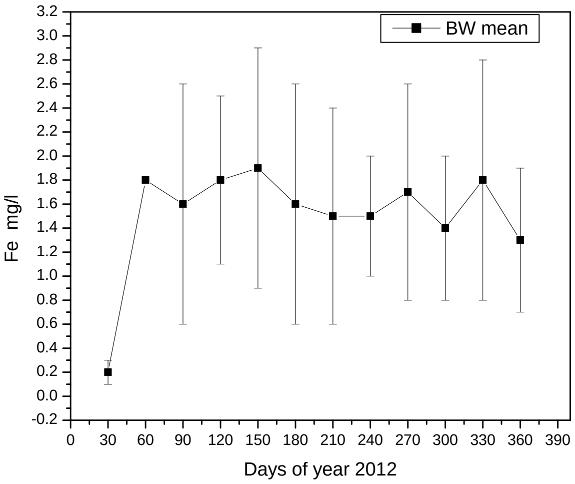

Figure: 4.30: Monthly variation of Iron of deep groundwater bore well(BW) sources & control well (CW) along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

The most common form of iron in solution in groundwater is the ferrous ion Fe^{2+}. This ion has an octahedral hydration shell of six water molecules. The monohydroxide complex $FeOH^{+}$ can be predominant above a pH of about 9.5 and may be significant at somewhat lower pH's.

4.3 Trace Element Study

Minor and trace constituents, which are present in concentrations less than 1.0mg/L, have vital importance to human health, plant nutrition, or other areas of general interest [18]. The trace elements include elements of *s-block* (*alkali metals& alkaline earth metals*), *p-block and d-block* (*transition metals*), majority of which are determined by *ICP-MS method.*

The result of the trace element study of BW strata are given in Table 4.3. In the present study area, the average concentration of lithium in deep bore wells is 2.43±1.9µg/l, rubidium is 9.87±4.0µg/l, cesium is 0.16±0.05µg/l, strontium is 533±348µg/l and barium is 56.1±29.3µg/l. The higher concentration of strontium is due to its presence in minerals of Ca and Mg as impurity. In BW strata the mean of vanadium is 0.28±0.2µg/l, chromium is 0.29±0.07µg/l, manganese is 25.1±14.4µg/l, nickel is 4.03±1.6 µg/l, copper is 2.5±1.4 µg/l, zinc is 13.9±12 µg/l, and silver is 0.2±0.06 µg/l. Cadmium and cobalt are detected only in two stations and its concentration is only 0.1µg/l.

Table 4.3: Trace element concentrations in deep groundwater (BW) sampling stations along Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Trace element	**Unit**	**Stations**								**IS:2012**
		BW1	**BW2**	**BW3**	**BW4**	**BW5**	**BW6**	**BW7**	$\bar{x} \pm \sigma$	
Li	µg/l	0.6	3.4	4.8	4.8	0.8	0.4	2.2	5.6±3.5	
Rb	µg/l	4.5	12.7	12.1	13.8	11.6	4.2	10.2	13.2±7.2	
Cs	µg/l	ND	0.2	0.1	0.1	0.2	ND	0.2	0.23±0.12	
Sr	µg/l	82.1	746.4	810.8	941.9	443.8	70.8	636.1	593±340	
Ba	µg/l	36.7	71.6	82.1	62.1	94.7	29.8	15.6	23±9	700
V	µg/l	0.6	0.1	ND	0.4	0.2	0.4	0.1	0.28± 0.2	
Cr	µg/l	0.3	0.2	0.3	0.3	0.2	0.4	0.3	0.29± 0.07	50
Mn	µg/l	5.1	29	33.5	35.1	37	3.5	32.4	25.1± 14.4	500
Co	µg/l	ND	ND	ND	0.1	ND	0.1	ND	0.1± 0	
Ni	µg/l	2.2	5.2	4	3.3	6.7	2.2	4.6	4.03± 1.6	20
Cu	µg/l	5.2	1.2	1.4	3.6	1.8	2	2.3	2.5± 1.4	1500
Zn	µg/l	6.9	12.7	6.1	40.3	12.9	8.5	10	13.9± 12	15000
Ag	µg/l	0.2	0.2	0.2	0.2	0.2	0.1	0.3	0.2± 0.06	
Cd	µg/l	ND	ND	0.1	ND	ND	ND	0.1	0.1± 0	5
Al	µg/l	50.5	7.3	13.5	51.3	10.4	48.3	17.8	28.4± 20	200
Ga	µg/l	7.8	14.8	16.7	12.5	19.3	6.3	19.6	13.9± 5	
In	µg/l	ND	0.1	ND	ND	0.1	ND	0.1	0.1± 0	
Pb	µg/l	0.6	0.5	0.3	1.5	0.3	0.5	0.6	0.6± 0.4	50
As	µg/l	0.2	ND	ND	0.2	ND	0.1	ND	0.17±0.06	50
Bi	µg/l	ND	0.3	ND	0.1	0.1	ND	0.2	0.18± 0.1	
Se	µg/l	3.8	4.2	4.8	4.5	4.2	4.7	4.5	4.4± 0.3	10

The mean of aluminium in BW strata is 28.4±20µg/l, gallium is 13.4-14.4µg/l, lead is 0.6±0.4µg/l and selenium is 4.4±0.3µg/l. Element indium is present in 3 stations and in all of them its concentration is 0.1 µg/l. Arsenic also is present in 3 BWs and its mean is 0.17±0.06µg/l. Bismuth is present in 4 stations and its mean value is 0.18±0.1μg/l. So all the trace elements studied, using *ICP-MS method*, are well within the standard limit and no contamination or pollution is observed.

4.4 Statistical Analysis

Since routine chemical analysis of water is time consuming it would be necessary to establish relationships between a common and easily determinable parameter (*independent variable*) and other parameters (*dependent variable*). The most familiar measure of dependence between two quantities is the *Pearson's correlation coefficient*. If the *correlation coefficient* 'r' between two variables X and Y is fairly large, it implies that these two variables are highly correlated [19-21].

Pearson Correlation matrix for bore well (BW) strata during year 2012 is given in Table 4.4.

Table 4.4: Pearson correlation matrix for Bore Well (BW) strata of Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

	pH	**EC**	**TDS**	**TH**	**Ca**	**Mg**	**Na**	**K**	**Fe**	**HCO_3**	**Cl**	**SO_4**	**PO_4**	**DO**	**BOD**
pH	1.00														
EC	-0.47	1.00													
TDS	-0.48	0.04	1.00												
TH	-0.31	0.57	0.35	1.00											
Ca	-0.30	0.54	0.28	0.89	1.00										
Mg	-0.19	0.39	0.30	0.74	0.36	1.00									
Na	-0.11	-0.04	-0.44	0.08	0.25	-0.21	1.00								
K	-0.03	0.49	0.28	0.43	0.29	0.47	-0.73	1.00							
Fe	0.80	-0.55	-0.37	-0.38	-0.37	-0.23	-0.18	0.06	1.00						
HCO_3	-0.30	0.06	0.64	0.21	0.26	0.05	-0.29	0.09	-0.49	1.00					
Cl	0.10	0.44	-0.19	0.28	0.15	0.35	-0.07	0.16	-0.14	0.23	1.00				
SO_4	-0.03	0.10	-0.26	0.07	0.03	0.08	0.13	0.11	0.18	-0.41	0.36	1.00			
PO_4	-0.16	0.37	-0.20	0.52	0.57	0.23	0.37	0.08	-0.30	-0.19	0.28	0.56	1.00		
DO	0.26	0.03	-0.47	-0.41	-0.28	-0.41	-0.12	0.11	0.37	-0.55	-0.40	-0.22	-0.14	1.00	
BOD	-0.27	0.36	0.11	0.36	0.38	0.18	0.26	0.17	-0.14	-0.48	-0.25	0.41	0.47	0.01	1.00

From Table 4.4 it is clear that pH is directly correlated to iron (r=0.80). Thus the chemical behaviour of iron and its solubility in water depend on the pH. From the matrix, we can see that pH doesn't show any other significant correlation. EC show slight positive correlation to TH and Ca (0.89) and a slight negative correlation to Fe (r= $^{-}$0.55). TDS show slight positive correlation to bicarbonate (r= 0.64). TH show significant positive correlation to Ca (r=0.89) and Mg (r=0.74). No other significant correlations are observed in the *Pearson correlation matrix* for BW strata.

4.5 Water quality Index (WQI)

By using *weighted arithmetic index method* WQI [22] of BW strata calculated in each month of year 2012 are given in Table 4.5.

Table 4.5: Monthly variation of WQI, Water Quality and Grading of CW & Bore Well strata of Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Year (2012)	CW			BW			
	WQI	Water Quality	Grading	WQI		Water Quality	Grading
				$\bar{x} \pm \sigma$	Range		
Jan	49	G	B	30.8±6.0	24.8-36.8	G	B
Feb	44	G	B	35.8±5.9	29.9-41.7	G	B
Mar	55	P	C	69.3±7.9	61.4-77.2	P	C
Apr	51	G	B	47.0±18.1	28.9-65.1	G-P	B-C
May	45	G	B	43.7±16.1	27.6-59.8	G-P	B-C
Jun	33	G	B	32.8±6.1	26.7-38.9	G	B
Jul	31	G	B	36.8±5.0	31.8-41.8	G	B
Aug	32	G	B	41.3±4.9	36.4-46.2	G	B
Sep	33	G	B	37.0±4.4	32.6-41.4	G	B
Oct	30	G	B	35.3±4.9	30.4-40.2	G	B
Nov	21	E	A	23.0±6.3	16.7-29.3	E-G	A-B
Dec	35	G	B	35.3±8.1	27.2-43.4	G	B
$\bar{x} \pm \sigma$	38±10			39±8.9			
μ	38±6.5			39±5.7			
CI	28-48	G	B		33.3-44.7	G	B

E-Excellent G-Good P-Poor

In January and February water show *good quality*. In March WQI range from 61.4 to 77.2 which define *poor quality water*. This is due to the high pH in that month. In April and May 2012, water quality ranges from *good to poor* *category*. After that in the monsoon season the WQI calculated is in the range 25-50 which suggest *good quality*. In November the water quality improves and WQI range from 16.7-29.3 which suggest the water is in *excellent to good category*. In December also WQI shows *good quality* water.

4.6 Sodium – Chloride Ratio

From Table 4.6 it is clear that for the BW strata *ion exchange* is occurring in all months of year 2012. The value of *Na/Na+Cl* is higher than 0.5 and that of *Na/Cl* is higher than 1.0 in all months. The annual mean $(\bar{x} \pm \sigma)$ is 0.68±0.12 for *Na/Na+Cl* and 2.76±1.9 for *Na/Cl*. In ion exchange process Ca & Mg in water replaces Na in clays. Since Ca & Mg are removed from water this process is also called *natural softening*.

Table 4.6: Monthly variation of Na/Na+Cl ratio, Na/Cl ratio & probable inference of CW & BW strata Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Year (2012)	**CW**			**BW**		
	$\frac{Na}{Na+Cl}$	$\frac{Na}{Cl}$	**Inference**	$\frac{Na}{Na+Cl}$	$\frac{Na}{Cl}$	**Inference**
Jan	0.75	3.06	Ion exchange	0.7±0.1	2.8±1.6	Ion exchange
Feb	0.60	1.52	Ion exchange	0.7±0.1	2.3±1.3	Ion exchange
Mar	0.58	1.40	Ion exchange	0.7±0.1	2.5±1.9	Ion exchange
Apr	0.45	0.81	Reverse ion exchange	0.6±0.1	2.4±2.2	Ion exchange
May	0.48	0.93	Reverse ion exchange	0.5±0.08	1.1±0.3	Ion exchange
Jun	0.51	1.03	Ion exchange	0.7±0.2	3.3±3.1	Ion exchange
Jul	0.63	1.70	Ion exchange	0.7±0.1	3.2±2.2	Ion exchange
Aug	0.61	1.57	Ion exchange	0.7±0.1	2.8±1.5	Ion exchange
Sep	0.69	2.18	Ion exchange	0.7±0.1	2.8±2.2	Ion exchange
Oct	0.70	2.30	Ion exchange	0.7±0.1	3.4±1.8	Ion exchange
Nov	0.56	1.29	Ion exchange	0.7±0.07	3.2±1.5	Ion exchange
Dec	0.59	1.46	Ion exchange	0.7±0.1	3.4±1.8	Ion exchange
$\bar{x} \pm \sigma$	0.6±0.1	1.6±0.6	Ion exchange	0.68±0.12	2.76±1.9	Ion exchange
μ	0.6±0.1	1.6±0.6		0.68±0.08	2.76±1.2	
CI	0.5-0.7	1-2.2		0.6 -0.76	1.56 -3.96	

4.7 Irrigation Quality Evaluation

In arid and semi-arid regions the crop production is affected by the high concentration of soluble salts in irrigated water [23, 24]. Continuous use of such water result in the development of saline or sodic soil and it require expensive treatment to make them productive again. There are three principal problems that can arise from the quality of irrigation water delivered to the agricultural fields 1) salinity hazard which is directly related to the quantity of dissolved salts in water and EC or TDS of water can give a direct indication of salinity hazard 2) Sodicity (alkali) hazard which arises due to the continuous use of water, which contain more sodium ions than divalent calcium and magnesium ions while the total concentration of salts is generally not very high, for irrigation. Accumulation of sodium ions onto the exchange site results in a breakdown of soil aggregates responsible for good soil structure needed for free movement of water and air through the soils 3) Toxicity hazard results from the existence of toxic substances as boron or heavy metals in water. Ions like chloride, sodium, etc., could prove toxic to specific crops if present in excessive quantities.

Boron is not detected in the present study area and the trace elements are not present in harmful levels. The extend of these problems in the deep groundwater of present study can be evaluated by calculating the various irrigation quality parameters.

To assess the irrigational water quality of the water analysed, 6 parameters are calculated using the concentrations of various ions obtained from chemical analysis after converting to milliequivalents per litre (meq/L). They are Sodium Adsorption Ratio (SAR), Sodium Percentage (Na %), Magnesium Adsorption Ratio (MAR), Residual Sodium Carbonate (RSC), Permeability Index (PI) and Kelly’s ratio (KR).

4.7.1 Electrical Conductivity, Total Hardness & Total Dissolved Solids

Three parameters already discussed namely EC, TH, TDS have special importance in determining the irrigation suitability of water (Table 4.7).

Table4.7: Monthly variation of EC, TH and TDS and the inferences of Bore Well strata Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Year (2012)	Parameters					
	EC µS/cm	**Inference**	**TH mg/l**	**Inference**	**TDS mg/l**	**Inference**
Jan	250±80	E-G	165±33	MH-H	532±120	F
Feb	350±90	G	178±31	MH-H	257±19	F
Mar	260±80	E-G	159±52	MH-H	193±57	F
Apr	260±90	E-G	151±68	MH-H	245±114	F
May	420±40	G	175±36	MH-H	428±138	F
Jun	290±100	E-G	123±51	MH-H	290±131	F
Jul	310±50	G	178±21	H	300±89	F
Aug	380±30	G	174±13	H	207±15	F
Sep	360±90	G	177±66	MH-H	164±54	F
Oct	400±60	G	182±26	H	234±31	F
Nov	350±100	G	186±23	H	537±86	F
Dec	360±60	G	164±22	MH-H	203±36	F
$\bar{x} \pm \sigma$	333±76	G	168±41	MH-H	299±86	F
μ	333±48		168±26		299±54	
CI	285-381		142-194		245-353	

E-Excellent G-good H-Hard MH-Moderately Hard F-Fresh

The Electrical Conductivity of BW strata is either less than 250 µS/cm or comes in the range 250-750 µS/cm in all months of year 2012 which suggest that the water quality is *excellent or good* for irrigation throughout the year.

The Total Hardness (TH) is less than 300mg/l throughout the year. So the irrigation quality ranges from *moderately hard to hard* (MHH). Weathering of rocks leads to the hardness of deep groundwater sources.

Total Dissolved Solids (TDS) for BW strata is less than 1000mg/l throughout the year which infers that the water is in *fresh* category and there is no salinity problem for using the water for irrigation

4.7.2 Kelly's ratio (KR)

Kelly's ratio is calculated as the ratio of Na concentration to the total concentration of Ca and Mg (all concentrations in meq/l).The ratio is less than 1 for BW strata throughout the year (Table 4.8), which suggest the water is suitable for irrigation throughout the year. The annual mean ($\bar{x} \pm \sigma$) of KR is 0.26±0.08 which is much lower than 1.

Table 4.8: Monthly variation of Kelly's ratio (KR), Magnesium Adsorption Ratio (MAR) & Permeability index (PI) of BW strata along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Year (2012)	**Parameters**								
	$KR = Na^+ / (Ca^{2+} + Mg^{2+})$			$MAR = Mg^{2+} \times 100 / (Ca^{2+} + Mg^{2+})$			$PI = [Na^+ + (HCO_3)^{1/2}] \times 100 / [Ca^{2+} + Mg^{2+} + Na^+]$		
	$\bar{x} \pm \sigma$	**Range**	**Water Quality**	**$\bar{x} \pm \sigma$**	**Range**	**Water Quality**	**$\bar{x} \pm \sigma$**	**Range**	**Water Quality**
Jan	0.24±0.09	0.15-0.33	S	34.7±8.7	26.0-43.4	S	76.4±14.4	62.0-90.8	G
Feb	0.25±0.05	0.2-0.3	S	37.1±5.9	31.2-43	S	67.3±5.1	62.2-72.4	G
Mar	0.26±0.09	0.17-0.35	S	35.9±7.1	28.8-43	S	69.3±12.9	56.4-82.2	G
Apr	0.22±0.04	0.18-0.26	S	43.4±21.6	21.8-65	S-US	74.4±21.1	52.5-95.5	G
May	0.16±0.09	0.07-0.25	S	38.7±5.5	33.2-44.2	S	64.6±1.9	62.7-66.5	G
Jun	0.26±0.05	0.21-0.31	S	36.9±14	22.9-50.9	S	87.7±25.9	61.8-113.6	G
Jul	0.22±0.04	0.18-0.26	S	35.7±6	29.7-41.7	S	62.6±4.7	57.9-67.3	G
Aug	0.28±0.07	0.21-0.35	S	32±6.2	25.8-38.2	S	65.4±4	61.4-65.8	G
Sep	0.28±0.07	0.21-0.35	S	36.5±21.8	14.7-58.3	S	70.7±28.4	42.3-99.1	G
Oct	0.26±0.04	0.22-0.3	S	34.8±2.8	32-37.6	S	57±5	52-62	G
Nov	0.25±0.06	0.19-0.31	S	33.7±10	23.7-43.7	S	63.4±4.4	59.0-67.8	G
Dec	0.4±0.2	0.2-0.6	S	25.7±15	10.7-40.7	S	83.4±30.4	50.0-113.8	G
$\bar{x} \pm \sigma$	0.26±0.08			35.4±12.1			70.2±16.7		
μ	0.26±0.05			35.4±7.7			70.2±10.6		
CI	0.21-0.31		S	27.7-43.1		S	59.6-80.8		G

S-Suitable US- Unsuitable G- Good for irrigation

4.7.3 Magnesium adsorption ratio (MAR)

MAR is the percentage of the ratio of magnesium concentration to the total concentration of Ca and Mg (all concentrations in meq/l). The MAR calculated for BW strata is less than 50% in all months except April which suggest the suitability of water for irrigation. In April the upper limit is 65 which is slightly higher than 50, the limit of MAR for irrigation suitability. The annual mean ($\bar{x} \pm \sigma$) of MAR is 35.4±12.1 which is lower than 50. Higher Magnesium concentration is mostly observed in dolomite rich areas.

4.7.4 Permeability Index (PI)

According to the PI percentage water is classified into *Class I, Class II & Class III*. If the PI is higher than 75% the water comes in *class I*, 25-75% *class II* and less than 25% *class III*. *Class I&II* water is *good* for irrigation. From the table it is clear that the water of BW strata of the study area comes in *class I and class II* throughout the year. The annual mean ($\bar{x} \pm \sigma$) PI is 70.2±16.7. So the water is *good* for irrigation.

4.7.5 Sodium Adsorption Ratio

SAR is a simple method of evaluating high sodium in water. From Table 4.9 it is clear that SAR value of BW strata is less than 10 throughout the year and so the water maintain *excellent quality* in the whole year. The annual mean of SAR is 0.65±0.18. So unlike DW strata higher sodium concentration is not a problem in BW strata.

Table 4.9: Monthly variation of Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC) and Sodium Percentage (Na%) of BW strata along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Year (2012)	**Parameters**								
	SAR = $Na^+ / [(Ca^{2+} + Mg^{2+}) / 2]^{1/2}$			RSC = $(CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$			Na% = $Na^+ \times 100 / (Ca^{2+} + Mg^{2+} + Na^+ + K^+)$		
	$\bar{x} \pm \sigma$	**Range**	**Water Quality**	**$\bar{x} \pm \sigma$**	**Range**	**Water Quality**	**$\bar{x} \pm \sigma$**	**Range**	**Water Quality**
Jan	0.61±0.18	0.43-0.79	E	1.82±0.9	0.92-2.72	G-US	22.0±5.6	16.4-27.6	E-G
Feb	0.67±0.15	0.52-0.82	E	0.71±0.38	0.33-1.09	G	22.7±2.9	19.8-25.6	E-G
Mar	0.63±0.11	0.52-0.74	E	0.34±0.3	0.04-0.64	G	23.6±5.7	17.9-29.3	E-G
Apr	0.51±0.2	0.31-0.71	E	0.19±0.93	-0.74-1.12	G	21.2±3.2	18.0-24.4	E-G
May	0.43±0.23	0.20-0.66	E	1.1±0.6	0.5-1.7	G-D	17.2±6.1	11.1-23.3	E
Jun	0.58±0.19	0.39-0.77	E	1.15±0.6	0.55-1.75	G-D	23.8±3.4	20.4-27.2	G
Jul	0.58±0.09	0.49-0.67	E	0.38±0.3	0.08-0.68	G	20.4±2.7	17.7-23.1	E-G
Aug	0.76±0.19	0.57-0.95	E	0.51±0.31	0.2-0.82	G	24.1±4.4	19.7-28.5	E-G
Sep	0.71±0.2	0.51-0.91	E	-0.08±0.8	-0.88-0.72	G	24.5±3.9	20.6-28.4	G
Oct	0.7±0.13	0.57-0.83	E	-0.7±0.8	-1.5-0.1	G	23.4±2.7	20.7-26.1	G
Nov	0.7±0.14	0.56-0.84	E	0.27±0.4	-0.13-0.67	G	22.7±3.5	19.2-26.2	E-G
Dec	0.9±0.3	0.6-1.2	E	1.2±0.7	0.5-1.9	G-D	29.5±8.9	20.6-38.4	G
$\bar{x} \pm \sigma$	0.65±0.18			0.57±0.62			22.9±4.76		
μ	0.65±0.11			0.57±0.39			22.2±3.0		
CI	0.54-0.76		E	0.18-0.96		G	19.0-25.9		E-G

E-Excellent G-good D-Doubtful US- Unsuitable

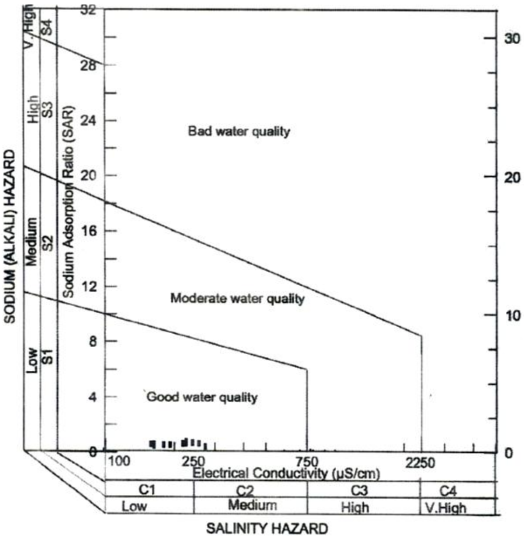

Figure 4.31 USSL Diagram for deep groundwater BW strata of Arattupuzha coast, Alappuzha, Kerala, India showing each month of year 2012

Sodium Adsorption Ratio (SAR**)** is plotted against Electrical Conductivity (EC) in *U. S. Salinity diagram* to further classify groundwater samples. From the *USSL diagram* it is clear that, in all months water comes in *C1S1*and *C2S1*regions showing ***l****ow to medium salinity hazard and low sodium or alkali hazard.* Thus the water of BW strata keep *good water quality* throughout the year.

4.7.6 Residual sodium carbonate (RSC)

In January the RSC range is 0.92-2.72 which suggest a water quality of *good to unsuitable*. The higher bicarbonate concentration in some of the bore wells result in the increase in RSC. If RSC is higher than 2.5 the water is considered *unsuitable* for irrigation. In the months May (0.5-1.7), June (0.55-1.75) and December (0.5-1.9) the water quality vary from *good to doubtful range*, since the upper limit is higher than 1.25 which is the limit for *good quality*. In all other months RSC is lower than 1.25suggesting *good quality* water. The annual mean ($\overline{x} \pm \sigma$) RSC is 0.57±0.62.

4.7.7 Sodium Percentage (Na%)

Sodium Percentage calculation again reveals the *excellent to good quality* of BW water. The Na % is lower than 40 in all months and its mean value is 22.9±4.76.

Calculated percent sodium for groundwater in the study area is plotted against electrical conductivity (EC) in *wilcox diagram*.

From *Wilcox diagram,* the points corresponding to all months are clustered in the region of *excellent to good quality*. So water of BW kept *good quality* throughout the year 2012.

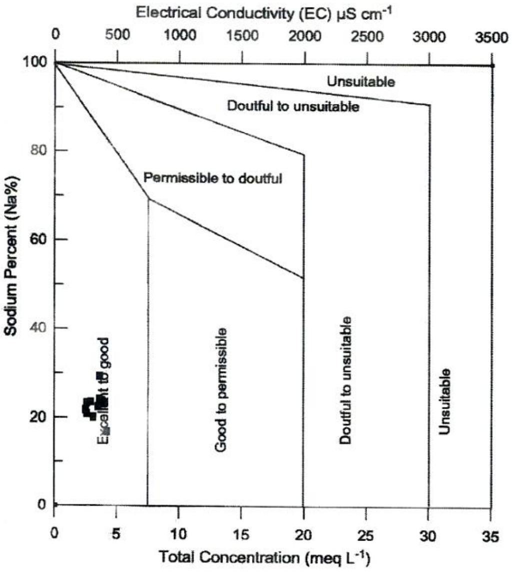

Figure 4.32: Wilcox Diagram for deep groundwater BW strata of Arattupuzha coast, Alappuzha, Kerala, India showing each month of year 2012

4.8 Saturation Indices (SI)

The determination of saturation indices is useful as an indicator of chemical stability and of probable behaviour of groundwater encountered in wells, where there may be concern over possible deposition of carbonate precipitates on well screens, gravel packs, and water-yielding rock faces

4.8.1 Aggressiveness Index (AI)

AI calculation suggest that the water of BW strata is *moderately aggressive* (Table 4.10).In the months March, April, August and December the tendency of water ranges *from moderately aggressive* **(**MA)*to non-aggressive* (NA). The annual mean $(\bar{x} \pm \sigma)$ AI is 11.8±0.4 which is lower than 12.

Table 4.10: Monthly variation of corrosion indices, Aggressiveness index(AI), Langelier Saturation Index(LSI) & Ryznar Stability index (RSI) of DW strata along the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Year (2012)	**Parameters & Tendency of water**					
	AI AI = pH + log (AH)	**Tendency of water**	**LSI** LSI = pH - pHs	**Tendency of water**	**RSI** RSI = 2pHs – pH	**Tendency of water**
Jan	11.7±0.2	MA	-0.18±0.22	SCNSF- SSFC	7.6±0.3	CS- HC
Feb	11.8±0.2	MA	-0.04±0.2	SCNSF- SSFC	7.5±0.3	CS- HC
Mar	12.7±0.5	MA-NA	0.9±0.5	SSFC- SFNC	6.7±0.8	LS-CS
Apr	11.7±0.9	MA-NA	-0.06±0.9	SC- SFNC	7.9±1.5	LSC- HC
May	11.8±0.2	MA	0.01±0.2	SCNSF- SSFC	7.4±0.3	CS- HC
Jun	11.5±0.2	MA	-0.34±0.22	SCNSF	8.1±0.6	CS-HC
Jul	11.8±0.2	MA	-0.05±0.2	SCNSF- SSFC	7.5±0.3	CS-HC
Aug	12.0±0.2	MA-NA	0.24±0.29	SCNSF - SFNC	7.1±0.4	LSC- CS
Sep	11.6±0.1	MA	-0.17±0.12	SCNSF- SFNC	7.8±0.4	CS- HC
Oct	11.5±0.3	MA	-0.3±0.3	SC-BP	7.9±0.5	CS- HC
Nov	11.4±0.2	MA	-0.49±0.22	SC-SCNSF	7.9±0.3	CS- HC
Dec	11.8±0.3	MA-NA	-0.01±0.34	SCNSF- SSFC	7.5±0.5	CS- HC
$\overline{x} \pm \sigma$	11.8±0.4	MA	-0.04±0.4	SCNSF- SSFC	7.6±0.6	CS-HC
μ	11.8±0.2		-0.04±0.23		7.6±0.4	
CI	11.6-12.0		-0.27 -0.19		7.21-7.99	

MA-moderately aggressive NA-nonaggressive SCNSF- slightly corrosive but non scale forming SSFC- slightly scale forming and corrosive SC- serious corrosion SFNC -Scale forming but non corrosive CS-corrosion significant HC- heavy corrosion LSC- little scale or corrosion

4.8.2 Langelier Saturation Index (LSI)

Langelier developed a saturation index (LSI) for corrosion protection by a thin film of $CaCO_{3(s)}$ on the interior walls of pipes. This index is calculated from readily obtainable analytical results and indicates the tendency of natural or finished water either to deposit or dissolve calcium carbonate.

LSI calculation show the tendency of water is mainly in the range from s*lightly corrosive but non scale forming* (SCNSF) to *slightly scale forming and corrosive* (SSFC).The annual mean ($\overline{x} \pm \sigma$) LSI is -0.04±0.4.

Since the LSI calculation is based upon the *thermodynamic solubility constant* of $CaCO_{3(s)}$, it can only predict whether precipitation or dissolution should occur. It does not predict how much $CaCO_{3(s)}$ will precipitate or whether its structure will provide resistance to corrosion, The LSI value alone cannot predict how much $CaCO_{3(s)}$ will precipitate.

4.8.3 Ryznar Stability index (RSI)

LSI does not indicate how much calcium carbonate will deposit, whether a precipitate will be produced or a protective film will be formed.

Calculation of RSI shows the corrosive nature of water. From the Table 4.10 it is clear that the value is between 6 and 9. RSI between 6-7 shows *little scale or corrosion* (LSC) tendency of water, 7-7.5 show *corrosion significant* (CS) tendency of water, 7.5-9.0 show *heavy corrosion* (HC) tendency of water. The annual mean value of RSI is 7.6±0.6.

Thermodynamic corrosion of iron and copper pipes cannot be eliminated. Corrosion control is accomplished by chemical treatment of the water or electrochemical treatment of pipes. Chemical controls include adjustment of water pH, removal of dissolved oxygen, adjustment of calcium content etc [25].

4.9 Piper Plot and Water Quality Evaluation

Piper plot for BW strata in each month of year 2012 cluster in one point which is the area of *temporary hardness*. The water is *$Ca–Mg–HCO_3$ type*. The prominent cation is calcium (Ca^{2+}) and prominent anion is bicarbonate (HCO_3^-). From the cation triangle, 50-60% Ca, 30% Mg and 20% Na+K are shown by the water samples of BW strata for the monthly study of year 2012. From anion triangle, 80-90% HCO_3^-, 10% Cl^- and negligible SO_4^{2-} are observed.

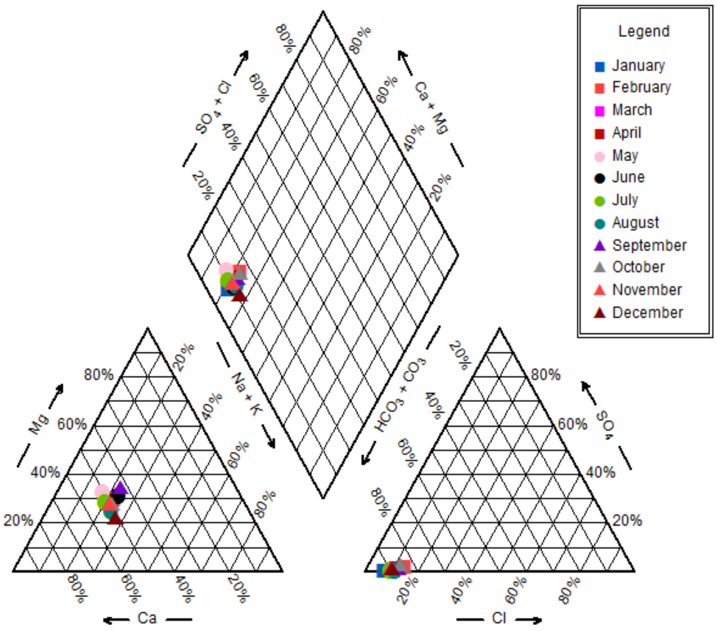

Figure 4.33: Hill-Piper Trilinear Diagram for bore well (BW) strata of Arattupuzha coast, Alappuzha, Kerala, Indiaduring each month of year 2012

Thus the deep bore well groundwater of the study area keep uniform character throughout the year 2012.

So Piper plot study is a useful tool in evaluating the overall hydrogeochemical behaviour of groundwater.

4.10 Gibb's plot

Identifying and understanding the hydrogeochemical processes are essential to evaluate the causes for changes in groundwater quality for planning groundwater protection. A number of factors influence water chemistry. Gibbs proposed that *rock weathering*, *atmospheric precipitation*, *evaporation* and *crystallisation* control the chemistry of water.

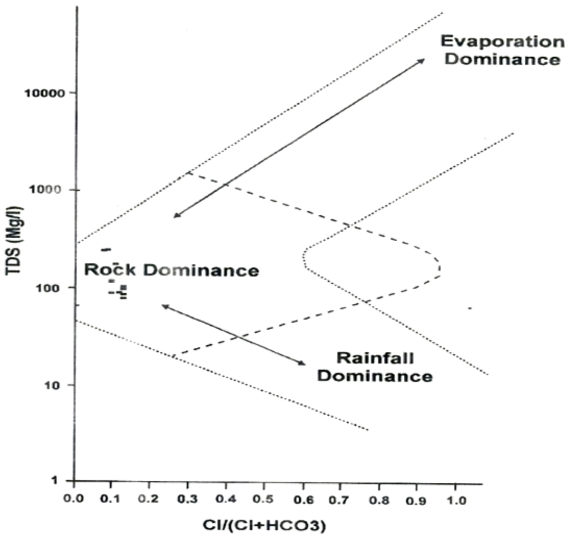

Figure 4.34: Gibb's plot of anion ratio against TDS for deep groundwater bore well (BW) strata of Arattupuzha coast, Alappuzha, Kerala, Indiaduring each month of year 2012.

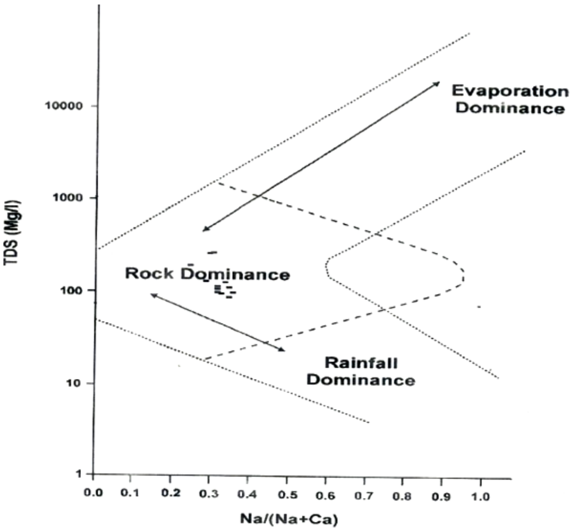

Figure 4.35: Gibb's plot of cation ratio against TDS for deep groundwater bore well (BW) strata of Arattupuzha coast, Alappuzha, Kerala, India during each month of year 2012.

Gibb's plot of anion ratio against TDS (Figure 4.34) & cation ratio against TDS (Figure 4.35) suggest that all of the data points occurs in the rock dominance zone which indicate that interaction between aquifer material and water is the major process controlling the groundwater chemistry of deep groundwater BW strata of the study area.

4.11 Total Carbon analysis

The carbon analysis of deep groundwater sources reveal that, major contribution is of inorganic origin and organic carbon is negligible in all source water (Table 4.11). The mean TC of BW strata is 29.4±10mg/l, TIC is 28.8±10.9mg/l and TOC is 0.65±0.89mg/l.

Table 4.11: Total carbon (TC), total inorganic carbon (TIC) & total organic carbon (TOC) of various deep groundwater sources of the study area Arattupuzha coast, Alappuzha, Kerala, India

Station	TCmg/l	TICmg/l	TOCmg/l
BW1	6.96	4.44	2.53
BW2	32.48	31.51	0.96
BW3	31.52	31.27	0.25
BW4	36.62	36.62	0.00
BW5	33.37	32.89	0.48
BW6	32.82	32.56	0.26
BW 7	32.16	32.06	0.10
$(\bar{x})$±SD(σ)	29.4±10.0	28.8±10.9	0.65±0.89

4.12 Designated Best Use

Central Pollution Control Board (CPCB), Ministry of Forest and Environment, Govt of India, New Delhi (BIS 2012) classifies water according to *designated best use*.

Table 4.12: Classification of deep groundwater sources of Arattupuzha coast, Alappuzha, Kerala, India based on designated best use by CPCB

Station	Total coliforms MPN/100ml	E. Coli	pH	DO mg/l	BOD mg/l	Class
BW1	Nil	Absent	7.14	4.2	2.5	C
BW2	240	Present	7.55	5.9	2.5	B
BW3	Nil	Absent	7.38	4.8	3.8	-
BW4	Nil	Absent	7.63	5.6	2.5	B
BW5	290	Present	7.23	4.2	1.3	C
BW6	Nil	Absent	7.75	7.1	2.5	B
BW7	4	Absent	7.43	6.3	2.5	B

Using the results of biological analysis of water samples in December 2012, deep groundwater sources are classified based on *designated best use* by CPCB (Table 4.12). The possibility of different stations to come in *A, B, C, or D class* is evaluated and it is found that BW2, BW4, BW6 & BW7 come in *class B* and BW1& BW5 in *class C*. To come in *class A* DO should be 6 or more and BOD should be less than 2mg/l. So the selected bore well water sources are not coming in *class A*.

4.13 Overall Water Quality of the Region

This chapter of the thesis elaborately discusses the monthly variation of groundwater quality of shallow groundwater sources along the study area in the year 2012. The mean values of various physico-chemical characteristics of shallow groundwater sources of the study area are compared with the IS and WHO standards in Table 4.13.

As per BIS (IS 10500: 2012) drinking water is water intended for human consumption for drinking and cooking purposes from any source. It includes water (treated or untreated) supplied by any means for human consumption. Drinking water shall comply with the requirements such as organoleptic and physical parameters, general parameters concerning substances undesirable in excessive amounts, parameters concerning toxic substances and parameters concerning radioactive substances. Analysis of pesticide residues shall be conducted by a recognized laboratory using internationally established test method meeting the residue limits. Drinking water shall also comply with bacteriological requirements, virological requirements and biological requirements.

Physico-chemical characteristics of deep groundwater sources of the study area during each month of year 2012 are given in Table 4.14.

Table 4.13: Physico-chemical characteristics of deep ground water sources of the study area Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Sl. No.	Parameter	Mean ($\bar{x}$)±SD(σ)	True Value(μ)	Confidence Interval (CI)	Drinking water standard as per IS 10500 : 2012		WHO2011	
					Acceptable	Permissible	Most desirable	Max. allowable
1	Temperature °C	31.1±1.5	31.1±0.95	30.1-32.1	-	-	-	
2	pH	7.5±0.24	7.5±0.15	7.35-7.65	6.5-8.5	No relaxation	6.5-8.5	No relaxation
3	EC (mS/cm)	0.33±0.04	0.33±0.04	0.28-0.38	-	-	1.5	-
4	Eh mV	-27.95±22.2	-27.95±13.9	-41.8 - -14	-	-	-	-
5	DO (mg/l)	4.7±1.6	4.7±1	3.7-5.7	-	-	-	-
6	BOD (mg/l)	3.8±1.7	3.8±1.1	2.7-4.9	-	-	-	-
7	TA(mg/l)asCaCO$_3$	198±45	198±28	170-226	200	600	-	-
8	TH(mg/l)as CaCO$_3$	168±41	168±26	142-194	300	600	100	500
9	TDS(mg/l)	299±86	299±54	245-353	500	2000	500	1500
10	Ca (mg/l)	43±11	43±7	36-50	75	200	75	200
11	Mg (mg/l)	16±6	16±4	12-20	30	100	50	150
12	Na (mg/l)	19±6	19±4	15-23	-	-	-	200
13	K (mg/l)	6±1.4	6±0.9	5.1-6.9	-	-	-	12
14	Fe (mg/l)	1.5±0.8	1.5±0.5	1.0-2.0	0.3	No relaxation	0.1	-
15	HCO$_3^-$ (mg/l)	241±58	241±37	204-278	-	-	-	-
16	Cl$^-$ (mg/l)	16±13	16±8	8-24	250	1000	250	600
17	SO$_4^{2-}$ (mg/l)	2.5±0.5	2.5±0.5	2.0-3.0	200	400	250	400
18	PO$_4^{3-}$ (mg/l)	0.1±0	0.1±0	0.1	-	-	-	-
19	NO$_3^-$ (mg/l)	1.1±0.4	1.1±0.4	0.6-1.5	45	No relaxation	50	-
				Trace Elements				
20	Li (μg/l)	2.4±2.0	2.4±1.8	0.6-4.2	-	-	-	
21	Rb(μg/l)	10±3.9	10±3.6	6.4-13.6	-	-	-	
22	Cs (μg/l)	0.16±0.05	0.16±0.05	0.11-0.21	-	-	-	
23	Sr (μg/l)	533±348	533±316	217-849	-	-	-	
24	Ba(μg/l)	56±29	56±27	29-83	700	No relaxation	700	No relaxation
25	V (μg/l)	0.28±0.15	0.28±0.14	0.14-0.42	-	-	-	
26	Cr (μg/l)	0.29±0.07	0.29±0.06	0.23-0.35	50	No relaxation	50	No relaxation
27	Mn (μg/l)	25.09±14.42	25.09±13.11	11.98-38.2	100	300	400	No relaxation
28	Co (μg/l)	0.1±0.0	0.1±0.0	0.1	-	-	-	
29	Ni (μg/l)	4.03±1.64	4.03±1.49	2.54-5.52	20	No relaxation	70	No relaxation
30	Cu (μg/l)	2.5±1.42	2.5±1.3	1.2-3.8	50	1500	2000	No relaxation
31	Zn (μg/l)	13.91±11.93	13.91±10.85	3.06-24.76	500	15000	-	-
32	Ag (μg/l)	0.2±0.06	0.2±0.05	0.15-0.25	100	No relaxation	-	-
33	Cd (μg/l)	0.1±0.0	0.1±0.0	0.1	3	No relaxation	-	-
34	Al (μg/l)	28.4±20.5	28.4±18.6	9.8-47	30	200	100	No relaxation
35	Ga (μg/l)	13.9±5.3	13.9±4.8	9.1-18.7	-	-	-	-
36	In (μg/l)	0.1±0.0	0.1±0.0	0.1	-	-	-	-
37	Pb (μg/l)	0.6±0.4	0.6±0.4	0.2-1.0	10	No relaxation	10	No relaxation
38	As (μg/l)	0.17±0.06	0.17±0.05	0.12-0.22	10	50	10	50
39	Bi (μg/l)	0.18±0.09	0.18±0.09	0.09-0.27	-	-	-	-
40	Se (μg/l)	4.4±0.3	4.4±0.3	4.1-4.7	10	No relaxation	40	No relaxation

Table 4.14: Physico-chemical characteristics of deep ground water sources of the study area during each month of year 2012

Strata	Data	pH	Eh	EC mS/cm	TH mg/l	Alkalinity mg/l	TDS mg/l	DO mg/l	BOD mg/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Fe mg/l	HCO$_3$ mg/l	Cl mg/l	SO$_4$ mg/l	PO$_4$ mg/l
CW2012	$\bar{x} \pm \sigma$	7.8± 0.3	-44±14	0.34± 0.04	196± 18	211± 27	280±125	4.98± 1.15	4.23± 1.9	67±12	7±5	67±12	2.1± 2	ND	258± 34	16± 7	4.8± 2.5	0.09± 0.05
	Range	7.5- 8.1	-58- -30	0.3- 0.38	178-214	184-238	155-405	3.83-5.13	2.33-6.13	55-79	2-12	55-79	1.9-4.1		224-292	9--23	2.3-7.3	0.04-0.14
BW2012	$\bar{x} \pm \sigma$	7.3 ±0.2	-16 ±8.9	0.26 ±0.08	165 ±33	255 ±38	533 ±119	3.1 ±1.3	2.7 ±0.6	43 ±9.3	14 ±5.0	18 ±4.5	5.6 ±0.1	0.2 ±0.1	312 ±46.3	13 ±88.5	ND	ND
January	Range	7.1-7.5	-24.9-7.1	0.18-0.34	132-198	217-293	414-652	1.8- 4.4	2.1-3.3	33.3-51.9	9.1-19.1	13.1-23.1	5.5-5.7	0.1-0.3	266-358	4.5-21.5	ND	ND
BW2012	$\bar{x} \pm \sigma$	7.4±0.2	-24±9.3	0.35± 0.09	178± 31	213± 25	258± 19	2.9± 0.9	4.5± 1.5	44± 6.2	16±5	21± 6	5.6± 0.1	0.8± 0	260± 30.5	24± 26.3	3±0	0.1±0
February	Range	7.2-7.6	-33.3-14.7	0.26-0.44	147-209	188-238	239-277	2.0-3.8	3.0-6.0	37.8-50.2	11-21	15-27	5.5-5.7	0.8	230-291	0-50	3	0.1
BW2012	$\bar{x} \pm \sigma$	8.7± 0.2	-60±63	0.26± 0.08	159± 52	176± 60	193± 57	4.8±1.2	7.7± 3.0	41±13	14± 6	18± 3.4	5.7± 0.4	1.6± 1.0	215± 73	16± 10	ND	ND
March	Range	8.5- 8.9	-123-+0.3	0.18-0.34	107-211	116-236	136-250	3.6- 6.0	4.7-10.7	28-54	8-20	14.6-21.4	5.3-6.1	0.6-2.6	142-288	6-26	ND	ND
BW2012	$\bar{x} \pm \sigma$	7.8± 0.5	-52± 24	0.3±0.1	146±73	155± 84	157±102	5.8± 1.7	3.0±1.0	37±24	13± 4.2	15± 8	6.2± 3.8	1.8± 0.7	189± 102	13.6± 9.9	2±0	ND
April	Range	7.3- 8.3	-76- 28	0.2-0.4	73-219	71- 239	55- 259	4.1-7.5	2.0-4.0	13- 61	8.8-17.2	7-23	2.4-10.0	1.1-2.5	87- 291	3.7-23.5	2	ND
BW2012	$\bar{x} \pm \sigma$	7.4±0.1	-25± 8	0.42± 0.04	184±8	237± 34.4	500± 73	4.8± 1.8	5± 3.6	45±5.2	17.3±2.2	13.4± 7.2	7.7± 0.2	1.9± 1	289± 42	18.8± 10	ND	ND
May	Range	7.3- 7.5	-33- 17	0.38-0.46	176-196	203-271	427-573	3.0- 6.6	1.4-8.6	39.8-50.2	15.1-19.5	6.2-20.6	7.5-7.9	0.9-2.9	247-331	8.8-28.8	ND	ND
BW2012	$\bar{x} \pm \sigma$	7.4± 0.3	-25±19	0.29± 0.1	129± 54	186± 75	290± 130	5.5± 1.6	2.5± 1.0	31±13	12.6±7	15.5± 7.2	5.1± 2	1.6± 1	227± 91	14.1± 13.4	ND	ND
June	Range	7.1- 7.7	-44-6	0.09-0.39	75-183	111-261	160-420	3.9- 7.1	1.5-3.5	18-44	5.6-19.6	8.3-22.7	3.1-7.1	0.6-2.6	136-318	0.7-27.5	ND	ND
BW2012	$\bar{x} \pm \sigma$	7.4± 0.2	-24±10	0.31± 0.05	187± 22	206± 25	301± 89	4.9± 1.8	2.5± 1.4	48.5± 8.9	16.1±1.9	18.3± 2.7	6.1± 0.7	1.5± 0.9	251± 30	14± 10.3	ND	0.1± 0
July	Range	7.2- 7.6	-14- 34	0.26-0.36	165-209	181-231	212-390	3.1-6.7	1.1-3.9	39.6-57.4	14.2-18.0	15.6-21.0	5.4-6.8	0.6-2.4	221-281	3.7-24.3	ND	0.1
BW2012	$\bar{x} \pm \sigma$	7.6±0.2	-35±8.6	0.38± 0.03	184± 14	209± 14	-	5.1± 1.5	4.3± 1.2	50.1± 6.3	14.3±2.8	23.8± 5.8	5.6± 0.6	1.5± 0.5	255± 17	18.1± 3.5	ND	0.1±0
August	Range	7.4- 7.8	-43.6-26.4	0.35-0.41	170-198	195-223	-	3.6- 6.6	3.1-5.5	43.8-56.4	11.5-17.1	18.0-39.6	5.0-6.2	1.0-2.0	238-272	14.6-21.6	ND	0.1
BW2012	$\bar{x} \pm \sigma$	7.4± 0.3	-26±15	0.36± 0.1	177± 66.4	173± 51.7	164± 54	4.5± 2.0	6.1± 2.4	40.2± 12.0	18.6±12.6	22± 8.2	5.8± 2	1.7± 0.9	211± 63	17± 12	ND	ND
September	Range	7.1- 7.7	-41- 11	0.26-0.46	110.6-243.4	121.3-224.7	110-218	2.5-6.5	3.7-8.5	28.0-52.2	6.0-31.2	13.8-30.2	3.8-7.8	0.8-2.6	148-274	5-29	ND	ND
BW2012	$\bar{x} \pm \sigma$	7.3± 0.2	-21±9	0.39± 0.06	182± 26.4	146.4±58.1	234± 31	4.9± 1.6	4.7± 2.0	47.3± 7.2	15.4±2.6	22± 5.1	6.4± 0.9	1.4± 0.6	179± 71	14.1± 10.9	2.6± 0.5	0.14± 0.01
October	Range	7.1-7.5	-30- 12	0.33-0.45	155.6-208.4	88.3-204.5	203-265	3.3-6.5	2.7-6.7	40.1-54.5	12.8-18.0	16.9-27.1	5.5-7.3	0.8-2.0	108-250	3.2-25.0	2.1-3.1	0.13-0.15
BW2012	$\bar{x} \pm \sigma$	7.0 ±0.2	-1 ±11	0.35 ±0.05	186 ±23	199 ±23	184 ±35	4.4 ±2.0	2.5 ±0.7	49 ± 8	15.4 ±5.4	22 ±4.5	5.6 ±0.7	1.8 ±1.0	243 ±28	12.8±7.1	ND	ND
November	Range	6.8- 7.2	-12- +11	0.3- 0.4	163-209	176-222	149-219	2.4- 6.4	1.8-3.2	41-57	10.0-20.8	17.5-26.5	4.9-6.3	0.8-2.8	215-471	5.7-19.9	ND	ND
BW2012	$\bar{x} \pm \sigma$	7.4 ±0.2	-27 ±12	0.36 ±0.06	147 ±48	206 ±28	113 ±38	5.4 ±1.1	2.5 ±0.7	42.1 ±13.1	10.3 ±6.5	23.3 ±7.2	5.5 ±0.8	1.3 ±0.6	251.2 ±34.5	15.5± 13.8	ND	ND
December	Range	7.2- 7.6	-39-15	0.3-0.42	99-195	178-234	75- 199	4.3- 6.5	1.8-3.2	29- 55.2	3.8-16.8	16.1-30.5	4.7-6.3	0.7-1.9	216.7-285.7	1.7-29.3	ND	ND
BW2012 Overall	$\bar{x} \pm \sigma$	7.5±0.24	-27.95± 22.2	0.33± 0.04	168± 41	198± 45	299± 86	4.7± 1.6	3.8± 1.7	43±11	16± 6	19±6	6± 1.4	1.5± 0.8		16±13	2.5± 0.5	0.1±0
	μ	7.5±0.15	-27.95± 13.9	0.33± 0.04	168± 26	198± 28	299± 54	4.7±1	3.8± 1.1	43±7	16±4	19±4	6± 0.9	1.5± 0.5	241± 37	16±8	2.5± 0.5	0.1±0
	CI	7.35-7.65	-41.8 - 14	0.28-0.38	142-194	170-226	245-353	3.7- 5.7	2.7-4.9	36-50	12- 20	15- 23	5.1-6.9	1.0-2.0	204-278	8-24	2.0-3.0	0.1
BIS2012		6.5- 8.5		-	200	200	500			75	30	-	-	0.3	-	250	200	
WHO2011		6.5- 8.5		1.5	-		500			75	50	200	12	0.3	500	250	250	

Results of ANOVA tests conducted to check the various hypotheses, suggested in the introduction chapter, give the following results:

a) *Whether there is any significant difference between* water quality parameters between CW and BW for the months of 2012.

Table 4.15: ANOVA table for the comparison of water quality parameters between CW and BW for the months of 2012 of Arattupuzha coast, Alappuzha, Kerala, India.

Source	SS	df	ms	F	P-value
Total	3686459.42	383			
Bet. CW & BW	295.44	1	295.4400	0.228	P>0.05
Bet. Months	72789.27	11	6617.2064	5.099	P<0.001
Bet. Parameters	3151361.89	15	8852.1401	6.821	P<0.001
Residuals	462012.82	356	1297.7888		

Inference

1) Between CW and BW there is no significant difference in the mean value of the parameters (P>0.05).
2) Between months difference is significant (P<0.001), January, May and November exhibited significantly higher mean parameter values than months.
3) Variation between parameters is also significant (P<0.001). TDS, HCO_3 and TH are significantly higher than rest of the parameters.

b) *Whether there is any significant difference between water quality index for different bore well stations for the months of 2012*

Table 4.16: ANOVA table for the comparison of water quality index for bore well stations for the months of 2012 of Arattupuzha coast, Alappuzha, Kerala, India

Source	ss	df	ms	F	p-value
Total	17777.02	83			
Month	9133.00	12	761.0833	9.351	P< 0.001
Bore well	2783.95	6	463.9917	5.701	P< 0.001
Residual	5860.05	72	81.3896		

Inference

1) There is significant difference between bore wells with respect to WQI ($P<0.001$). BW1 is having significantly less WQI compared to other bore wells.
2) The WQI differ significantly between months ($P<0.001$). WQI is significantly higher in March.

4.14 Conclusion

This chapter of the thesis elaborately discusses the groundwater quality of deep groundwater sources along the study area in the year 2012. The annual mean of important water quality parameters are; pH 7.5±0.24, Eh $^{-}$27.95±22.2mV, EC 0.33±0.04mS/cm, TH 168±41mg/l, Alkalinity 198±45mg/l, TDS 299±86mg/l, DO 4.7±1.6mg/l, BOD 3.8±1.7mg/l, Ca 43±11mg/l, Mg 16±6mg/l, Na 19±6mg/l, K 6±1.4mg/l, Fe 1.5±0.8mg/l, $HCO_3$241±58mg/l, Cl 16±13mg/l, SO_4 2.5±0.5mg/l, $PO_4$0.1±0mg/l (Table 4.11). Spatial distribution of the prominent water quality parameters help to understand the variation in the study area. Trace elements analysed are not present in harmful levels. The mean values of various parameters of BW strata during each month of year 2012 are compared with IS2012& WHO standards in Table 4.12.

Correlation matrix for Bore well (BW) strata suggests positive correlation of pH to Iron, TH to Ca and Mg.WQI of BW strata suggest mostly good quality. In March overall poor quality and in April & May poor quality in some stations are observed whereas in November WQI from 17 to 29 suggest that the water is in excellent to good category. From Sodium – Chloride ratio calculations it is inferred that only ion exchange is observed to be prominent phenomena that control the chemistry of deep groundwater in BW strata.

A detailed study of irrigational quality give the following conclusions. Electrical conductivity of BW strata suggests that the water quality is excellent or good for irrigation throughout the year. Based on TH, bore well water is moderately hard to hard category. TDS suggest fresh category for BW strata. Kelly's ratio of BW strata is less than 1.0 throughout the year suggesting suitability of water for irrigation. MAR is less than 50 suggesting good irrigational quality in all months except April. PI lower than 25 is not observed in BW strata suggesting good irrigational quality throughout the year.SAR is less than 10 suggest in good quality. In USSL in all months water comes in C1S1and C2S1 regions showing low to medium salinity hazard and low sodium or alkali hazard and water is good for irrigation.RSC suggest unsuitability of some stations in January and doubtful quality of some stations in May, June and December. %Na suggests good quality of BW water and from wilcox diagram, water of BW kept good quality throughout the year 2012.

Saturation indices calculations suggest the slightly corrosive nature of deep groundwater (BW) of the region. Piper plot for BW strata suggest temporary hardness throughout the year. The water is Ca–Mg–HCO_3 type. Gibb's plots suggest rock weathering as the major process controlling deep groundwater composition.

Results of ANOVA tests conducted suggest that, there is no significant difference in the mean value of the parameters between CW and BW and for BW strata January, May and November 2012 exhibited significantly higher mean parameters with TDS, HCO_3 and TH significantly higher than rest of the parameters. There is significant difference between bore wells with respect to WQI and it differ significantly between months with significantly higher in March.

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Chapter 5

GROUNDWATER QUALITY OF A TSUNAMI DEVASTATED COASTAL SEGMENT: POST TSUNAMI STUDIES OF SHALLOW GROUNDWATER (2005-2016)

Contents

5.1 Introduction

There is a continuing need for long-term studies of groundwater composition for such purposes as surveillance of pollution, maintenance of water quality standards and observation of the long term influence of changing land-use or water-use patterns [1-3]. These studies require considerable detailed sampling and analysis. But there are little studies regarding the continuous evaluation of coastal disasters like tsunami impact on devastated regions. This type of work is expensive in money and professional talent. A programme involving the collection of large volumes of groundwater data tends to develop a system of evaluation of impact on coastal environment over a period of time. The data obtained is continuously examined and studied in a logical framework, mathematically designed, and come out with hydrogeochemical interpretation is essential for groundwater source protection and abatement. In the present study, a detailed investigation was carried out with an objective of identifying the groundwater quality, prominent water quality parameters controlling the hydro chemical evolution of a tsunami devastated coastal segment of Kerala after 26th December 2004 Indian Ocean tsunami specifically at Arattupuzha coast, Kerala, India, as a post tsunami disaster groundwater study programme.

This chapter discusses the temporal variation of groundwater quality of shallow groundwater sources of the tsunami affected region. Study discussed in chapter 3 give a detailed discussion of groundwater quality parameters of 6 dug wells in the area in each month of year 2012.The study continued in the years 2013, 2014, 2015 and 2016 with one sampling event in December of the respective year. From the reported study of the year 2001, the groundwater quality parameters of 4 shallow dug wells in the study area is known [4-9]. Results of post tsunami studies of year 2005 (12 months data) and 2008, the groundwater quality parameters of 5 dug wells are systematically evaluated [10]. The data obtained for the study period 2012-2016 are outcome of a continued effort of research specifically as a post tsunami impact on groundwater. In this study research findings of the tsunami affected Arattupuzha region with respect to groundwater quality for a period 2001-2016 are discussed.

5.2 Water Quality Parameters

The variation of major water quality parameters of dug wells (DW) over year 2001 to 2016 are discussed in the following sections, as function of days since April of the year 2001, the pre tsunami period, the early data available as a bench mark for the situation existed before 26th December 2004 Indian Ocean Tsunami struck the above coastal area. Results are plotted as function of days 2001 (0 day), January 2005- December 2005 (1460-1790 days), 2008 (2890 days), January 2012 – December 2012 (3980-4310 days), 2013 (4675 days), 2014 (5040 days), 2015 (5405 days), 2016 (5770 days). For the critical evaluation of temporal and spatial profile of the respective years are also marked on the graphs.

5.2.1 pH

In 2001 the pH of dug well (DW) strata is 7.5±0.6 (Figure 5.1). In 2005 post tsunami study data reveal that the pH of shallow groundwater sources vary from 7.6 to 8.2. From the monthly variation it can be seen that pH shows a distinct alkaline nature. In 2008 the mean pH of DW strata is 7.3±0.2, which shows near neutral situation and water got stabilised. From the results of 2012 study pH range from 7.6 to 8.1which is much similar to 2005 range. The results of the subsequent years analysis reveal that the mean ($\bar{x} \pm \sigma$) pH is 7.9±0.3 (2013), 9 ±0.3 (2014), 7.7±0.3 (2015) and 8.2±0.3 (2016). So in 2015 slight decrease in pH, and in 2016 it increases indicating higher alkalinity. Thus, the data generated over the last 16 years reveal that the pH of DW strata is within the standard limit of 6.5-8.5 although in some months the pH is close to 8.5.pH higher than 8 are associated with *sodium carbonate-bicarbonate* waters, while moderately high pH are associated with waters *high in bicarbonate*.

One of the main objectives for pH study is to produce water that minimizes corrosion or incrustation. These processes, which can cause considerable damage to the water supply systems, result from complex interactions between pH and other parameters, such as dissolved solids, dissolved gases, hardness, alkalinity, and temperature. There exists a situation for progressive decline in the efficiency of chlorine disinfection processes with high level of pH.

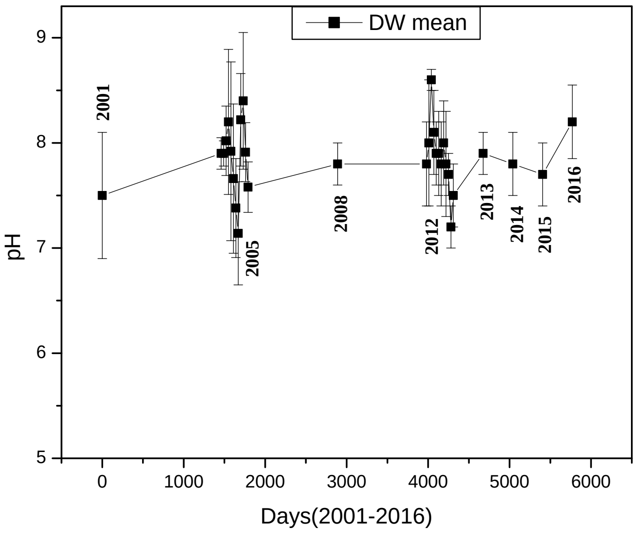

Figure 5.1: Temporal variation of pH of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

5.2.2 Electrical Conductivity (EC)

Electrical conductivity (EC) is very important parameter in determining the water quality because it is an indicator of salinity of groundwater. In 2001 the EC of DW strata is 0.4±0.07mS/cm (Figure 5.2). In 2005 post tsunami study data reveal that the EC of shallow groundwater sources vary from 2.3 to 4.7mS/cm. From the monthly variation in the post tsunami year, there is a hike in EC which is a normal result of sea water inundation. In 2008, the mean EC of DW strata is 0.6±0.3mS/cm. From the results of 2012 study the EC ranges from 0.3 to 2.1mS/cm. The results of the subsequent years analysis reveal that mean ($\overline{x} \pm \sigma$) EC is 1.7±2.0 (2013), 1.5 ±1.8 (2014), 0.9±0.9 (2015) but increases to 1.3±1.4 mS/cm in 2016. Thus the data generated over the last 16 years reveal that the EC of DW strata exceed the standard limit of 1.5 mS/cm in many occasions.

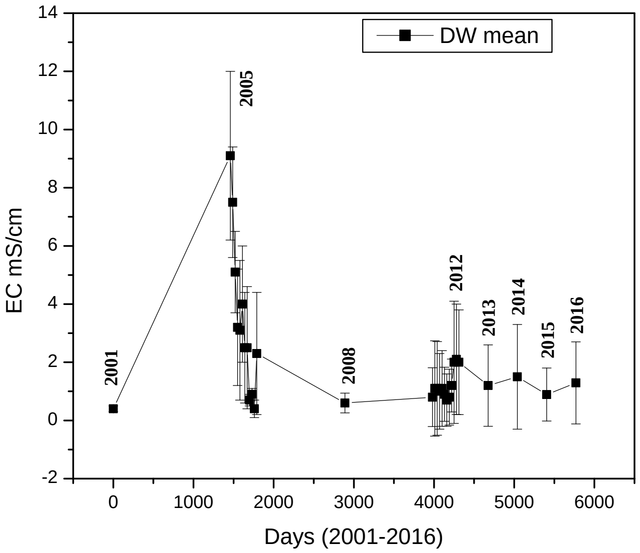

Figure 5.2: Temporal variation of shallow EC of groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

5.2.3 Total Hardness (TH)

In 2001 the TH of DW is 71±57mg/l (Figure 5.3). In 2005 post tsunami study data reveal that the TH of shallow groundwater sources vary from 294 to 718mg/l. Monthly variation shows that in the post tsunami year 2005, similar to EC, there is a hike in TH. In January 2005, TH is 1002mg/l. From January to August 2005, the value decreases successively and a minimum of 340mg/l is observed in August 2005 afterwards. TH increases slightly and reaches 620mg/l in September 2005.

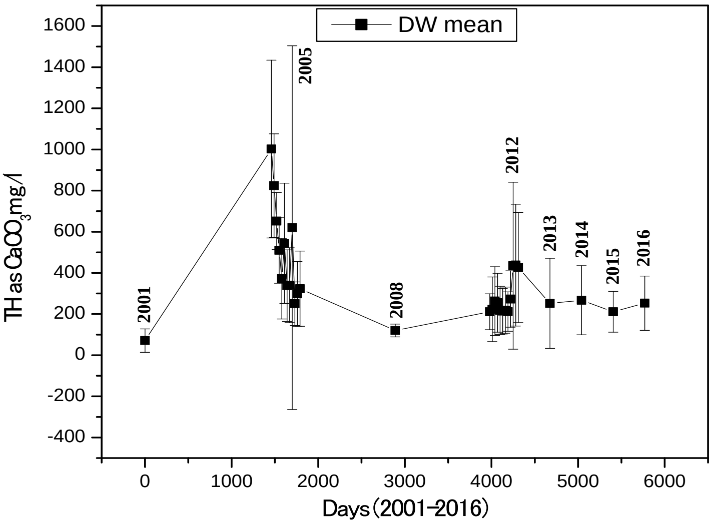

Figure 5.3: Temporal variation of TH of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

In December 2008 the mean TH of DW strata is 120±31mg/l. From the 2012 study, the TH range is 156-408mg/l. The results of the subsequent years analysis reveal almost steady level of total hardness, observed as 252±219 (2013), 267±168 (2014), 211±99 (2015) and 253±132mg/l (2016). Thus the results obtained over the last 16 years reveal that the TH of DW strata is higher than the standard limit of 200mgl in most of the analysis. Hardness maintains a high value throughout the study period. Hardness is caused by divalent metallic ions dissolved in water, principally calcium and magnesium. The most important anions with which they are associated are HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, etc.

5.2.4 Calcium (Ca^{2+})

The Ca concentration of DW strata in 2001 is 21±21mg/l (Figure 5.4). In 2005 post tsunami study data reveal that the Ca of shallow groundwater sources is 107±58mg/l. From the monthly results, in January 2005, just after tsunami event, the concentration is 230mg/l which decreases to less than

100mg/l in December 2005. In 2008 the mean value of Ca of DW strata is 25±8mg/l. The mean $(\bar{x} \pm \sigma)$ Ca is 69± 47mg/l in the year 2012. Monthly data shows that, there is an increase in Ca from October to December 2012 which infers sea water mixing. The results of the subsequent years analysis reveal mean $(\bar{x} \pm \sigma)$ Ca 80±51 (2013), 66±24 (2014), 47±21 (2015) and 61±19mg/l (2016). Thus the data generated over the last 16 years reveal that the Ca of DW strata is higher than standard limit of 75mg/l in the post tsunami year, 2005 and towards the end of year 2012. Afterwards by year 2016, it comes to less in the range. The concentration of calcium in groundwater is generally between 10 and 100mg/l.

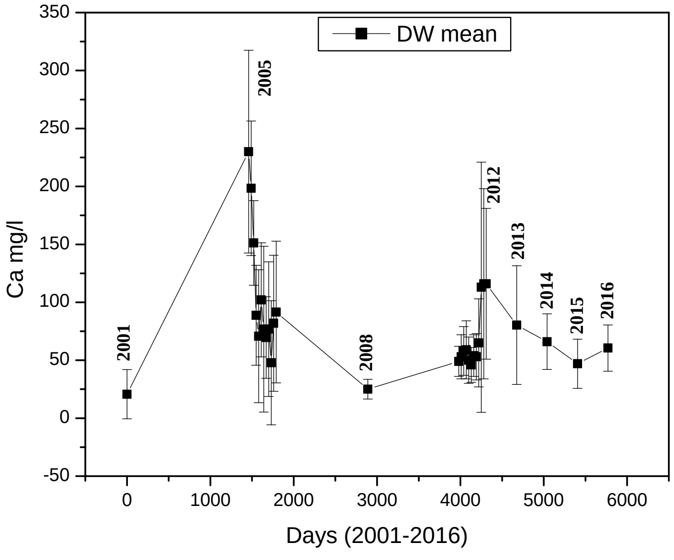

Figure 5.4: Temporal variation of Ca of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

5.2.5 Magnesium (Mg^{2+})

The Mg conccentration of DW strata in 2001 is 5±3mg/l (Figure 5.5). In post tsunami year 2005 study data reveal that the Mg of shallow groundwater sources is 58±61mg/l. From the monthly variation, the concentration of Mg show higher than 100mg/l in January and September 2005. In 2008 the mean of Mg of DW strata is14±7.6mg/l. Mg conccentration is 28± 29mg/l in the year 2012. The results of the subsequent years analysis reveal the mean 13±24 (2013), 25±33 (2014), 23±18 (2015) and 25±25mg/l (2016). Thus the data generated over the last 16 years reveal that the Mg concentration of DW strata shows higher than standard limit of 30mgl (according to BIS 2012 and 50mg/l according to WHO 2011) in the post tsunami year 2005 and towards the end of year 2012.

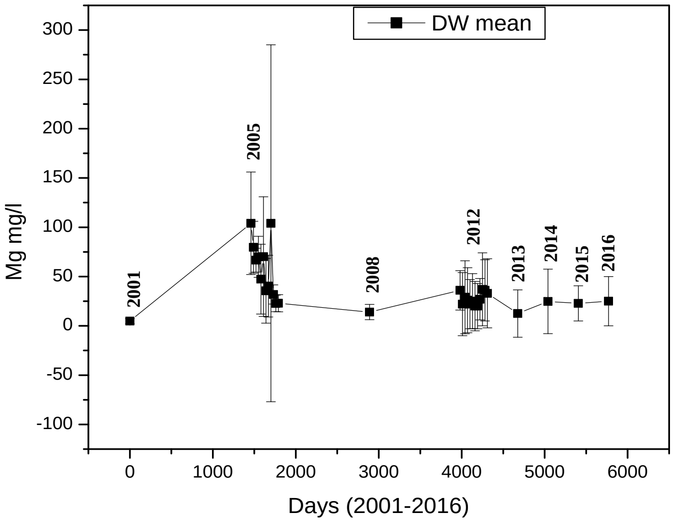

Figure 5.5: Temporal variation of Mg of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

5.2.6 Sodium (Na^+)

The Na conccentration of the DWstrata in 2001 is 39±8.3mg/l (Figure 5.6). Post tsunami study data (2005) reveal that the Na of shallow groundwater sources vary from 156 to 886mg/l. From the monthly variation it can be seen that just after tsunami (in January 2005) the concentration is 1296mg/l Na^+ which decreases and keeps almost steady value of around 200mg/l in the subsequent months till December 2005. In 2008 the mean of Na of DW strata has been 106±59mg/l. We can see that the Na concentration is 26-188mg/l during 2012 as annual mean. The results of the subsequent years analysis reveal the mean 119±140mg/l (2013), 141±162 (2014), 58±52 (2015) and increases to 143±229mg/l in 2016. Thus the data generated over the last 16 years reveal that the Na concentration of DW strata is much higher than the standard limit of 200mg/l in the post tsunamic year 2005. Last 5 years data indicates the increased sodium level in number of stations than the conditions existed in 2001.

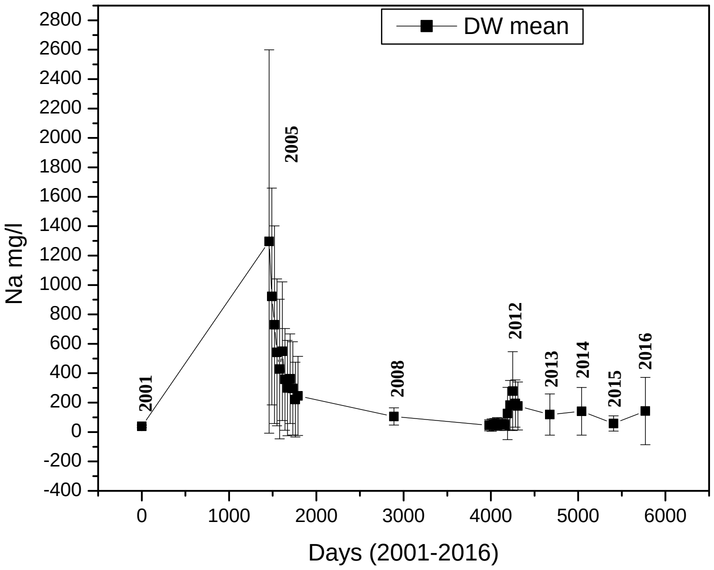

Figure 5.6: Temporal variation of Na of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

5.2.7 Potassium (K^+)

The K conccentration of the groundwater DW strata in 2001 is 6.3±6mg/l in the pre-tsunami period (Figure 5.7). In 2005 post tsunami study data reveal that the K conccentration of shallow groundwater sources is 24±18mg/l with very high observed in January (42±23mg/l) and February (36±22mg/l).

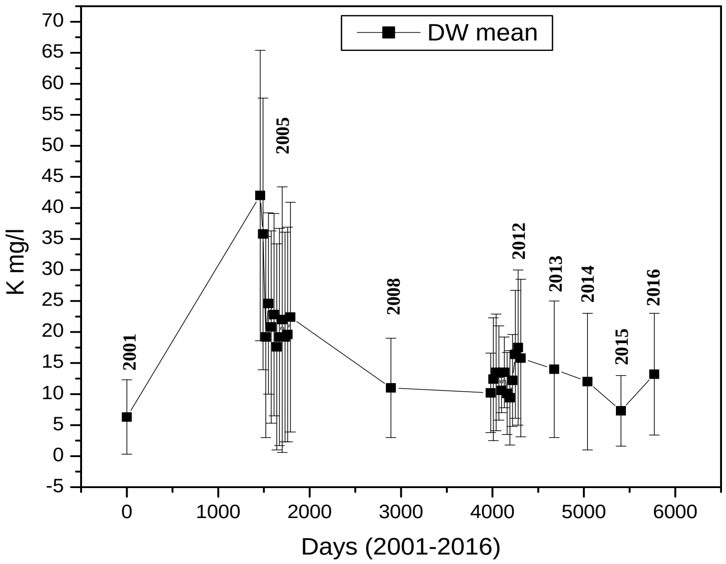

Figure 5.7: Temporal variation of K of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

In 2008 the mean K of DW strata is11±8mg/l. From the results of 2012 study the, K concentration is 12.9± 8.7mg/l. The results of the subsequent years analysis reveal the mean 14±11mg/l (2013), 12±11mg/l (2014), 7.3±5.7mg/l (2015) and it is 13±10mg/l in 2016. Thus the data generated over the last 16 years reveal that the K concentration of DW strata is much higher than the BIS standard limit of 12mg/l.

5.2.8 Bicarbonate (HCO_3^-)

In the pre-tsunamic period 2001, the bicarbonate concentration of the DW strata is 43±58mg/l (Figure 5.8). In 2005 post tsunami study data reveal that the HCO_3^- of shallow groundwater sources vary from 229 to 345mg/l. Study of monthly variation reveal bicarbonate concentration remain almost steady. In 2008 the bicarbonate of DW strata is 32±14mg/l which is much lower than 2005. Bicarbonate concentration is 242± 98mg/l in the year 2012 which is almost comparable to 2005. The results of the subsequent years analysis reveal the mean 411±249 (2013), 284±114 (2014), 227±105 (2015) and it is 269±106mg/l (2016). Thus the data generated over the last 16 years reveal that the HCO_3^- of DW strata is within the maximum permissible limit of 500mg/l. Increased bicarbonate level suggest the prominence of rock weathering in the region in the post tsunamic period.

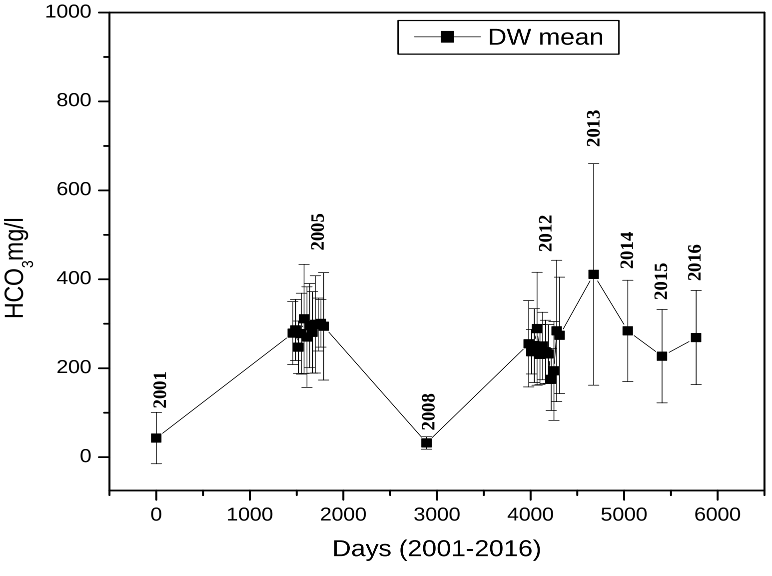

Figure 5.8: Temporal variation of HCO_3 of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

5.2.9 Chloride (Cl^-)

The Cl^- conccentration of the DW strata in pre-tsunamic situation (2001) has been 63±5.3mg/l (Figure 5.9). In 2005 post tsunami study results reveal that the Cl^- of shallow groundwater sources is 2302±2044mg/l. Monthly variation shows that from January to May 2005, very high concentration of Cl^- is observed due to tsunami wave inundation in the area.

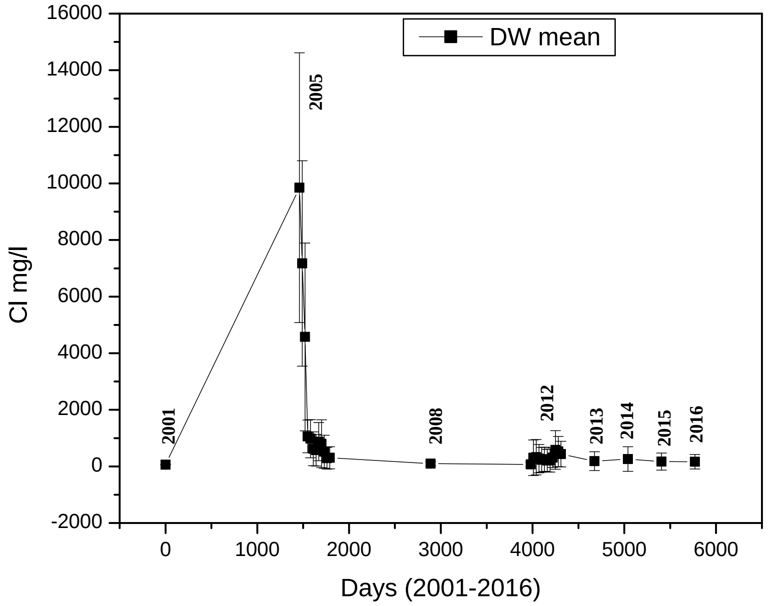

Figure 5.9: Temporal variation of Cl of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

The concentration decreases in the subsequent months till December 2005. In 2008, the mean of Cl^- of DW strata is 97±80mg/l. From the results of 2012 study the Cl^- conccentration is 311± 484mg/l which is very much lower than that in the early months of 2005.The results of the subsequent years analysis reveal Cl^- 186±332mg/l (2013), 259±434mg/l (2014), 171±302mg/l (2015) and 166±254mg/l (2016). Thus the data generated over the last 16 years reveal that the Cl^-concentration of DW strata show much higher than standard limit of 250mg/l in early months of 2005. In most of post-tsunamic periods the Cl^- concentration has been less than the standard limit being geologically some reduction of the Cl^- occurs, in the coastal area.

5.2.10 Sulphate (SO_4^{2-})

The SO_4^{2-} conccentration of the DW strata in 2001 has been 21±24mg/l (Figure 5.10).

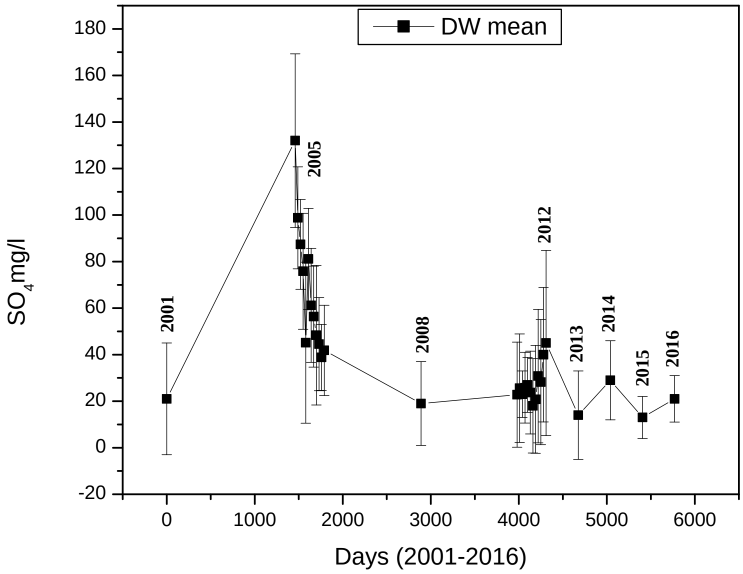

Figure 5.10: Temporal variation of SO_4^{2-} of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

In 2005 post tsunami study data reveals that the SO_4^{2-} of shallow groundwater sources is 68±25mg/l. From the monthly variation it can be seen that from January to April 2005, high concentration of SO_4^{2-} is observed and after that almost steady is observed. In 2008 the mean of SO_4^{2-}

of DW strata is 19±18mg/l. From the results of 2012 study the annual mean SO_4^{2-} is 27± 24mg/l, which is very much lower than that in the year of 2005. The results of the subsequent years analysis reveal 14±19mg/l (2013), 29±17mg/l (2014), 13±9mg/l (2015) and it is 21±10mg/l in 2016. Thus results over the last 16 years reveal that the SO_4^{2-} concentration of DW strata of the region is within the standard limit of 200mg/l. After 26th December 2004 Indian Ocean tsunami, SO_4^{2-} is considerebly reduced, through the mighty wave inundation enhanced the SO_4^{2-} of the groundwater.

5.2.11 Redox Potential (Eh)

From the post tsunami studies done in the year 2005, annual mean Eh of DW strata is $^-33$±24 mV (Figure 5.11), water exist in the reducing environment.

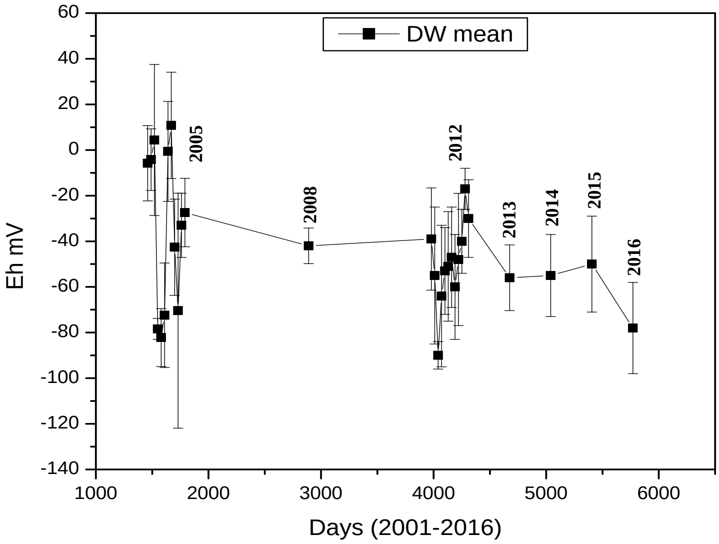

Figure 5.11: Temporal variation of Eh of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

In March and August 2005, oxidising environment is observed whereas in all other months, reducing environment is prevalent in DW strata. In 2008 the mean Eh of DW strata is $^{-}42$±7.7mV, a condition passive behaviour, where water is more immense to reactive environment. As discussed in chapter 3 in all months of year 2012 reducing environment is observed in DW strata with a mean of $^{-}50$±22. The results of the subsequent years analysis have $^{-}56$±14 mV (2013), $^{-}55$ ±18 mV (2014), $^{-}50$±21 mV (2015) and it is $^{-}78$±20 mV (2016). Thus, the data generated over the last 16 years reveal that the Eh of DW strata show the presence of a reducing environment in shallow groundwater sources of the study area.

5.2.12 Alkalinity (AL)

In 2001 the Alkalinity of the DW strata is only 35±48mg/l as evidenced in Figure 5.12. From the post tsunamic studies of 2005 the monthly variation of Alkalinity of DW strata is presented.

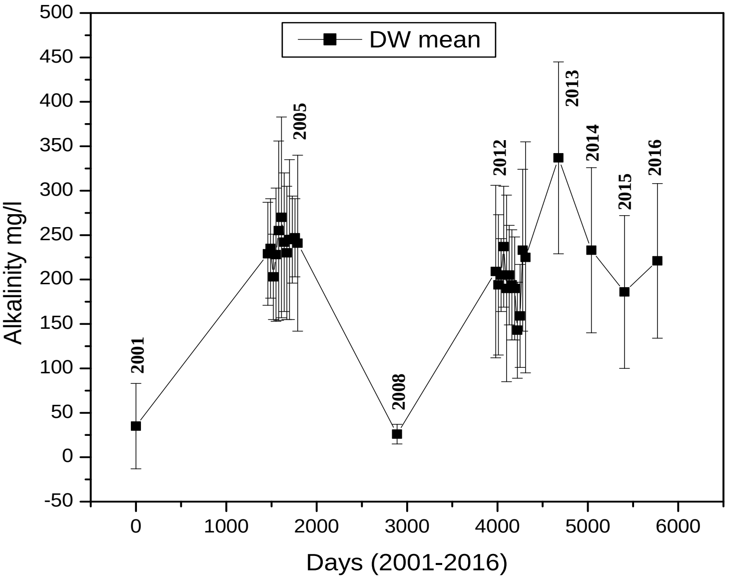

Figure 5.12: Temporal variation of Alkalinity of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

The annual mean of Alkalinity is 261±167mg/l with a confidence interval of 55-367. Alkalinity variation is similar to bicarbonate variation. In 2008 the mean Alkalinity of DW strata is 26±11mg/l. From the results of 2012 study the Alkalinity range is 148-250mg/l. The results of the subsequent years analysis reveal the mean 337±204mg/l (2013), 232±93mg/l (2014), 186±86mg/l (2015) and 221±87mg/l (2016). Alkalinity of DW strata show value higher than standard limit of 200mg/l in certain periods, mostly recent years 2013 onwards, where carbonate equilibria/carbonate weathering is more prominent.

5.2.13 Dissolved Oxygen (DO)

The concentration of DO in water regulates the sustence of flora and fauna. Seasonally the DO concentration is more during monsoon and least during summer. From the post tsunamic studies of 2005 the monthly variation of DO of DW strata 4.8±1.8mg/l is obtained. The annual mean DO is 4.8±1.8mg/l with a confidence interval of 3.7-5.9. In 2008, the mean DO of DW strata is 2.4±1.6mg/l; more quality degradation is distinct. From the results of 2012 study the annual mean DO is 4.83± 1.96mg/l with a CI of 3.6-6.1mg/l. The results of the subsequent years analysis reveal the mean 3.9±1.6mg/l (2013), 5.6±2.6mg/l (2014), 5±2mg/l (2015) and it is 4.4±1.6mg/l in 2016. Thus DO is relatively lower in DW strata of the study area (Figure 5.13). Only in a single event reaches 8.0mg/l in 2005, whereas most of the time DO has been in the range 3.6-6.1mg/l. Oxygen saturation is inhibited, may be due to organic contamination and lack of reaeration or O_2 is actively used up in many of the biogeochemical processes augmented in the local environment

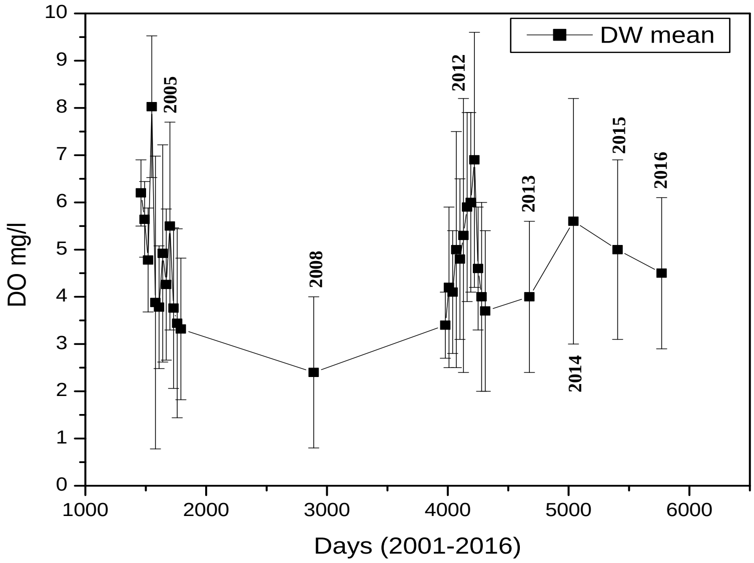

Figure 5.13: Temporal variation of DO of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

5.2.14 Biochemical Oxygen Demand (BOD)

BOD is defined as the amount of oxygen required by bacteria and other microorganisms in the biochemical degradation and transformation of organic matter under aerobic condition. The basic principle underlying the BOD determination is the measurement of the dissolved oxygen content of the sample before and after 5 days incubation at 20 °C. From the post tsunamic studies of 2005 the monthly variation of BOD of DW strata is obtained. The annual mean BOD is 9.7±3.5mg/l with a confidence interval of 7.5-11.9mg/l. In 2008 the mean BOD of DW strata is 9.0±5.1mg/l. From the results of 2012 study the annual mean BOD is 5.9± 3.5mg/l with a CI 3.7-8.1. The results of the subsequent years analysis reveal decreasing of BOD level, the mean 3.6±1.2mg/l (2013), 3.6±1.9mg/l (2014) and it is 2.1±2.0mg/l in 2015 (Figure 5.14). As per the classification of a fresh water source of India (Central

Pollution Control Board -CPCB) a drinking water source without conventional treatment but after disinfection must have a BOD of 2mg/l or less to qualify *category A* of designated best use. Throughout the study particularly after 2013, the groundwater has a stable BOD acceptable for category C type at least for a limited months, BOD remains 2.4-4.8mg/l (2013), 1.7-5.5mg/l (2014) and ¯0.1- 4.1mg/l (2015). This indicate that groundwater requires conventional treatment disinfect, being the BOD is not less than 2mg/l (for Class A) or 3mg/l (for Class B).

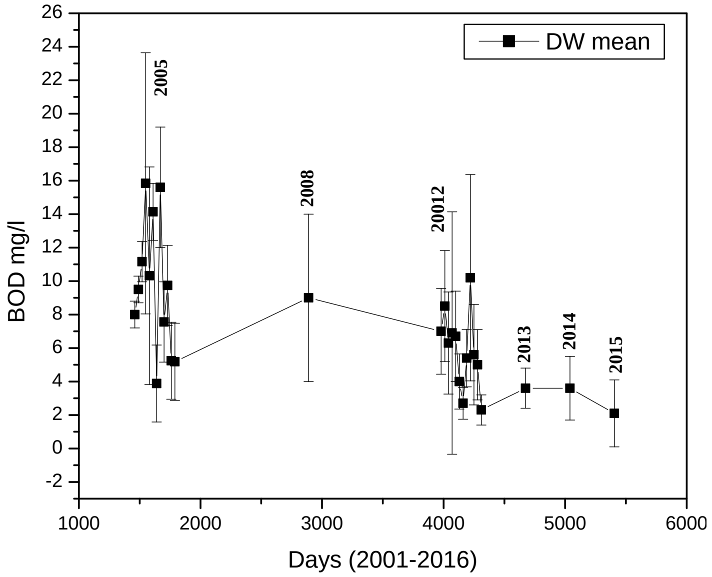

Figure 5.14: Temporal variation of BOD of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

5.2.15 Phosphate (PO_4^{3-})

Phosphate is one of the trace constituent of water < 0.1mg/l. Regarding PO_4^{3-}, the pre-tsunamic data (2001) is not available for a comparison. However the extensive studies have been done in 2005 in the post-tsunamic period.

Phosphate are not toxic to people or animals unless they are present in very high levels. Digestive problems could occur from extremely high levels of phosphate. Phosphate itself does not have notable adverse health effects. However, phosphate levels greater than 1.0mg/l may interfere with coagulation and encrustation in water treatment plants and distribution systems. As a result, organic particles that harbour microorganisms may not be completely removed before distribution.

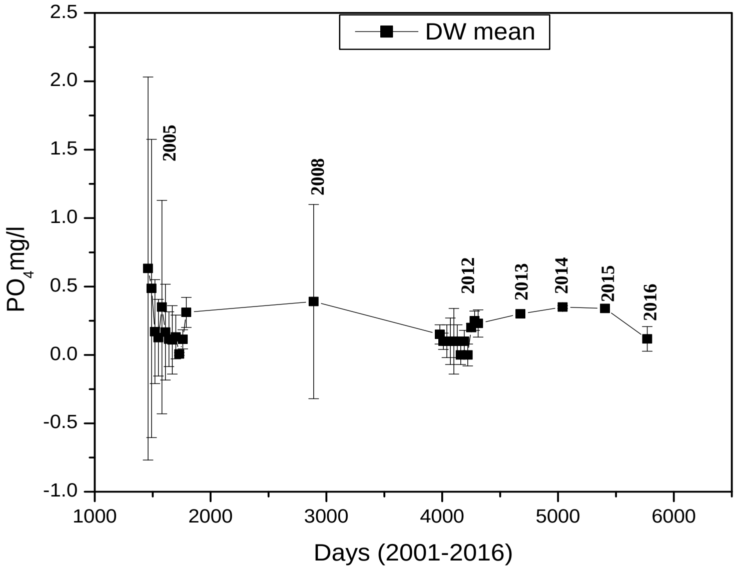

Figure 5.15: Temporal variation of PO_4 of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

From the post tsunamic studies of 2005 the monthly variation of phosphate of DW strata is obtained. The annual mean is 0.23±0.5mg/l. In 2008 the mean of phosphate of DW strata is 0.4±0.7mg/l. From the results of 2012 study the annual mean phosphate is 0.19±0.14mg/l. The results of the subsequent years analysis reveal the mean 0.3±0 (2013), 0.35±0.01 (2014) and 0.34±0.0 (2015) and it is 0.12±0.09mg/l in 2016 (Figure 5.15).

Thus very low phosphate concentration is observed in the DW strata of the study area, specifically for the recent times. Tsunami affected dug well sources, just after tsunami event in January 2005 have 0.17±0.15mg/l and the control well has 0.23mg/l. Bore well have 0.42±0.72mg/l. It has been seen that PO_4^{3-} has been very prominent even after 1430 days (2008) with 0.08±0.108mg/l and 0.26mg/l for control well. This decline in PO_4^{3-} over years may be due to change in pH of the water to alkaline range [10].

5.2.16 Nitrate (NO_3^-)

Concentration of nitrates above permissible limits indicates large scale anthropogenic activity and leachates from landfill sites and domestic sewage. In the present study area the nitrate in 2005 is 0.5±0.2mg/l. In 2008 the mean nitrate is 0.9±0.7mg/l. During year 2012 and December 2013, NO_3-was below detectable limit. The mean nitrate in subsequent year is 2.2±0.6mg/l (2014), 1.6±0.7mg/l (2015) and 2.8±1.0mg/l (2016) (Figure 5.16). There is very low nitrate level but its increasing value suggests anthropogenic influence, in the region. It is seen that the NO_3^- level is getting more with time since, tsunami event 2005 to 2016. However, it is less than the maximum permissible NO_3^- (45mg/l), suggesting the quality is within the acceptable limit.

Nitrogen is contained in all enzymes essential for all plant functions. However, when swallowed, they are converted to nitrites that can react with haemoglobin in the blood, oxidizing its divalent iron to the trivalent form and creating methaemoglobin. Thus Nitrate compounds can prevent haemoglobin from binding with oxygen at levels above the permissible limit. Thus the drinking water that is contaminated with nitrates can prove fatal especially to infants as it restricts the amount of oxygen that reaches the brain causing the ‘blue baby’ syndrome or methaemoglobinaemia.

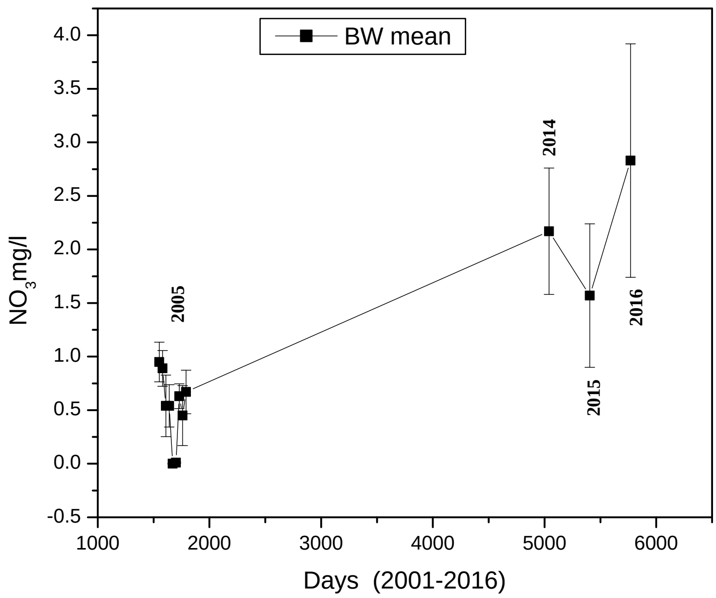

Figure 5.16: Temporal variation of NO_3 of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

5.2.17 Iron (Fe)

There are 2.17 lakh water quality affected inhabitations in India by 2012 as per the statistics of XI plan document, mostly affected by excess iron, fluoride, salinity, nitrate and arsenic. Hence, surveillance and monitoring of groundwater with respect to iron whose IS standard is 0.3mg/l maximum acceptable limit is pertinent. The fate of Fe is decided by the presence of O_2 and H_2S. In the reducing environment Fe is precipitated as pyrite FeS_2 (marcasite). In the present study area the iron concentration in 2005 is 0.04±.02mg/l. In 2008 the iron concentration is 0.13±0.04mg/l. The annual mean in 2012 analysis is 0.08±0.14mg/l. The 2014 analysis shows that the mean iron concentration is 0.9±0.2mg/l and it is 0.01±0.01mg/l in 2016 (Figure 5.17). In 2012 and in 2014 slightly higher concentration than the permissible limit of 0.3mg/l are observed in certain wells.

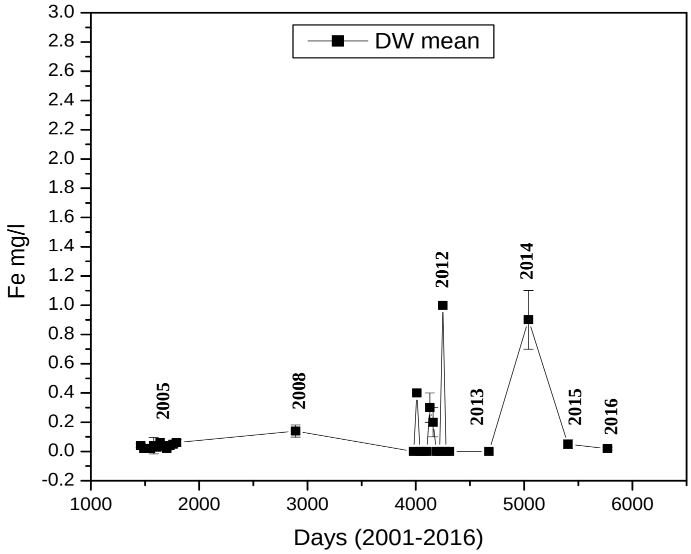

Figure 5.17: Temporal variation of Fe of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

Toxic effects have resulted from the ingestion of large quantities of iron, but there is no evidence to indicate that concentrations of iron commonly present in food or drinking water constitute any hazard to human health. At concentrations above 0.3mg/l, iron can stain laundry and plumbing fixtures and cause undesirable tastes. Iron may also promote the growth of certain microorganisms, leading to the deposition of a slimy coat in piping.

5.2.18 Total Dissolved Solids (TDS)

TDS is one of the most important organoleptic and physical parameters comprise all dissolved matter present in a water sample. In pre-tsunami year 2001 shallow dug wells have a TDS of 240.5mg/l and 182.0mg/l for bore well waters. Just after tsunami event, the TDS content has enhanced to 2103.5±1729mg/l for shallow groundwater and observed for deep groundwater has been 369±140mg/l. In 2008 these TDS 390mg/l and 195mg/l, a decline with respect to change of time is observed. Total dissolved solids affect the taste, hardness, corrosivity and incrustation of water. Waters with less than 500mg/l TDS (IS 10500: 2012) are generally satisfactory for domestic use and those with more than 1000mg/l usually contain minerals which give it a disagreeable taste or make it unsuitable for other purposes and it is observed in slightly saline water. In any occasions permissible limit in the absence of alternate source it is limited to 2000mg/l.

TDS data of the present study area is available from 2012 onwards. The annual mean of 2012 is 1210±1491mg/l with a CI of 261-2159 at 95% confidence level. The mean of TDS in subsequent year is 463±761mg/l (2013), 832±1069mg/l (2014), 494±624mg/l (2015) and is 684±737mg/l in 2016. Thus higher than 1000mg/l is observed in some occasions which show high salinity (Figure 5.18).

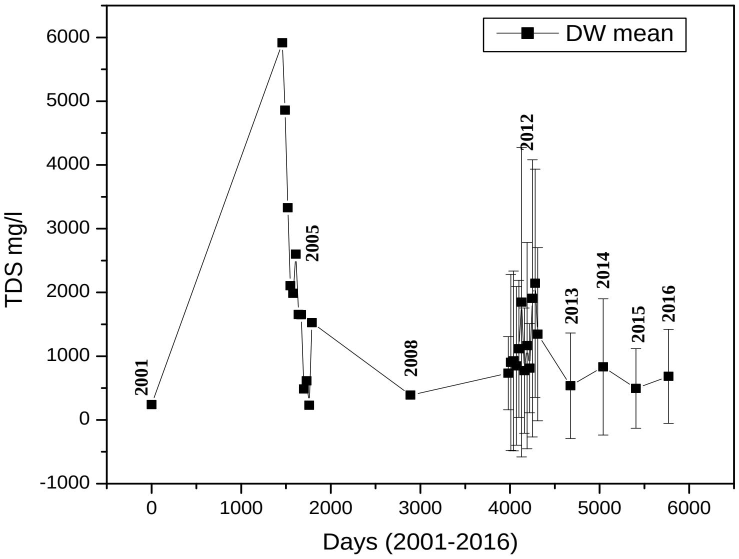

Figure 5.18: Temporal variation of TDS of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, Indiafor the period 2001-2016.

5.3 Water Quality Index (WQI)

The water quality index reflects the quality of any water under study by means of a single number, calculated by considering combined effect of important physico-chemical parameters [11-13]. In the present study, WQI calculation is done by Weighted Arithmetic Water Quality Index Method (WAWQI) using the prominent 10 parameters, pH, EC, TH, Ca, Mg, Na, K, HCO_3, Cl & SO_4. WQI calculated, using the mean of the above parameters are given in Table 5.1.

Table 5.1: Temporal variation of WQI, Water Quality & grade of dug well (DW) water sources along the study area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016

Year/Month	WQI	Water Quality	Grading
Apr 2001	37	Good	B
Jan 2005	263	Unfit for Human use	E
Feb 2005	217	Unfit for Human use	E
Mar 2005	148	Unfit for Human use	E
Apr 2005	141	Unfit for Human use	E
May 2005	112	Unfit for Human use	E
Jun 2005	119	Unfit for Human use	E
Jul 2005	84	Very Poor	D
Aug 2005	79	Very Poor	D
Sep 2005	134	Unfit for Human use	E
Oct 2005	112	Unfit for Human use	E
Nov 2005	99	Very Poor	D
Dec 2005	97	Very Poor	D
Dec 2008	46	Good	B
Jan 2012	66	Poor	C
Feb 2012	76	Very Poor	D
Mar 2012	99	Very Poor	D
Apr 2012	84	Very Poor	D
May 2012	68	Poor	C
Jun 2012	69	Poor	C
Jul 2012	63	Poor	C
Aug 2012	69	Poor	C
Sep 2012	74	Poor	C
Oct 2012	90	Very Poor	D
Nov 2012	79	Very Poor	D
Dec 2012	81	Very Poor	D
Dec 2013	79	Very Poor	D
Dec 2014	77	Very Poor	D
Dec 2015	51	Poor	C
Dec 2016	89	Very Poor	D

In 2001 the WQI of 37 for DW strata suggests good quality of water (B Grade) existed there. WQI of the 4 stations are 19,21,82 & 24, three are having *excellent* category and one is in very *poor* quality state. Using the post tsunami data of 2005, WQI is calculated for each month. It'svery high value, 263 in January and 217 in February, show that the water is *unfit for human use* (E Grade).

The WQI of individual five dugwell stations in January are 252, 229, 409, 217 & 204 suggests high deterioration in quality of one station compared to the rest. Thus the WQI calculation confirm the deterioration of DW water sources, due to tsunami wave inundation. By July 2005 the WQI value become less than 100 but still the quality of water is in *very poor* category (D Grade). In July the WQI of different stations are 145, 24, 160, 38 & 44 suggesting the improvement in quality, still 2 stations are coming in the category of *unfit for human use*. In 2008 the WQI calculation using mean of 10 parameters give a value 46 which suggest *good* quality water (B Grade), these too, WQI of individual stations are 85, 30, 37, 41 & 33; one maintains in *very poor* category and all others are in *good* category.

As regards to year 2012 monthly variation suggest *poor* to *very poor* water quality for shallow groundwater. In January WQI of individual stations (six dug wells) are 66, 122, 49, 77, 33 & 49, suggesting considerable deterioration in quality of one station compared to the rest. In July 2012, they are 68, 122, 31, 61, 44 & 51 and in December 2012, they are 38, 151, 35, 59, 98 & 106. In 2013 WQI calculated using mean parameters is 79 suggesting *very poor* water quality (D Grade) with individual stations having WQI of 66,160,41,64,68 & 73. In 2014 mean WQI is 77 suggesting *very poor* water quality (D Grade) with individual stations having WQI of 66, 164, 30, 64, 75 & 63. In 2015, WQI mean 51 suggests quality becomes good for all stations with values 49, 84, 23, 50, 46 & 55. But in 2016 the WQI calculated is 89 which suggest a character of *very poor quality*. So water quality damage occured in shallow groundwater sources of the study area in 2016. The WQI of individual stations (six dug wells) are noted as 86, 150, 57, 108, 77 & 54 suggests a marked deterioration in quality for 2 stations compared to the rest.

Thus on an average the shallow dug well water of the area is not having good quality water.But as we see in chapter 3, the control dug well selected in the area show good quality water with WQI 38±10 in 2012.

Figure 5.19 give the temporal variation of WQI of dug well water sources. In years, 2005 & 2012 monthly mean data is plotted. Two cut off points, one at 50 below which water has good quality and another at 100 above which water is unfit for direct human use are shown.

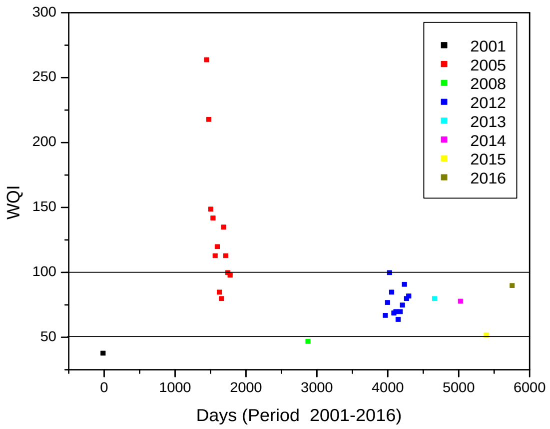

Figure 5.19: Temporal variation of WQI of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

Thus WQI calculation using major water quality parameters give a consolidation of the quality of water.

5.4 Sodium – Chloride Ratio

Sodium-chloride ratio for the groundwater for the period 2001-2016 has been analysed. If the value of *Na/(Na+Cl)* is higher than 0.5 and that of *Na/Cl* is higher than 1.0, it suggest *ion exchange processes* (all concentrations in meq/l) [7].

Table 5.2: Temporal variation of $\frac{Na}{Cl}$, $\frac{Na}{Na+Cl}$ & Inference of Dug well water sources along the study areaArattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

Year/ Month	$\frac{Na}{Cl}$	$\frac{Na}{Na+Cl}$	**Inference**
Apr 2001	1.0	0.5	Ion exchange
Jan 2005	0.2	0.2	Reverse ion exchange
Feb 2005	0.3	0.2	Reverse ion exchange
Mar 2005	0.4	0.2	Reverse ion exchange
Apr 2005	0.7	0.4	Reverse ion exchange
May 2005	0.5	0.3	Reverse ion exchange
Jun 2005	2.6	0.5	Ion exchange
Jul 2005	2.1	0.5	Ion exchange
Aug 2005	0.4	0.3	Reverse ion exchange
Sep 2005	1.3	0.4	Ion exchange
Oct 2005	0.9	0.5	Ion exchange
Nov 2005	1.5	0.5	Ion exchange
Dec 2005	1.5	0.5	Ion exchange
Dec 2008	2.3	0.7	Ion exchange
Jan 2012	1.6	0.5	Ion exchange
Feb 2012	1.1	0.5	Ion exchange
Mar 2012	0.8	0.4	Reverse ion exchange
Apr 2012	0.8	0.4	Reverse ion exchange
May 2012	0.9	0.4	Reverse ion exchange
Jun 2012	0.9	0.5	Ion exchange
Jul 2012	1.2	0.5	Ion exchange
Aug 2012	1.9	0.6	Ion exchange
Sep 2012	1.5	0.6	Ion exchange
Oct 2012	1.5	0.6	Ion exchange
Nov 2012	1.1	0.5	Ion exchange
Dec 2012	1.3	0.5	Ion exchange
Dec 2013	1.8	0.6	Ion exchange
Dec 2014	1.5	0.6	Ion exchange
Dec 2015	1.3	0.5	Ion exchange
Dec 2016	1.3	0.6	Ion exchange

Table 5.2, shows mean of these ratios of DW strata. It is clear that in 2001, *ion exchange* is the main process occurring in shallow groundwater sources of the study area. During the post tsunamic year 2005, till May *reverse ion exchange* occur as the main process. This is due to the high concentration of sodium in water. In June and July 2005 *ion exchange* is prominent. In August again reverse *ion exchange* occur. After that to December *ion exchange* is observed.

In March, April and May 2012, *reverse ion exchange* was very prevalent. In all other months *ion exchange* is observed. From subsequent years study it is clear that *ion exchange* is the main process that control hydrogeochemistry of the region in December month of years 2013, 2014, 2015 & 2016.

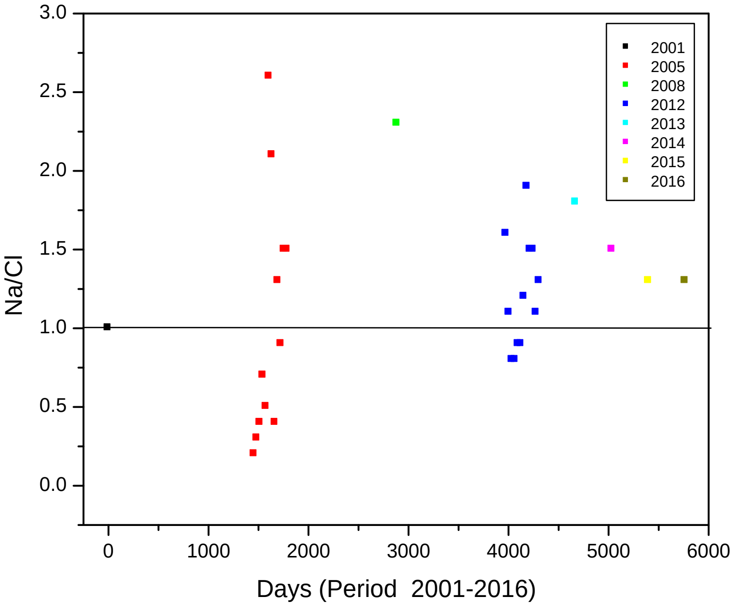

Figure 5.20: Temporal variation of Na/Cl ratio of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

Figure 5.20 give the temporal variation of Na/Cl ratio of dug well water sources. The groundwater that has Na/Cl = 1.0; Na/Na+Cl = 0.5, the condition for *ion exchange* shifted through different mechanism. The ratio below 1.0 suggests *reverse ion exchange* observed in the early months of post tsunami study year 2005 and towards the end of the year 2012, onwards it is changed into *ion exchange*.

5.5 Irrigation Quality Evaluation

In order to evaluate the quality of the water used for the irrigation, it is important to take into consideration the characteristics that are crucial for plant growth as well as the admissible levels of concentrations [14-19]. The testing of water and accurate interpretation of the results is of significance in the selection process of fertilizers and irrigation techniques in order to avoid crop damage. The irrigation suitabilityof water is evaluated by calculating the various parameters representing irrigation quality of groundwater.

5.5.1 Electrical Conductivity & Total Hardness

The higher the EC, the lesser the water available to plants, even though the soil may seen wet and saturated. So irrigation water with high EC reduces yield potential of the crops. Temporal variation of mean EC of DW strata is given in Table 5.3. In 2001 EC is 370 µS/cm show good quality of water. In the post tsunami period of January 2005, very high EC of 9100 µS/cm is observed which decreases in successive months and till June the quality of water is in the range *unsuitable category*. In July and August 2005, EC decreases to less than 3000 µS/cm and the quality of water is in *doubtful category*. In September 2005, EC decreases to 746 µS/cm and the quality become *good for irrigation*. In October 2005, again increase and belongs to *permisible category.*

Table 5.3: Temporal variation of EC, TH, Alkalinity, Permanent hardness (PeH) and Inferences of dug well water sources along the study area, Arattupuzha coast, Alappuzha, Kerala, India for the period 2001-2016.

Year/ Month	**EC µS/cm**	**Inference**	**TH mg/l as $CaCO_3$**	**Inference**	**Alkalinity mg/l**	**PeH**
Apr 2001	370	G	71.0	S	35.0	36
Jan 2005	9100	U	1002	VH	229	773
Feb 2005	7476	U	824	VH	235	589
Mar 2005	5122	U	652	VH	203	449
Apr 2005	3240	U	510	VH	228	282
May 2005	3056	U	372	VH	255	117
Jun 2005	4000	U	544	VH	270	274
Jul 2005	2544	D	338	VH	242	96
Aug 2005	2542	D	340	VH	230	110
Sep 2005	746	G	620	VH	245	375
Oct 2005	944	P	250	H	245	6
Nov 2005	354	G	298	H	247	52
Dec 2005	2346	D	323	VH	241	82
Dec 2008	600	G	120	MH	26	94
Jan 2012	800	P	211	H	209	2
Feb 2012	1100	P	223	H	194	29
Mar 2012	1100	P	263	H	205	58
Apr 2012	1000	P	255	H	237	18
May 2012	1100	P	218	H	190	28
Jun 2012	900	P	214	H	205	9
Jul 2012	700	G	219	H	194	25
Aug 2012	800	P	212	H	190	22
Sep 2012	1200	P	273	H	143	130
Oct 2012	2000	P	435	VH	159	276
Nov 2012	2100	D	438	VH	233	205
Dec 2012	2000	P	426	VH	225	201
Dec 2013	1200	P	252	H	337	0
Dec 2014	1500	P	267	H	233	34
Dec 2015	890	P	211	H	186	25
Dec 2016	1290	P	253	H	221	32

G-good P-Permissible D-Doubtful S-Soft H-Hard VH-very Hard

In November again quallity become *good* but in December there is a hike in EC and water quallity become *doubtful for irrigation*. In 2008, mean EC of 600 µS/cm suggest *good quality*. In 2012, the water quality is *permissible for irrigation* in most of the months except July and November. In July mean EC is 700 µS/cm suggesting *good water quality* and in November 2012, 2100 µS/cm suggesting *doubtful category*. In the subsequent years the quality change to *permissible range*.

TH variation of DW strata is given in Table 5.3, show 71mg/l in 2001which infers *soft water*(S). In 2005 the water become *very hard* (VH) as TH exceed 300mg/l and it persist towards the end of the year except in October and November when the hardness become less than 300mg/l and quality improves to *hard* (H) category. In the 2008 analysis, the water is *moderately hard* (MH). In 2012 analysis, water show *hard* nature which change to *very hard* towards the end of the year due to sea water ingress. In the subsequent years also water is *hard*. Thus the higher concentration of Ca and Mg in shallow groundwater sources of the area can be confirmed. It is seen that the water in the region once have been 'soft' in character has become *hard water* after 24 December 2004 Indian Ocean Tsunami.

Hardness as $CaCO_3$ exceeds the alkalinity as $CaCO_3$, the difference is termed as non-carbonate hardness or permanent hardness (PeH) most unsuitable in post-tsunami period, has become *hard* water after 26th December 2004 Indian Ocean Tsunami. It is contributed by chlorides and sulphates of calcium and magnesium. Except in 2013, Permanent Hardness is present in all other analysis. In 2013 the higher alkalinity suggests the contribution of bicarbonate of sodium.

5.5.2 Kelly's ratio

Kelly's ratio more than 1.0 indicates an excess level of sodium in water and therefore the water is not suitable for irrigation. KR for DW strata in year 2001 is 2.09 suggesting unsuitability of water for irrigation. In 2005 study, throughout the year KR higher than 1.0 and so water quality is *unsuitable for irrigation*. In 2008 study KR is 2.13, again suggesting unsuitability. In 2012 study, from January to July and also in November and December KR lower than 1.0 suggest water is suitable for irrigation. But from August to October 2012, KR becomes higher than 1.0 suggesting unsuitability of water for irrigation. In 2013 analysis also the KR is 1.02 and water is unsuitable. In 2014, 2015 & 2016 KR lower than 1.0 and water is *suitable for irrigation*. Figure 5.21 give the temporal variation of Kelly's ratio of dug well water sources.

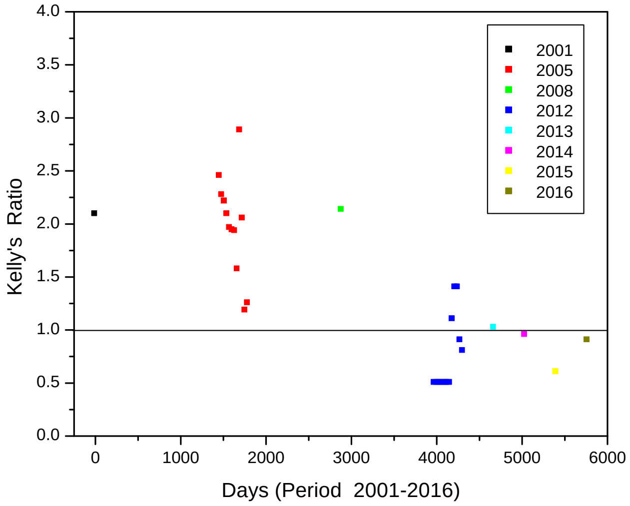

Figure 5.21: Temporal variation of Kelly's ratio of shallow groundwater dug well sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India.

5.5.3 Magnesium Adsorption Ratio (MAR)

More magnesium in water adversely affects the crop yield and it is evaluated by calculating Magnesium adsorption ratio (MAR). If MAR is less than 50 water is *suitable* for irrigation. In 2001, MAR is 34 suggesting water is *suitable* for irrigation. In 2005, MAR higher than 50 is observed in April, May, September and October 2005, showing *unsuitability* of water for irrigation.

Table 5.4: Temporal variation of Kelly's ratio (KR), Magnesium Adsorption Ratio (MAR) & Permeability index (PI) of dug well water sources along the study area, Arattupuzha coast, Alappuzha, Kerala, India for the period 2001-2016.

Year/Month	KR	Inference	MAR	Inference	PI	Inference
Apr 2001	2.09	US	34	S	77	classI
Jan 2005	2.45	US	42	S	72	classII
Feb 2005	2.27	US	39	S	71	classII
Mar 2005	2.21	US	42	S	70	classII
Apr 2005	2.09	US	57	US	72	classII
May 2005	1.96	US	53	US	78	classI
Jun 2005	1.94	US	50	S	69	classII
Jul 2005	1.93	US	45	S	78	classI
Aug 2005	1.57	US	43	S	74	classII
Sep 2005	2.88	US	51	US	73	classII
Oct 2005	2.05	US	63	US	81	classI
Nov 2005	1.18	US	36	S	74	classII
Dec 2005	1.25	US	32	S	75	classII
Dec 2008	2.13	US	46	S	74	classII
Jan 2012	0.5	S	39	S	73	classII
Feb 2012	0.5	s	33	S	68	classII
Mar 2012	0.5	S	37	S	62	classII
Apr 2012	0.5	S	37	S	65	classII
May 2012	0.5	S	37	S	68	classII
Jun 2012	0.5	S	38	S	70	classII
Jul 2012	0.5	S	31	S	68	classII
Aug 2012	1.1	US	33	S	74	classII
Sep 2012	1.4	US	39	S	72	classII
Oct 2012	1.4	US	33	S	70	classII
Nov 2012	0.9	S	32	S	64	classII
Dec 2012	0.8	S	28	S	62	classII
Dec 2013	1.02	US	11	S	84	classI
Dec 2014	0.95	S	29	S	74	classII
Dec 2015	0.6	S	37	S	68	classII
Dec 2016	0.9	S	31	S	72	classII

S- Suitable US- Unsuitable

From Table 5.4, it is clear that in all other analysis MAR is lower than 50 and water is *suitable* (S) for irrigation. Figure 5.22 give the temporal variation of magnesium adsorption ratio (MAR) of dug well water sources. Except in few months of 2005, water is suitable for irrigation based on MAR.

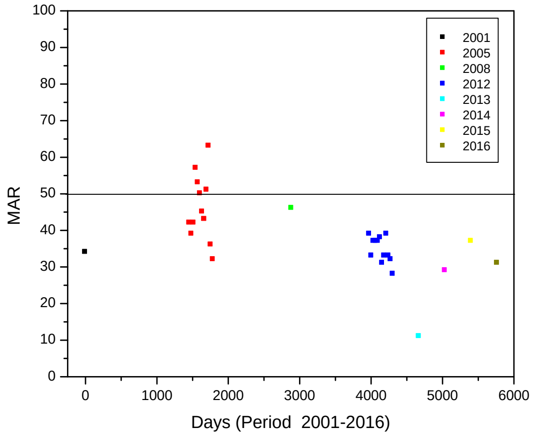

Figure 5.22: Temporal variation of Magnesium Adsorption Ratio of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

5.5.4 Permeability Index (PI)

Excess sodium in water produces the undesirable effects of changing soil properties and reducing soil permeability. The soil permeability is affected by long term use of irrigation water. A criterion for assessing the suitability of water for irrigation is based on PI. Water can be classified as class I, Class II and Class III. Class I and Class II waters are categorised as *good* for irrigation with 75% or more maximum permeability. Class III water was *unsuitable* with 25 % of maximum permeability. In the present study area in all analysis of the DW water sources PI is higher than 25which shows that the water comes in class I or class II and is *Good* (G) for irrigation.

5.5.5 Sodium Adsorption Ratio (SAR)

SAR is an easily measured property that gives information on the comparative concentrations of Na^+, Ca^{2+} and Mg^{2+} in soil solutions. From Table 5.5, it is clear that, in all analysis of DW strata over the year 2001-2016, the SAR shows *excellent to good quality* of water. Figure 5.23 give the temporal variation of sodium adsorption ratio (SAR) of dug well water sources. SAR below 10 suggests *excellent quality* and below 18 suggests *good quality* of water.

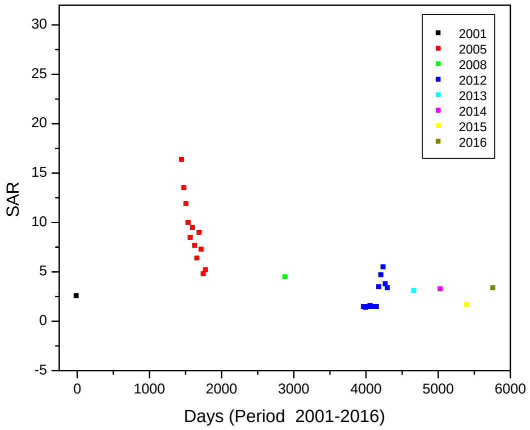

Figure 5.23: Temporal variation of Sodium Adsorption Ratio of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016 .

5.5.6 Residual sodium carbonate (RSC)

The concentration of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) influences the suitability of water for irrigation purpose. RSC is calculated to determine the hazardous effect of carbonate and bicarbonate on the quality of water used for agricultural activities. The RSC value calculated for DW strata over the year from 2001 to 2016 shows higher than 1.25 only in 2013 (1.7). So except in this time, in all other occasions the water shows *good quality*. In 2013, higher bicarbonate make water *doubtful* for irrigation.

5.5.7 Sodium Percentage (Na%)

Sodium percentage calculated for water reveal that in 2001 the water of DW strata show *permissible category*.

Table 5.5: Temporal variation of sodium adsorption ratio (SAR), residual sodium carbonate (RSC) and sodium percentage (Na %) of dug well (DW) water sources along the study area, Arattupuzha coast, Alappuzha, Kerala, India for the period 2001-2016.

Year/Month	SAR	Inference	RSC	Inference	% Na	Inference
Apr 2001	2.5	E	-0.7	G	56	P
Jan 2005	16.3	G	-15.4	G	67	D
Feb 2005	13.4	G	-11.8	G	65	D
Mar 2005	11.8	G	-9.0	G	64	D
Apr 2005	9.9	E	-5.6	G	62	D
May 2005	8.4	E	-2.3	G	58	P
Jun 2005	9.4	E	-5.4	G	58	P
Jul 2005	7.6	E	-1.9	G	60	P
Aug 2005	6.3	E	-2.2	G	52	P
Sep 2005	8.9	E	-7.5	G	58	P
Oct 2005	7.2	E	-0.1	G	56	P
Nov 2005	4.7	E	-1.0	G	45	P
Dec 2005	5.1	E	-1.6	G	48	P
Dec 2008	4.4	E	-1.9	G	60	P
Jan 2012	1.4	E	0.3	G	31	G
Feb 2012	1.3	E	-0.6	G	29	G
Mar 2012	1.4	E	-1.2	G	29	G
Apr 2012	1.5	E	-0.4	G	30	G
May 2012	1.4	E	-0.6	G	30	G
Jun 2012	1.4	E	-0.06	G	30	G
Jul 2012	1.4	E	-0.5	G	30	G
Aug 2012	3.4	E	-0.4	G	43	P
Sep 2012	4.6	E	-2.6	G	50	P
Oct 2012	5.4	E	-5.5	G	50	P
Nov 2012	3.7	E	-4.1	G	43	P
Dec 2012	3.3	E	-4	G	39	G
Dec 2013	3.0	E	1.7	D	45	P
Dec 2014	3.2	E	-0.6	G	43	P
Dec 2015	1.6	E	-0.4	G	34	G
Dec 2016	3.3	E	-0.6	G	39	G

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

In 2005, the monthly analysis in the beginning shows that the water is in *doubtful category* since the Na% is higher than 60, and after that, the quality improves to *permissible category*. From May 2005, till the end of the year 2005 Na% is lower than 60%. In 2008 water belongs permissible category. In 2012 till July, water show *good category* and after that *permissible category*. In 2013 and 2014 the Na% are 45 and 43 which show again *permissible category*. In 2015 and 2016 the DW strata show Na% 34 and 39 which are less than 40 and so the water quality is *good.*

Figure 5.24 give the temporal variation of sodium percentage of dug well water sources. Na % below 40 suggest *good* (G), 40-60 *permissible* (P), 60-80 *doubtful* (D) and above 80 *unsuitable* category (US).

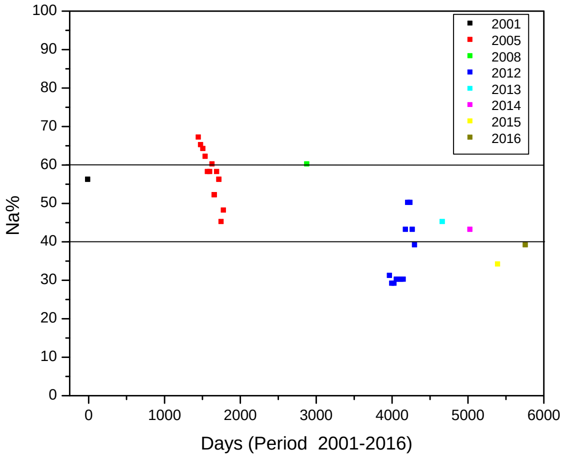

Figure 5.24: Temporal variation of sodium percentage of shallow groundwater dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

5.6 Piper Plot and Water Quality Evaluation

The chemical quality data of the Arattupuzha coastal area are plotted on Hill-Piper Trilinear Diagram for quality analysis. In Piper diagram, the percentages of the major cations and anions determined in milli equivalent are plotted in separate triangles. The plotted points in the triangular fields are projected further into the central diamond field, which provides the overall character of the water [20, 21].

Figure 5.19 give the Hill-Piper-Trilinear diagram for the DW strata of the study area in the years 2001, 2005, 2008, 2012, 2013, 2014, 2015 & 2016.

In 2001 in the diamond area the data point comes in the saline area. In the cation triangle the point corresponds to 56% Na+K, 32% Ca & 12% Mg. In the anion triangle the point correspond to 60% Cl, 25% HCO_3 & 15% SO_4. So the prominent hydrochemical facies is Na-Cl which suggest salinity. In 2005 using the monthly data of post tsunami study the mean values of different parameters are determined and plotted in the Piper diagram. In the diamond area the point come in the saline region, with 68% Na+K, 18% Ca & 12% Mg from cation triangle and 88% Cl, 10% HCO_3 & almost 2% SO_4 from anion triangle (the point comes near to zero sulphate line). Thus in 2005, as expected due to tsunami, Na-Cl is the prominent hydrochemicalfacies., The lower concentration of Na compared to Cl is due to the *reverse ion exchange*. In 2008, the data point in the diamond area cluster with the 2005 point, in the cation triangle also the point cluster with 2005 point and in the anion triangle 75% Cl, 16% HCO_3 & 9%SO_4 are observed. Thus the mean values of the various parameters in 2001, 2005 and 2008 when plotted in Piper diagram, the points come in the saline area of the diamond. That is the major cation is Na+K and major anion is Cl^-.

In 2012 the point moves slightly towards the temporary hardness region in the diamond. That is there is slight increase in concentrations of Ca^{2+} and HCO_3^- and the point lies in the no dominant area. From the cation triangle 48% Na+K, 32% Ca & 20% Mg and from the anion triangle 68% Cl and 30% HCO_3 & 2% SO_4 are observed. In 2013, the point move slightly towards the alkali carbonate region which is due to increase in HCO_3^- concentration and the point lies in the no dominant area of the diamond. In the cation triangle 52% Na+K, 38% Ca & 10% Mg and in the anion triangle 58% HCO_3, 42% Cl & negligible concentration of SO_4 are observed. In 2014 again the data plot shows saline character. From the cation triangle

55% Na+K, 28% Ca & 7% SO_4 and from the anion triangle 60% Cl, 38% HCO_3& 2% SO_4 are observed. In 2015 plot, the point comes in the no dominant region between temporary hardness [(Ca^{2+}+Mg^{2+}) and HCO_3^-] and saline nature [(Na^++K^+) and (Cl^-+ SO_4^{2-})]. From the cation triangle 38% Na+K, 32% Ca& 30% Mg and from the anion triangle 60% Cl , 40% HCO_3 & negligible concentration of SO_4 are observed. In 2016, the point move slightly towards the alkali carbonate region and the point lies in the no dominant area of the diamond. In the cation triangle point is in Na+K region and in anion triangle in between bicarbonate and chloride regions.

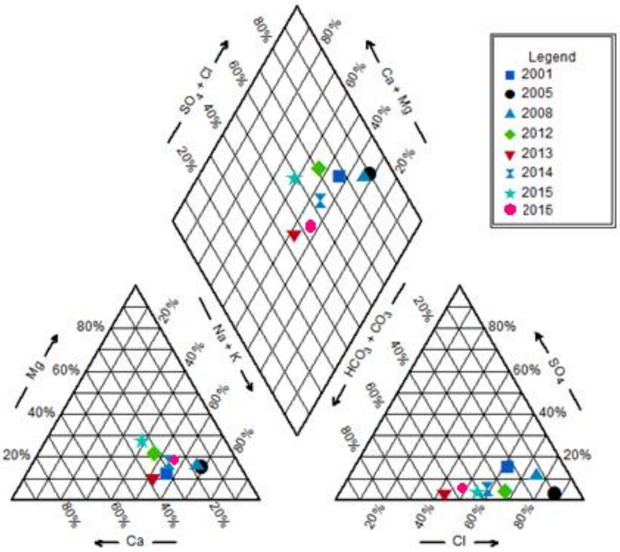

Figure 5.25: Hill-Piper Trilinear diagram for the DW strata of the study area in the years 2001, 2005, 2008, 2012, 2013, 2014, 2015 & 2016.

5.7 Overall Shallow Groundwater Quality of the Region (2001-2016)

This chapter of the thesis elaborately discusses the temporal variation of groundwater quality of shallow groundwater sources along the study area from year 2001 to 2016. The mean of various physico-chemical characteristics of shallow groundwater sources are compared with the IS and WHO standards in Table 5.6 .

Table 5.6: Physico-chemical characteristics of shallow ground water sources of the study area during years 2001, 2005, 2008, 2012, 2013, 2014, 2015 & 2016

Strata	Data	pH	Eh	EC mS/cm	TH mg/l	Alkalinity mg/l	TDS mg/l	DO mg/l	BOD mg/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Fe mg/l	HCO_3 mg/l	Cl mg/l	SO_4 mg/l	PO_4 mg/l	NO_3 mg/l
DW2001	$\bar{x} \pm \sigma$	7.5 ±0.6	-	0.4±0.07	71± 57	35±48	240± 46	-	-	21± 21	5±3	39±8.3	6.3±6	-	43±58	63± 5.3	21±24	-	-
	μ	7.5 ±0.8	-	0.4±0.09	71± 79	35±66	240± 68	-	-	21± 29	5±4	39± 11.5	6.3± 8.4	-	43±80	63± 7.3	21±33	-	-
	CI	6.7- 8.3	-	0.31-.49	0- 150	0-101	172- 308	-	-	0-50	1-9	17.5-50.5	0- 14.7	-	0-123	55.7-70.3	0-54	-	-
DW2005	$\bar{x} \pm \sigma$	7.9± 0.5	-33± 24	3.5± 1.8	506± 333	261± 167	2246±1742	4.8±1.8	9.7± 3.5	107± 58	58± 61	521± 574	24±18	0.04±.02	287±91	2302±2044	68± 25	0.23± 0.5	0.5± 0.2
	μ	7. 9± 0.3	-33± 15	3.5± 1.2	506± 212	261± 106	2246± 1098	4.8±1.1	9.7± 2.2	107± 37	58± 39	521± 365	24±12	0.04±.01	287±58	2302±1301	68± 16	0.23± 0.3	0.5±0.1
	CI	7.6- 8.2	-48- -18	2.3- 4.7	294-718	55- 367	1142-3344	3.7-5.9	7.5-11.9	70- 144	19- 97	156-886	12- 36	0.03-0.05	229-345	1001-3603	52- 84	0-0.53	0.4-0.6
DW2008	$\bar{x} \pm \sigma$	7.3± 0.2	-42± 7.7	0.6± 0.3	120± 31	26± 11	390± 221	2.4±1.6	9.0± 5.1	25±8	14± 7.6	106± 59	11± 8	0.13±0.04	32±14	97±80	19± 18	0.4±0.7	0.9± 0.7
	μ	7.3± 0.2	-42±9	0.6± 0.4	120± 37	26±13	390± 241	2.4±1.8	9.0± 5.9	25±10	14± 9	106± 69	11±9	0.13±0.05	32±16	97±93	19± 21	0.4± 0.8	0.9± 0.8
	CI	7.1- 7.5	33- 51	0.2- 1.0	83- 157	13- 39	149- 631	0.6- 4.2	3.2-15.0	15-35	5- 23	37- 175	2-20	0.08-0.18	16-48	4-190	0-40	0-1.2	0.1-1.7
DW2012	$\bar{x} \pm \sigma$	7.8± 0.4	-50± 22	1.2± 1.4	282± 198	199± 80	1210±1491	4.83± 1.96	5.9± 3.5	69± 47	28± 29	107± 127	12.9± 8.7	0.08±0.14	242± 98	311± 484	27± 24	0.19± 0.14	-
	μ	7.8± 0.2	-50± 14	1.2±0.9	282± 126	199± 51	1210± 949	4.83± 1.24	5.9± 2.2	69±30	28± 19	107± 81	12.9± 5.5	0.08±0.14	242± 62	311± 308	27± 15	0.19± 0.09	-
	CI	7.6- 8.1	-64- -36	0.3-2.1	156-408	148- 250	261-2159	3.6- 6.1	3.7 - 8.1	39- 99	9-47	26- 188	7.4-18.4	0-0.22	180-304	3-619	12- -42	0.1-0.28	-
DW2013	$\bar{x} \pm \sigma$	7.9± 0.2	-56± 14	1.7± 2.0	252± 219	337± 204	463± 761	3.9± 1.6	3.6± 1.2	80± 51	13± 24	119± 140	14± 11	-	411±249	186± 332	14± 19	0.3±0	-
	μ	7.9± 0.2	-56± 15	1.7± 2.0	252± 223	337± 208	463± 775	3.9±1.6	3.6± 1.3	80±52	13± 25	119± 143	14± 12	-	411±253	186± 339	14± 19	0.3±0	-
	CI	7.7- 8.1	-71- -41	0- 3.7	29- 475	129- 545	0- 1238	2.3-5.5	2.3- 4.9	28- 132	0-38	0-262	2-26	-	158-664	0-525	0-33	0.3	-
DW2014	$\bar{x} \pm \sigma$	7.9 ±0.3	-55 ±18	1.5 ± 1.8	267± 168	232± 93	832± 1069	5.6±2.6	3.6± 1.9	66±24	25± 33	141± 162	12± 11	0.9±0.2	284±114	259± 434	29± 17	0.35± 0.01	2.2± 0.6
	μ	7.9 ±0.3	-55 ±18	1.5 ± 1.8	267± 171	232± 95	832± 1090	5.6±2.7	3.6± 1.9	66±24	25± 33	141± 165	12± 12	0.9±0.2	284±116	259± 443	29± 17	0.35± 0.01	2.2± 0.6
	CI	7.6- 8.2	-73- -37	0-2.3	96- 438	137- 327	0- 1922	2.9- 8.3	1.7- 5.5	42- 90	0-58	0- 306	0-24	0.7-1.1	168-400	0-702	12- 46	0.34-0.36	1.6-2.8
DW2015	$\bar{x} \pm \sigma$	7.7± 0.3	-50± 21	0.9± 0.9	211± 99	186± 86	494± 624	5±2	2.1± 2.0	47±21	23± 18	58± 52	7.3±5.7	-	227±105	171± 302	13±9	0.34	1.6± 0.7
	μ	7.7± 0.3	-50± 21	0.9± 0.9	211± 101	186± 87	494± 636	5±2	2.1± 2.0	47±22	23± 18	58± 53	7.3± 5.8	-	227±107	171± 308	13±9	0.34	1.6± 0.7
	CI	7.4- 8.0	-71- -29	0-1.8	110-312	99- 273	0- 1130	3-7	0.1- 4.1	25- 69	5-41	5-111	1.5-13.1	-	120-334	0-479	4-22	0.34	0.9-2.3
DW2016	$\bar{x} \pm \sigma$	8.2± 0.3	-78± 20	1.3± 1.4	253± 132	221± 87	684± 737	4.4±1.6	-	61± 19	25± 25	143± 229	13± 10	0.01±0.01	269±106	166± 254	21± 10	0.12± 0.09	2.8± 1.0
	μ	8.2± 0.4	-78± 20	1.3±1.4	253± 134	221± 88	684± 751	4.4±1.6	-	61±20	25± 25	143± 234	13± 10	0.01±0.01	269±108	166± 259	21± 10	0.12± 0.09	2.8± 1.1
	CI	7.8- 8.6	-98- -58	0- 2.7	119-387	133- 309	0- 1435	2.8- 6.0	-	41- 81	0-50	0-377	3-23	0-0.02	161-377	0-425	11- 31	0.03-0.21	1.7-3.9
BIS2012		6.5- 8.5		-	200	200	500			75	30	-	-	0.3	-	250	200		50
WHO2011		6.5- 8.5		1.5	-		500			75	50	200	12	0.3	500	250	250		50

Results of ANOVA tests conducted to check the various hypotheses, suggested in the introduction chapter, give the following results:

a) *Whether there is any significant difference in the mean values of the parameters in DW strata at different time periods (2001-2016)*

Table 5.7: ANOVA table for the comparison of mean values of the parameters in DW strata at different time periods (2001-2016)

Source	**ss**	**df**	**ms**	**F**	**p-value**
Total	3205833.03	79			
Years	509014.27	7	72716.3249	2.911	$p<0.05$
Parameters	1123214.06	9	124801.5622	4.966	$p<0.001$
Residual	1573604.68	63	24977.8522		

Inferences

1) There is significant difference in the mean values of parameters between years ($p<0.05$). In 2005 the mean value of the parameters are significantly higher compared to other years
2) Mean values of the parameters also showed a significant difference ($p<0.001$). TH, HCO_3 and Cl are significantly higher than the rest.

b) *Whether the water quality index for Dug well strata differ significantly for the years 2013-2016*

Table 5.8: ANOVA table for the comparison of water quality index for dug well strata for the years of 2013-2016

Source	**ss**	**df**	**ms**	**F**	**p-value**
Total	31828.625	23			
Years	4603.125	3	1534.375	6.224	$p< 0.01$
Dugwell	23527.375	5	4705.475	19.086	$p< 0.001$
Residual	3698.125	15	246.542		

Inference

1) There is significant difference in the mean WQI between the years ($p < 0.01$). WQI in 2013, 2014 and 2016 are significant than that of 2015.
2) WQI also differe significantly between dug wells. Dug wells DW1, DW3, DW4, DW5 and DW6 registered significantly lower WQI compared to DW2 ($p<0.001$)

c) *Whether the water quality index for Dug well strata differ significantly in the months of 2005 for 5 strata DW1, DW2, DW3, DW4, DW5*

Table 5.9: ANOVA table for the comparison of water quality index for dug well strata for the months of 2005 for 5 strata DW1, DW2, DW3, DW4, DW5

Source	**ss**	**df**	**ms**	**F**	**p-value**
Total	346544.58	59			
Months	161840.18	11	14712.7436	131.972	P< 0.001
Dug wells	179799.10	4	44949.7750	403.194	P< 0.001
Residual	4905.30	44	111.4841		

Inference

1) The mean value of WQI between the month exhibited a high significant difference ($p<0.001$). January and February experienced significantly higher WQI, the highest in the month of January.

2) There is highly significant difference between Dug wells with respect to WQI. ($p<0.001$). DW1 and DW 3 are having significantly higher WQI compared to D4 and D5. Among DW1 and DW3, DW3 is having significantly higher WQI.

5.8 Conclusion

The long term variation of water quality parameters of shallow groundwater sources of the study area is discussed in this chapter .The study reveal the impact of tsunami inundation in the coastal segment, the present level of various parameters and also the prominent parameters which damage the quality of water sources. High electrical conductivity and high hardness are 2 factors deteriorating the irrigational suitability of shallow groundwaters. WQI calculation suggest poor quality of DW water. Sodium-chloride ratio suggest mainly ion exchange in DW strata. But salinity leads to reverse ion exchange occasionally.Irrigational quality study suggest unsuitability based on Kelly’s ratio and mostly suitability based on other parameters. Hill-Piper Trilinear plot suggest Na-Cl facies in the years

2001,2005 & 2008. In the present study period (2012,2013,2014, 2015 & 2016), points come in no dominant area between temporary hardness and saline regions.Thus this study is useful for evaluating the change and also for future reference.

Results of ANOVA test conducted to check whether there is any significant difference in the mean values of the parameters in DW strata at different time periods (2001-2016)suggests that there is significant difference between years and in 2005 the mean value of the parameters are significantly higher compared to other years. The parameters also showed a significant difference.TH, HCO_3 and Cl are significantly higher than the rest. Comparison of Water quality index (WQI) of years 2013-2016 showed significant difference. WQI in 2013, 2014 and 2016 are significantly higher than that of 2015.WQI also differ significantly between dug wells. Dug wells DW1, DW3, DW4, DW5 and DW6 registered significantly lower WQI compared to DW2. Comparing WQI in different months of post tsunami year and between stations suggest high significant difference. January and February experienced significantly higher WQI, the highest in the month of January. Between Dug wells also there is highly significant difference with respect to WQI.

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Chapter 6

GROUNDWATER QUALITY OF A TSUNAMI DEVASTATED COASTAL SEGMENT: POST TSUNAMI STUDIES OF DEEP GROUNDWATER (2005 -2016)

Contents

6.1 Introduction

This chapter discusses the temporal variation of groundwater quality of deep groundwater sources of tsunami affected Arattupuzha coast for a period of 2001 to 2016. The dependence on deep groundwater has reached high in recent decades in the study areas due to many reasons; mostly shortage in availability as a result of over exploitation. Moreover, the region is prone to coastal erosion and salinity hazard. Study discussed in chapter 4 give a detailed discussion of groundwater quality parameters of 7 bore wells in the study area in each month of year 2012. The study continued in the years 2013, 2014, 2015 and 2016 with one sampling in December of the respective years. The groundwater quality parameters of one deep bore well in the study area is available for the year 2001[1-6]. From the data of post tsunami studies the groundwater quality parameters in each month of year 2005 and December 2008 are known [7]. The data of these years are further seperated as dug well and deep bore well strta and are evaluated to study the temporal variation of deep groundwater quality for a period 2001-2016. GIS maps of years 2013, 2014 & 2015 are used to study variation in spatial distribution of parameters over the year [8-12].

6.2 Water Quality Parameters

The variation of major water quality parameters of bore wells (BW) over year 2001 to 2016 are discussed in the following session along with GIS maps.

6.2.1 pH

In 2001, the pH of the sampled bore well (BW) is 8.0 (Figure 6.1). Post tsunami study data of 2005 reveals that the pH of deep groundwater sources vary from 7.4 to 7.8. From the monthly variation study, in August 2001 the mean pH is 6.7 and in September the it is 8.3. In all other months the pH is near neutral. So unlike in DW strata pH goes to slightly acidic range. Presence of iron has an influence on pH.

$$FeS_2+7/2O_2+H_2O \rightarrow Fe^{2+}+2SO_4^{2-}+2H^+ \text{ .... } (6.1)$$

In 2008, the mean ($\bar{x} \pm \sigma$) pH of BW strata is 7.2±0.05. pH range in 2012 is 7.4-7.7. The results of the subsequent years analysis reveal mean ($\bar{x} \pm \sigma$) 7.5±0.2 (2013), 7.2 ±0.2 (2014), 7.4 ±0.2 (2015) and 7.5±0.3 (2016). Thus the data generated over the last 16 years reveal that the pH of BW strata is within the standard limit of 6.5-8.5. pH higher than 8 are associated with sodium carbonate-bicarbonate waters, while moderately high values are associated with waters high in bicarbonate.

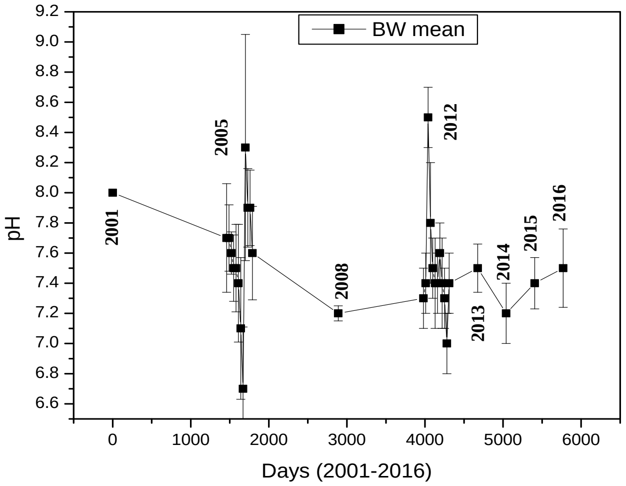
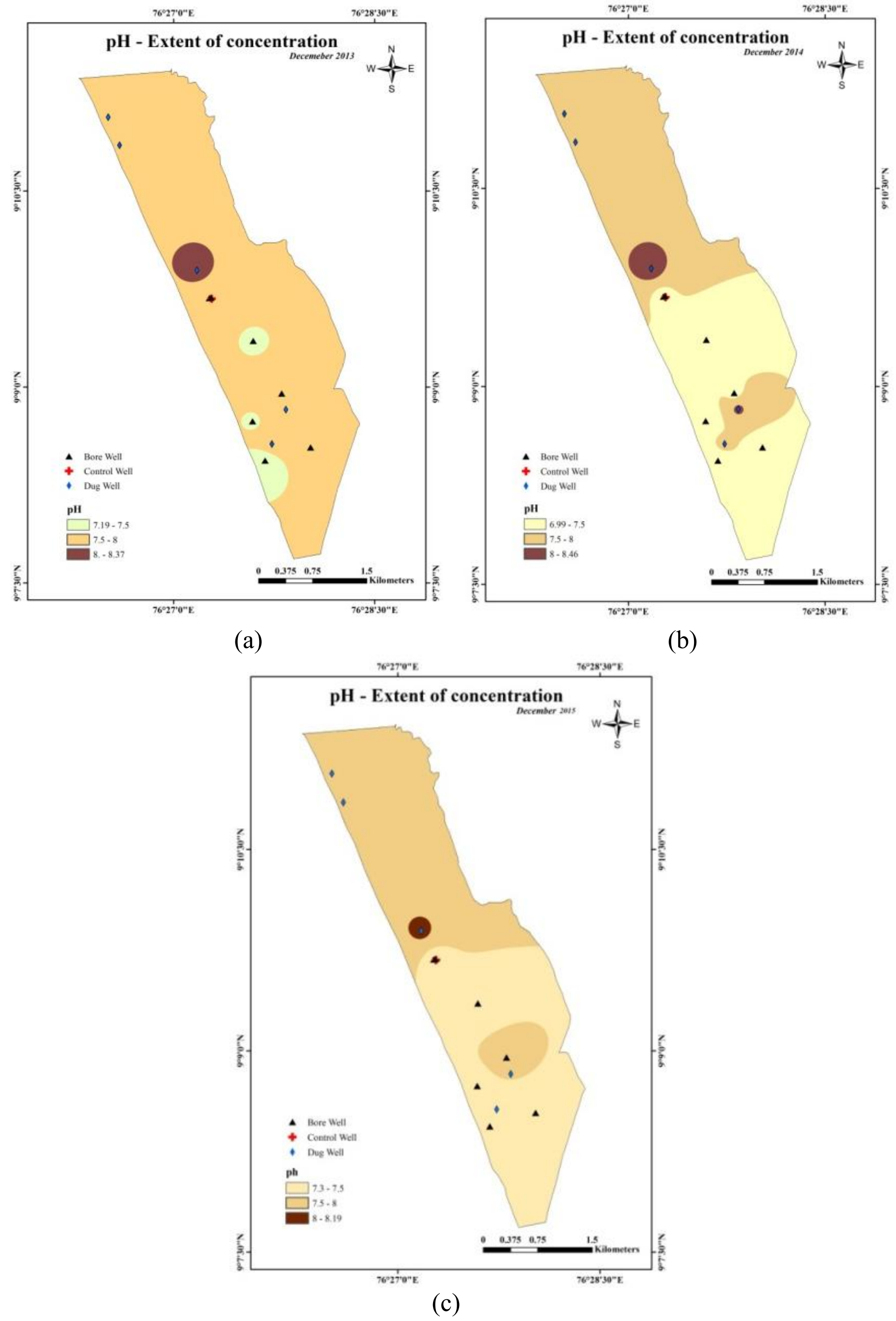


Figure 6.1: Temporal variation of pH of deep groundwater bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001 – 2016).

To study variation in spatial distribution GIS maps are given in Figure 6.2. In the year 2013 majority area shows slightly alkaline range of 7.5-8.0. In certain pockets, slightly lower pH of 7.2-7.5 is observed. There is a pocket at the central area where distinct alkaline pH of 8.0-8.4 is observed. In 2014 in the upper area and in a pocket in the southern area a pH range of 7.5-8.0 is observed. There is a pocket in the central part and in the southern part where pH is in the range 8-8.5 and in the rest of the lower part pH range is 7.0-7.5. In 2015, in the northern area and in a small area in the southern region pH 7.5-8.0 is observed. In the southern area, slightly lower pH 7.3-7.5 is observed. There is a pocket of high alkalinity 8.0-8.5 in the central area. The observations are almost similar to that in year 2014.



(a) (b)

(c)

Figure 6.2: Spatial distribution map for pH of the study area Arattupuzha coast, Alappuzha, Kerala, India during December of a) 2013 b) 2014 and c) 2015

6.2.2 Electrical Conductivity (EC)

Electrical conductivity is a measure of capacity of water to convey electric current. Electrical conductivity is directly proportional to its dissolved mineral content. The ionic mobility depends on its charge, size, the way it interact with solvent and other factors. EC shows good relation with hardness of Ca + Mg, Cl, SO_4 etc. But it is less closely related to bicarbonate concentration.

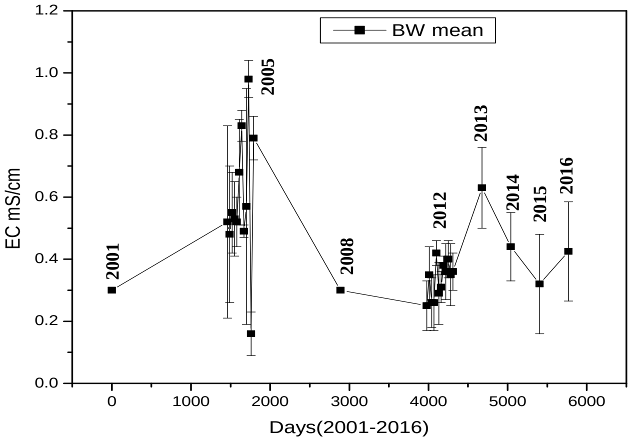
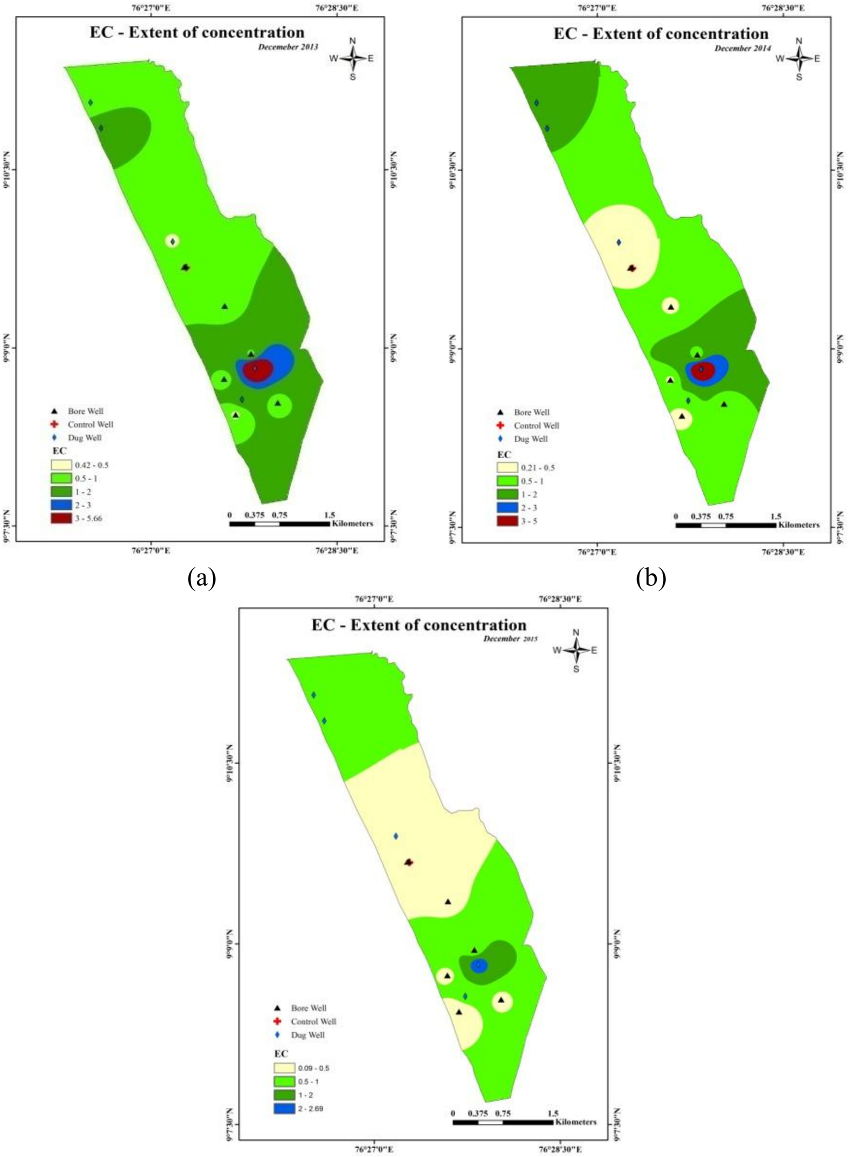


Figure 6.3: Temporal variation of EC of deep groundwater bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001 – 2016).

In 2001, the EC of the sampled bore well (BW) is 0.28 mS/cm (Figure 6.3). In 2005 post tsunami study data reveal that the EC of deep groundwater sources vary from 0.5 to 0.7. From the monthly variation a hike in EC, which is a normal result of sea water inundation, is observed. In January 2005, an EC of 0.52 mS/cm increases to 0.83 in July 2005. In 2008 the mean ($\overline{x} \pm \sigma$) EC of BW strata is 0.3±0. In 2012 study the EC range is 0.28 to 0.38. The results of the subsequent years analysis reveal mean ($\overline{x} \pm \sigma$) EC 0.6±0.1 (2013), 0.4 ±0.1 (2014) , 0.3 ±0.2 (2015) and 0.4±0.2 mS/cm (2016). Thus the data generated over the last 16 years reveal that the EC of BW strata is within the standard limit of 1.5 mS/cm and it is much lower compared to DW strata.

The spatial variation map for EC of the study area is presented in Figure 6.4.



(a) (b)

(c)

Figure 6.4: Spatial distribution map for EC of the study area Arattupuzha coast, Alappuzha, Kerala, India during December a) 2013 b) 2014 and c) 2015

In 2013, major part of northern area and small pockets in southern part show EC 0.5-1.0mS/cm. One small pocket in the southern area show much higher EC of 3.0-5.6mS/cm. In rest of the southern area and small part of northern side EC is 1-2mS/cm. In 2014, northern end completely and a small part of southern area show EC of 1-2mS/cm. In major portion slightly lower EC of 0.5-1.0mS/cm is observed. There are small pockets with still smaller EC of 0.2-0.5mS/cm. One small pocket as in the previous studies maintained the high EC range of 3-5mS/cm. In 2015, in the central area lower conductivity in the range 0.09-0.5mS/cm is observed. There is a pocket with very high conductivity in the southern end having EC higher than 2mS/cm.

6.2.3 Total Hardness (TH)

In 2001, the TH of the sampled bore well (BW) is 56 mg/l (Figure 6.5). In 2005, post tsunami study data reveal that the TH of deep groundwater sources vary from167 to 251. The monthly variation shows that in January (2005) TH is 317 which decrease to 137 in August. After that TH increases slightly. In 2008, the mean ($\bar{x} \pm \sigma$) TH of BW strata is 107±15 mg/l. In 2012, the TH range is142 to 194. The results of the subsequent years analysis reveal mean ($\bar{x} \pm \sigma$) 151±34 mg/l (2013), 173 ±44 mg/l (2014), 126±72 mg/l (2015) and 147±60 mg/l (2016). Thus the data generated over the last 16 years reveal that the TH of BW strata is within the standard limit of 200mg/l except in first 3 months of 2005 which is due to the tsunami inundation. The hardness of water varies considerably from place to place. Groundwater is harder than surface water since it is rich in carbonic acid and dissolved oxygen, which have a high solubilising potential towards rocks containing calcite, gypsum and dolomite.

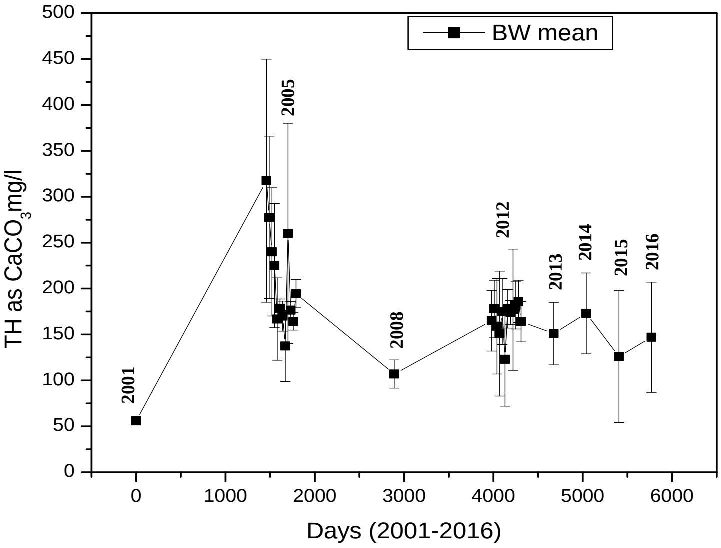
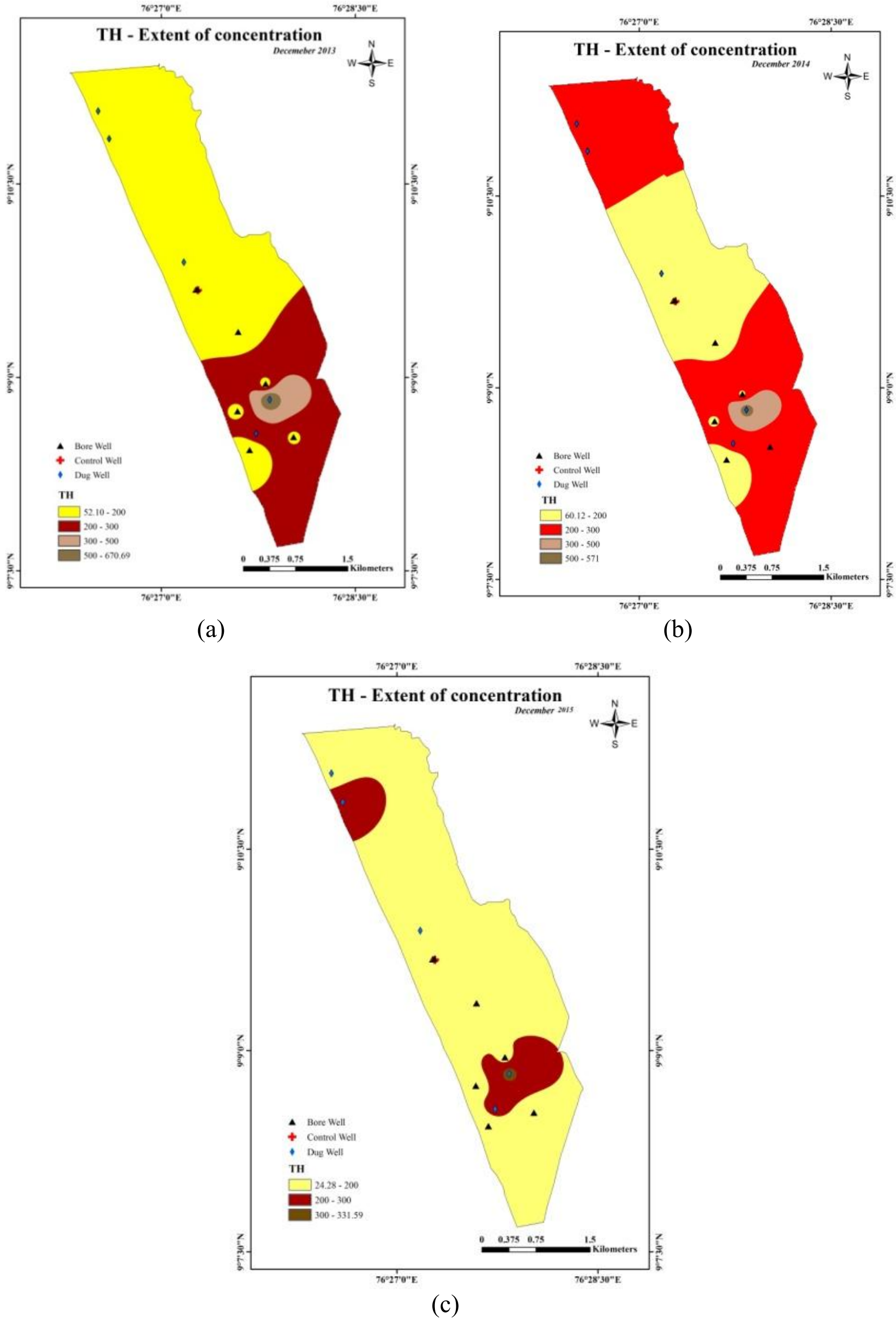


Figure 6.5: Temporal variation of TH of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001 – 2016).

The spatial variation map for TH of the study area is presented in Figure 6.6. In 2013, major area and small pockets in the south show TH range 52-200mg/l. In the southern area higher TH range of 200-300mg/l is observed. In 2014, a major change noticed is the increase in TH in the northern end. This region and the southern region show TH range 200-300mg/l. The central area and small pocket areas in the south have TH range 60-200mg/l. There is a small pocket area of TH higher than 500mg/l. In 2015, TH distribution shows that, in major part of the study area 24-200mg/l is observed. There is a small pocket area with higher TH, greater than 300mg/l, however it decreases compared to previous years analysis.



(a) (b)

(c)

Figure 6.6: Spatial distribution map for TH of the study area Arattupuzha coast, Alappuzha, Kerala, India during December a) 2013 b) 2014 and c) 2015.

6.2.4 Calcium (Ca^{2+})

Calcium is one of the most common ions in groundwater, being both abundant in the earth's crust and extremely mobile in the hydrosphere. The Ca conccentration of the deep groundwater in 2001 is 14 mg/l (Figure 6.7). In 2005 post tsunami study data reveal that the Ca of deep groundwater sources vary from 33.2 to 56.2 mg/l. Monthly variation shows that in January (2005) Ca is 81mg/l which decreases to 60 mg/l in February and 56 mg/l in March respectively. After that, there is not much variation in Ca concentration. In 2008, the mean ($\overline{x} \pm \sigma$) Ca of BW strata is 22±3 mg/l. In 2012, the Ca range is 36 to 50 mg/l. The results of the subsequent year's analysis reveal mean ($\overline{x} \pm \sigma$) Ca 54±15 mg/l (2013), 42 ±11 mg/l (2014), 32±20 mg/l (2015) and 38±17 mg/l (2016). Thus, the data generated over the last 16 years reveal that the Ca of BW strata is within the standard limit of 75mg/l except in January 2005. The concentration of calcium in groundwater is generally between 10 and 100mg/l.

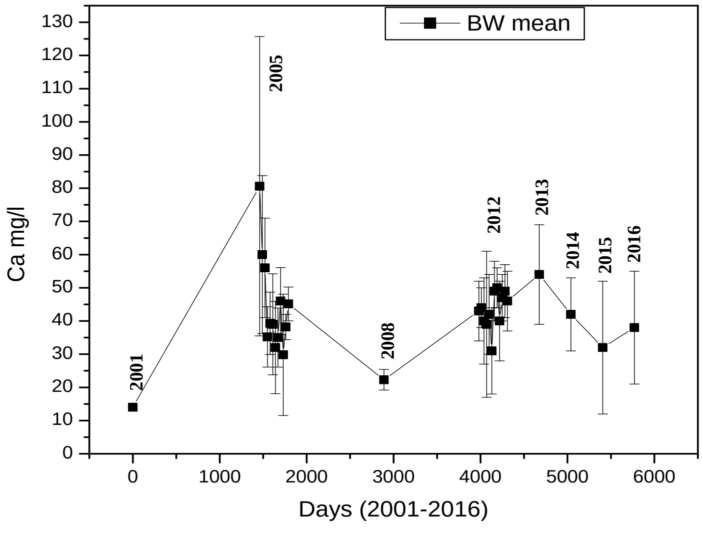
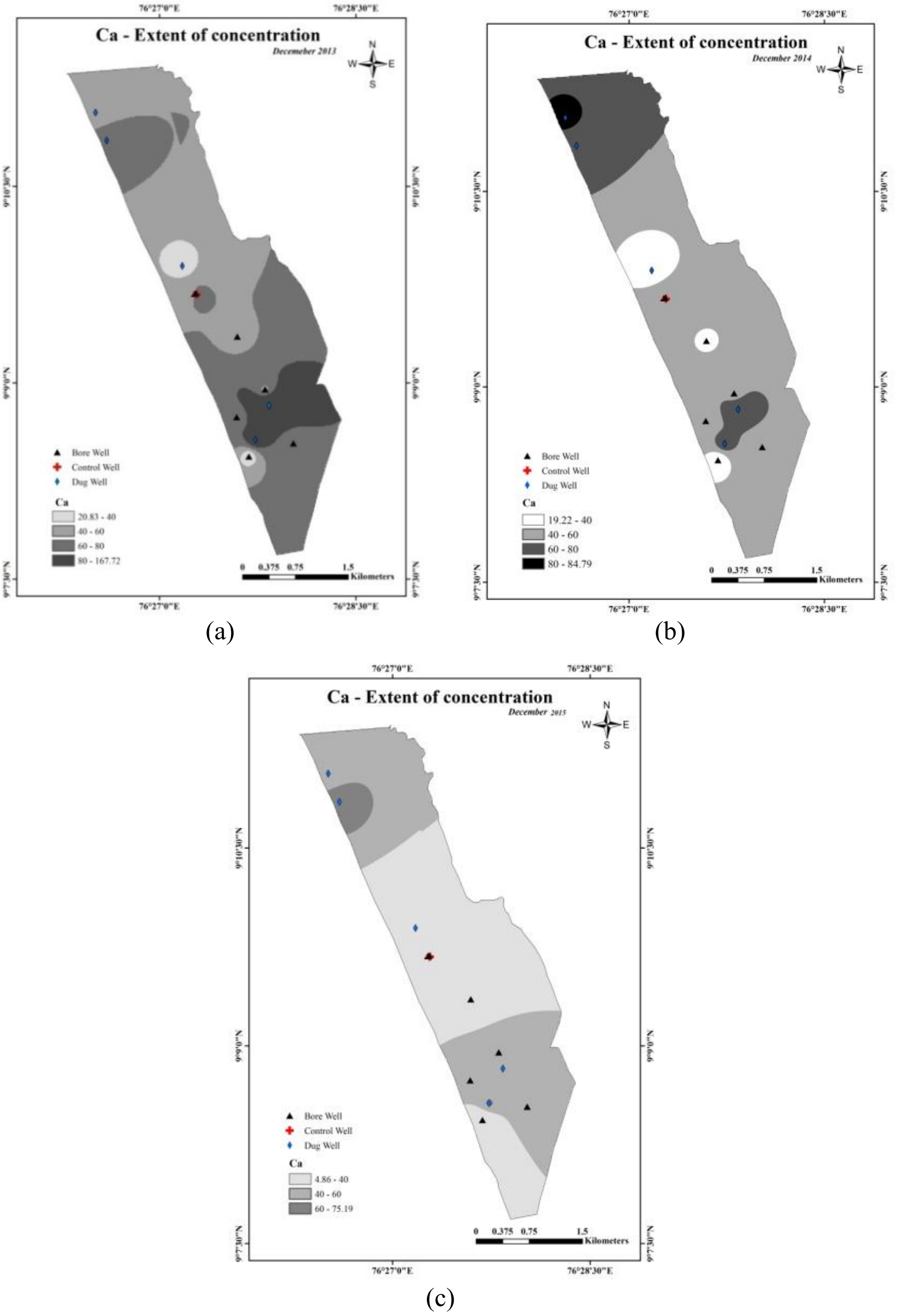


Figure 6.7: Temporal variation of Ca of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001 – 2016).

The spatial variation map for Ca of the study area is presented in Figure 6.8.



(a) (b)

(c)

Figure 6.8: Spatial distribution map for Ca of the study area Arattupuzha coast, Alappuzha, Kerala, India during December a) 2013 b) 2014 and c) 2015.

In 2013, lowest calcium range of 20-40mg/l is observed in central, upper areas and small pocket areas in south. In the lower area and small pockets show 60-80 mg/l range of calcium. Higher than 80mg/l in a pocket area in the lower part. In 2014, major area exhibit calcium in the range of 40-60mg/l. Small pockets of lower range 19-40 mg/l is also observed. In the upper part small pocket of higher than 80mg/l is present. Remaining upper part and a pocket on lower part show calcium range 60-80mg/l. In 2015, lower calcium concentration of 4-40mg/l is observed in central and lowermost areas. In the upper end, there is a pocket of high calcium, more than 60mg/l. In the rest of the upper and lower area, calcium range is 54-60mg/l.

6.2.5 Magnesium (Mg^{2+})

The Mg conccentration of the deep groundwater bore well in 2001 is 4.9 mg/l (Figure 6.9). In 2005 post tsunami study data reveal that the Mg of deep groundwater sources vary from 15.9 to 31.3 mg/l. Considering month wise data not much variation is observed. In 2008 the mean ($\bar{x} \pm \sigma$) Mg of BW strata is 12.5±4.2 mg/l. From the results of 2012 study the Mg range is from 12 to 20mg/l. The results of the subsequent years analysis reveal mean ($\bar{x} \pm \sigma$) Mg 3.9±2.9 mg/l (2013), 16.4 ±5.6 mg/l (2014), 11±6.7 mg/l (2015) and 13±5.2 mg/l (2016). Thus the data generated over the last 16 years reveal that the Mg concentration of BW strata is within the standard limit of 30 mg/l according to BIS 2012 and 50mg/l according to WHO 2011. A slight increase from 30mg/l is observed in some months of 2005. Magnesium is generally found in lesser concentration in natural waters than calcium, due to the slow dissolution of dolomite. Common concentrations of $Mg^{2+}$are between 1.0 and 40 mg/l.

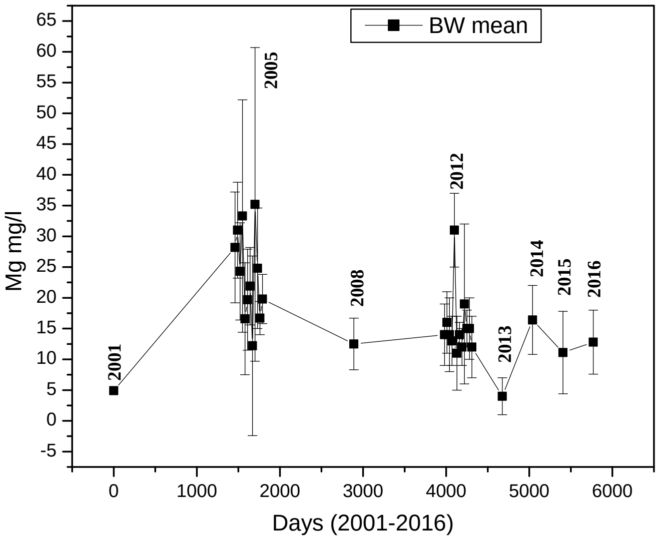
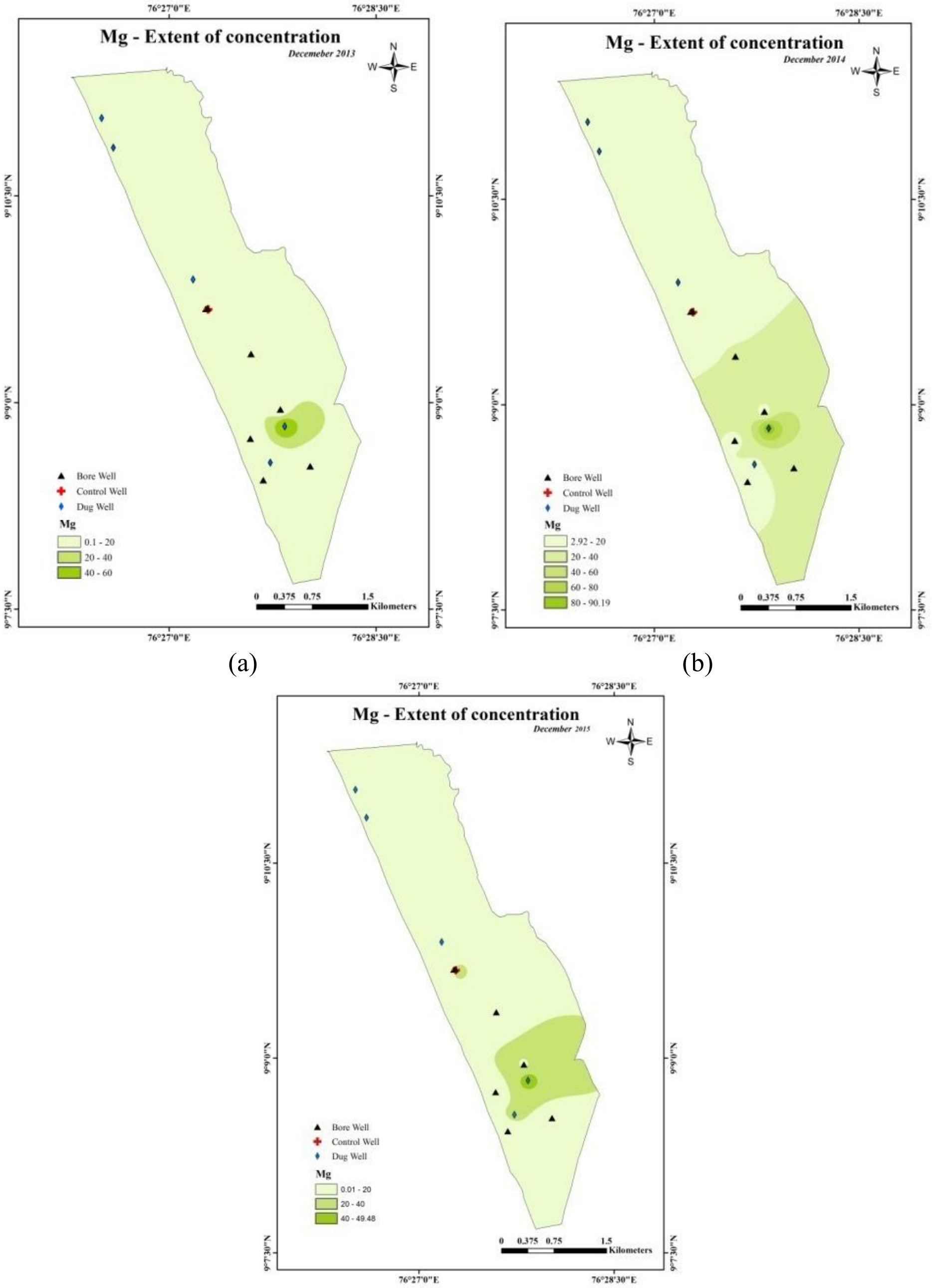


Figure 6.9: Temporal variation of Mg of deep groundwater bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001 – 2016).

The spatial variation map for Mg of the study area is presented in Figure 6.10. In 2013, major part shows much lower Mg concentration, in the range 0.1-20mg/l. There is a small pocket area near the southern end where higher Mg of above 40mg/l is observed. In 2014, slight higher concentration of 20-40mg/l is observed in southern area. Remaining area shows low Mg in the range of 2-20mg/l. There is a small pocket area of higher Mg (>80mg/l). In 2015, similar distribution of Mg as in 2013 is observed, major area below 20mg/l and small pocket area of higher than 40mg/l.



(a) (b)

(c)

Figure 6.10: Spatial distribution map for Mg of the study area Arattupuzha coast, Alappuzha, Kerala, India during December a) 2013 b) 2014 and c) 2015.

6.2.6 Sodium (Na^+)

The Na concentration of the deep groundwater bore well in 2001 is 11 mg/l (Figure 6.11). In 2005 post tsunami study data reveal that the Na of deep groundwater sources vary from 13 to 34 mg/l. Monthly variation shows that in January 2005 the concentration is 35mg/l which decreases and keeps almost steady in the subsequent months except a hike to 38mg/l in July 2005. In 2008, the mean ($\bar{x} \pm \sigma$) Na of BW strata is 60±7 mg/l which is an unusually high value. Clay minerals may release large quantities of exchangeable sodium. In 2012 study Na range is 15-23 mg/l. The results of the subsequent year's analysis reveal that mean ($\bar{x} \pm \sigma$) Na 20.8±6.3 mg/l (2013), 24 ±7.2 mg/l (2014), 16.4±7.7 mg/l (2015) and 23±4.5 mg/l (2016). Thus the data generated over the last 16 years reveal that the Na concentration of BW strata is well within the standard limit of 200 mg/l.

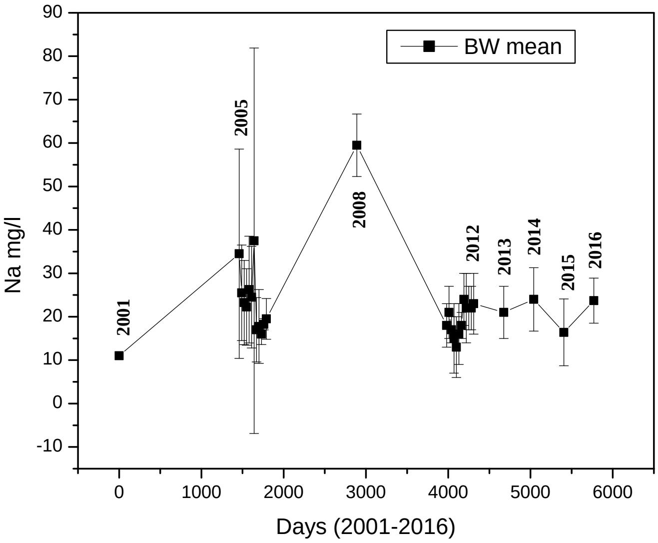
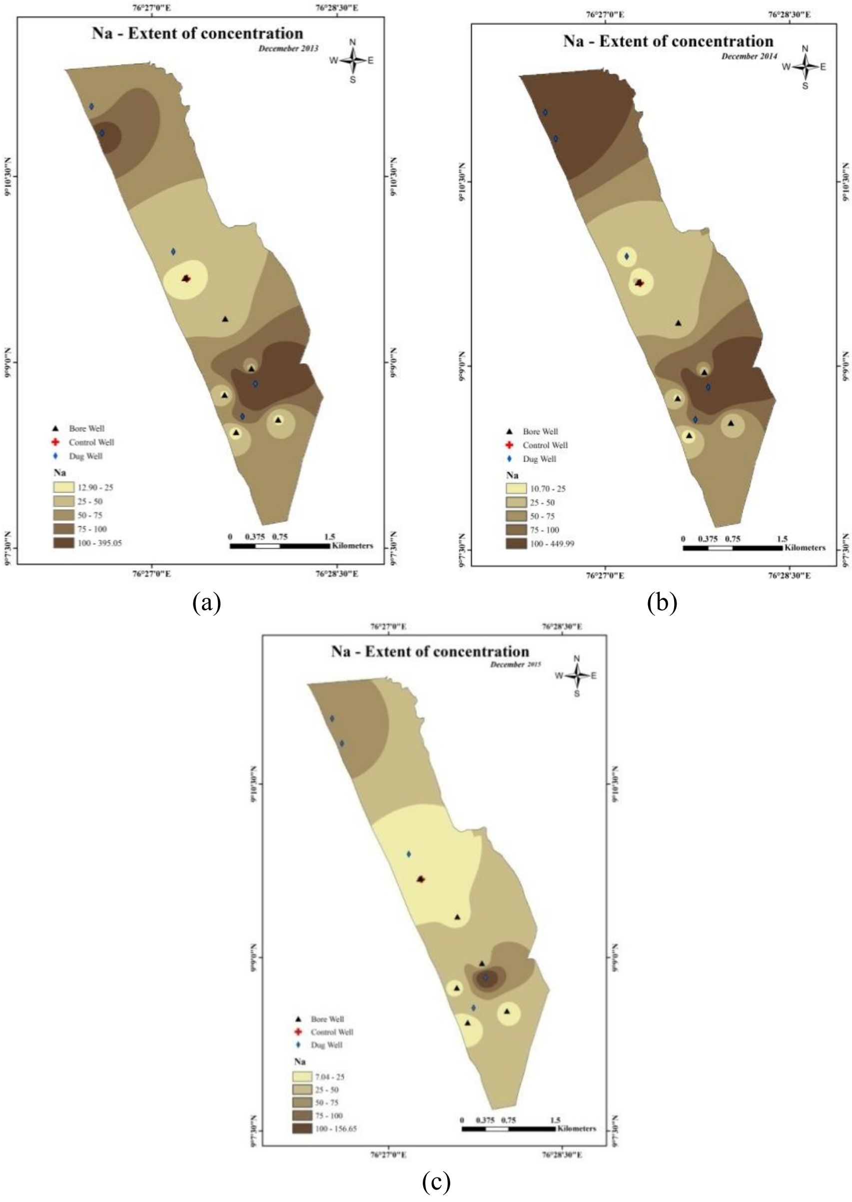


Figure: 6.11: Temporal variation of Na of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001 – 2016).

The spatial variation map for Na of the study area is presented in Figure 6.12



(a) (b)

(c)

Figure 6.12: Spatial distribution map for Na of the study area Arattupuzha coast, Alappuzha, Kerala, India during December a) 2013 b) 2014 and c) 2015.

In 2013, major areas of upper and lower parts show sodium concentration in the range 50-75mg/l. Small pocket areas in the upper and lower parts having sodium higher than 100mg/l. Central part is having 25-50 mg/l range of sodium and a small pocket of less than 25mg/l. In 2014, an increase in sodium with higher than 100 mg/l in the uppermost end and small pocket in the lower most part. In 2015, major area has Na range 25-50 mg/l. Central area and small pockets of lower range, less than 25 mg/l are also observed.

6.2.7 Potassium (K$^+$)

The K concentration of the deep bore well sources in 2001 is 25mg/l (Figure 6.13). In 2005, post tsunami study data reveal that the K of deep groundwater sources vary from 5.5 to 7.3mg/l. The monthly variation of K shows, almost a steady value. In 2008, the mean ($\bar{x} \pm \sigma$) K of BW strata is 7.0±0.8mg/l. From the results of 2012 study K ranges from 5.1 to 6.9. The results of the subsequent years analysis has mean is ($\bar{x} \pm \sigma$) K of 5.7±1.2mg/l (2013), 5.8 ±1.4mg/l (2014), 4.4±2.1mg/l (2015) and 4±2.3mg/l (2016). Thus the data generated over the last 16 years reveal that the K concentration of BW strata is well within the standard limit of 12mg/l.

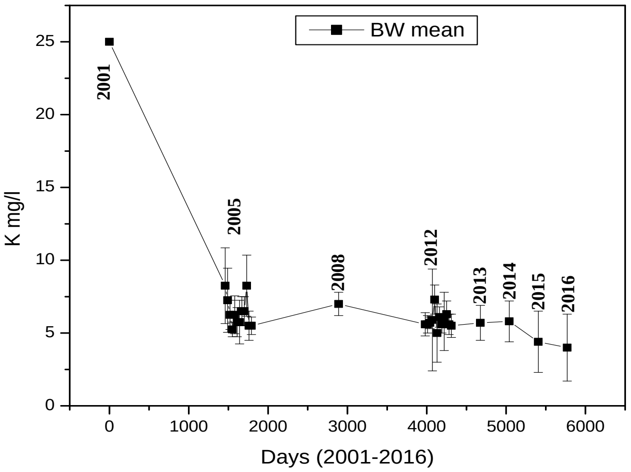
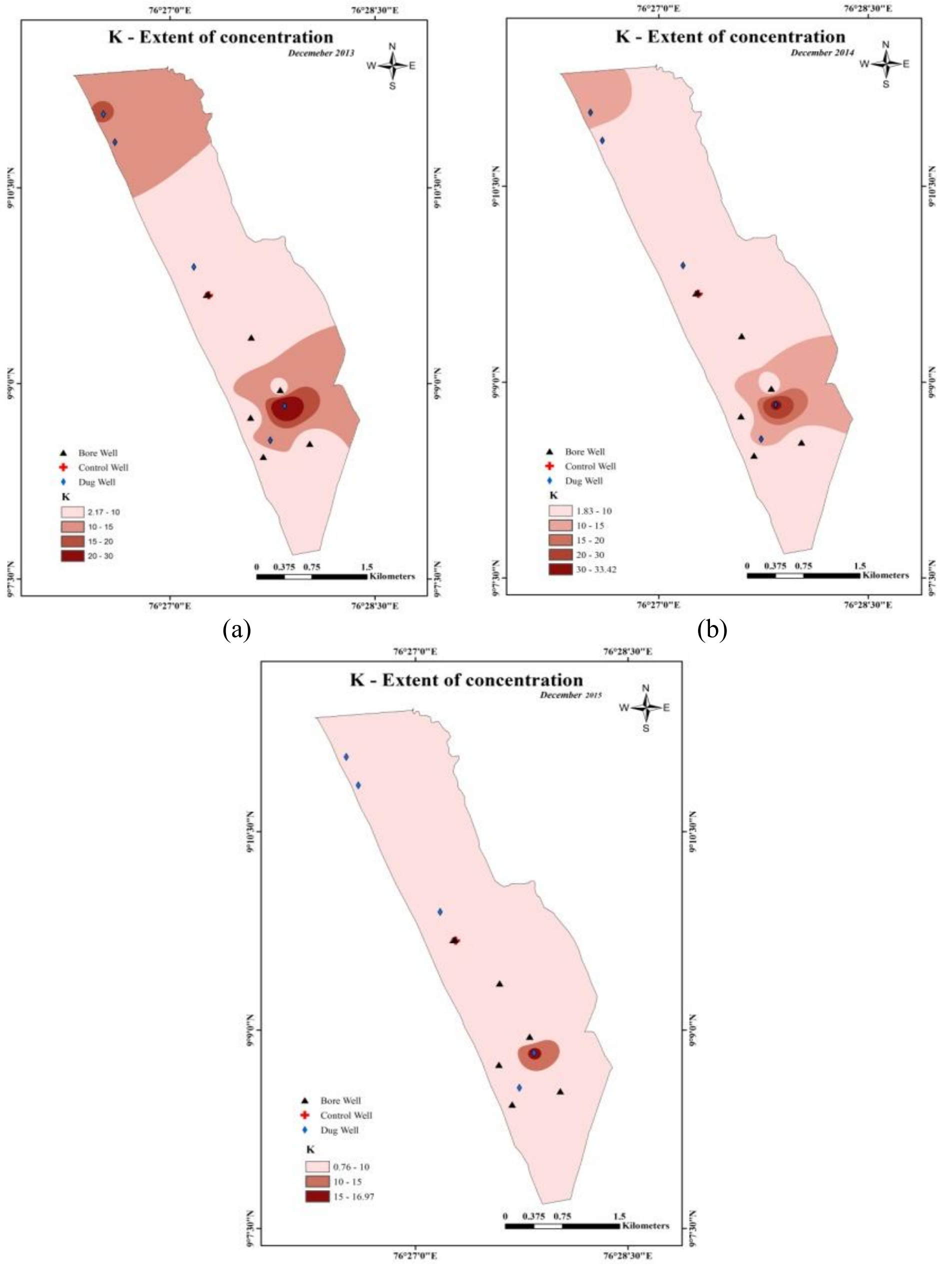


Figure 6.13: Temporal variation of K of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001 – 2016).

The spatial variation map for K of the study area is presented in Figure 6.14.



(a) (b)

(c)

Figure 6.14: Spatial distribution map for K of the study area Arattupuzha coast, Alappuzha, Kerala, India during December a) 2013 b) 2014 and c) 2015.

In 2013, increased potassium in the upper area and pocket area in lower part is observed. In 2014, there is lowering of potassium in upper part. In 2015, almost uniform distribution of less than 10mg/l potassium.

6.2.8 Bicarbonate (HCO_3^-)

In 2001, the bicarbonate concentration of the deep bore well (BW) is only 5.3mg/l (Figure 6.15). In 2005, post tsunami study data reveal that the HCO_3^- of deep groundwater sources vary from 257 to 303. The monthly variation of bicarbonate concentration shows almost steady value. In 2008, the mean ($\overline{x} \pm \sigma$) bicarbonate of BW strata is 27±15 mg/l which is much lower than the 2005 mean value of 276±36 mg/l. From the 2012 study, the bicarbonate concentration range is 204-278 which is almost similar to 2005 value. The results of the subsequent years analysis reveal mean ($\overline{x} \pm \sigma$) 312±2.9 mg/l (2013), 255 ±69 mg/l (2014), 182±91 mg/l (2015) and 213±101 mg/l (2016). Thus, the data generated over the last 16 years reveal that the $HCO_3^-$of BW strata is within the standard limit of 500mgl.

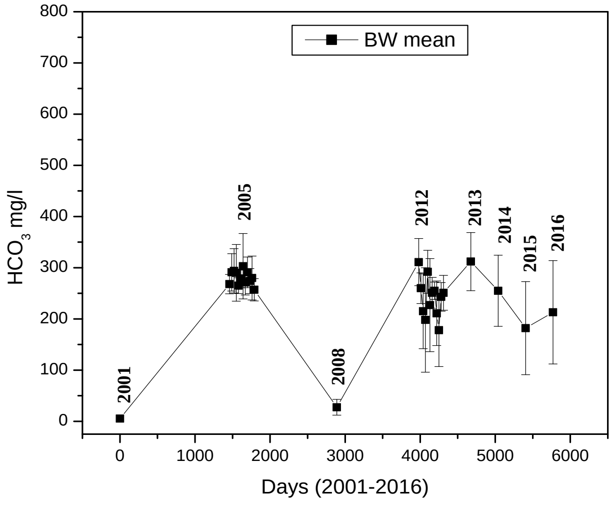
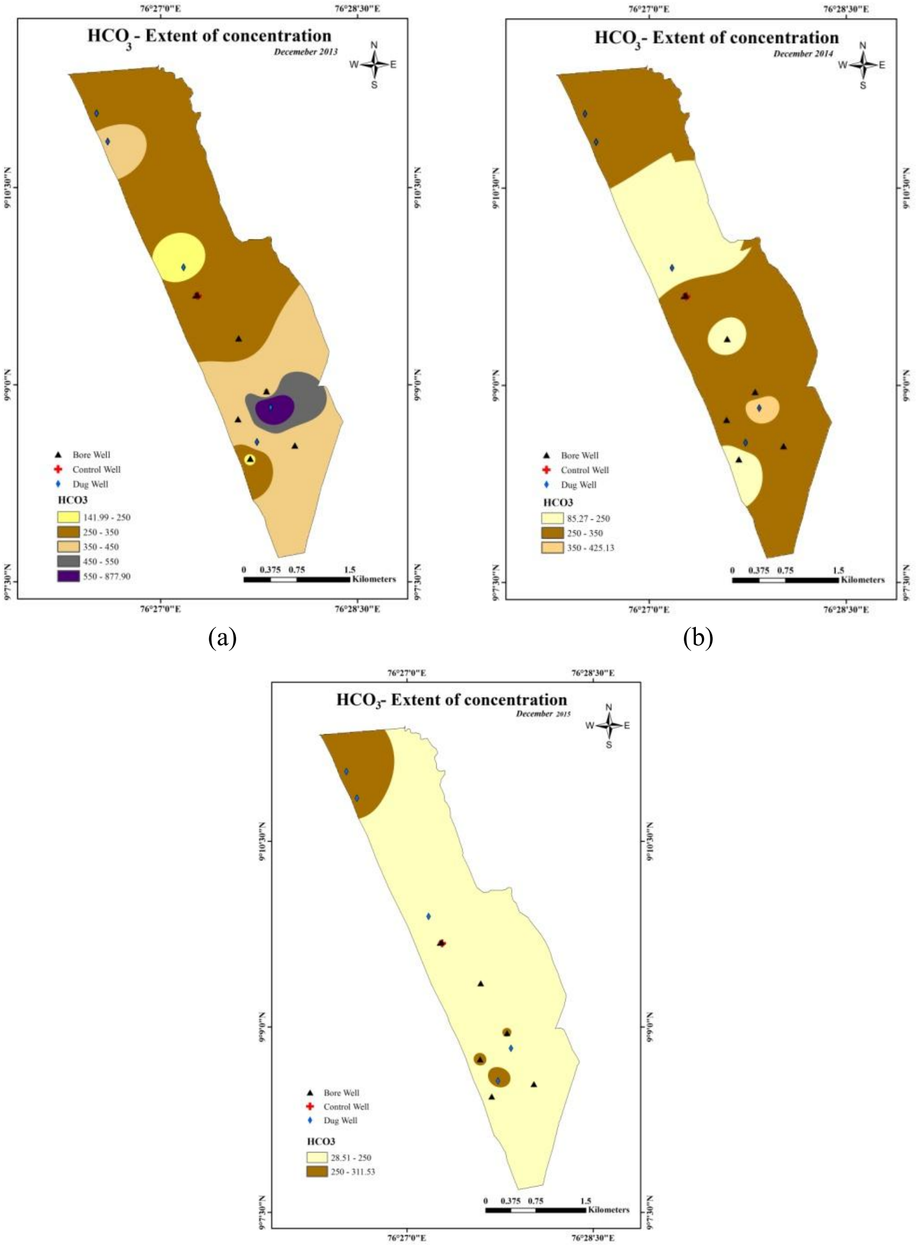


Figure 6.15: Temporal variation of HCO_3 of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001 – 2016).

The spatial variation map for HCO_3^- of the study area is presented in Figure 6.16.



(a) (b)

(c)

Figure 6.16: Spatial distribution map for HCO_3^- of the study area Arattupuzha coast, Alappuzha, Kerala, India during December a) 2013 b) 2014 and c) 2015

In 2013, increase in bicabonate is visible in the entire study area. In 2014, central area shows lower (85-350 mg/l) bicarbonate. In 2015, except in small area near top and small pocket in lower part, almost uniform distribution of bicarbonate is prominent.

6.2.9 Chloride (Cl)

The Cl$^-$ concentration of the bore well in 2001 is 31 mg/l (Figure 6.17). In 2005 post tsunami study data reveal that the Cl$^-$ of deep groundwater sources vary from 69 to 255mg/l. Monthly variation shows that from January to May 2005, very high concentration of Cl$^-$ is observed due to tsunami inundation. The highest value observed in May is 412mg/l. The concentration decreases in the subsequent months. In 2008, the mean ($\bar{x} \pm \sigma$) Cl$^-$ of BW strata is 14±3.5mg/l. In 2012 the range of Cl$^-$ is 8-24mg/l which is very much lower than that in the early months of 2005.The results of the subsequent years analysis reveal mean ($\bar{x} \pm \sigma$) Cl$^-$ 13.5±8.5 (2013), 19 ±10 (2014), 13.6±7.7 (2015) and 20±8.2mg/l (2016). Thus, the data generated over the last 16 years reveal that, the Cl$^-$ of BW strata show higher than standard limit of 250mg/l in early months of 2005. In all other periods, the Cl$^-$ concentration is much lower than the standard limit.

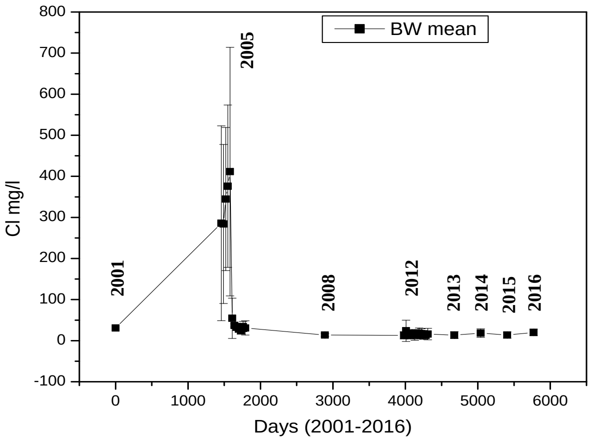
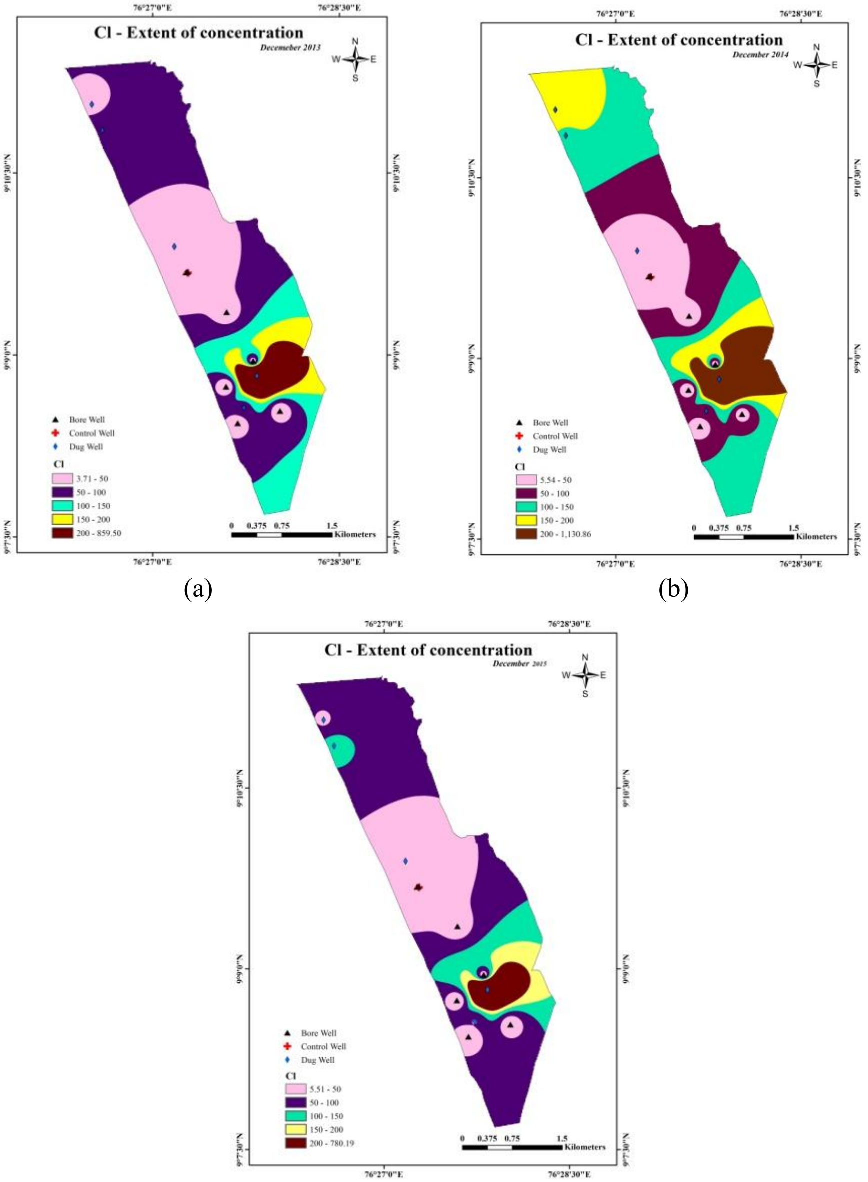


Figure: 6.17: Temporal variation of Cl$^-$ of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001 – 2016).

The spatial variation map for Cl of the study area is presented in Figure 6.18. In 2013, except a small pocket area, chloride level is lower than 200mg/l. In 2014 and 2015 almost similar distribution of chloride is observed.



(a)

(b)

(c)

Figure 6.18: Spatial distribution map for Cl^- of the study area Arattupuzha coast, Alappuzha, Kerala, during December a) 2013 b) 2014 and c) 2015.

6.2.10 Sulphate (SO_4^{2-})

The SO_4^{2-} concentration of the sampled bore well in 2001 is 20 mg/l (Figure 6.19). In 2005 post tsunami study data reveal that the SO_4^{2-} of deep groundwater sources vary from 5.7 to 19.3mg/l. Monthly variation shows that after October high concentration of SO_4^{2-} is observed. In 2008 the mean ($\bar{x} \pm \sigma$) SO_4^{2-} of BW strata is 3±1mg/l. In 2012 study SO_4^{2-} range is 2.0-3.0mg/l which is very much lower than that in the months of 2005. The results of the subsequent year's analysis reveal mean ($\bar{x} \pm \sigma$) SO_4^{2-}1.8±0.8 (2013), 4.6 ±0.5 (2014), 3.4±1.3 (2015) and 12.6±3.8mg/l (2016). Thus, the data generated over the last 16 years reveal that the SO_4^{2-} concentration of BW strata show much smaller than standard limit of 200mg/l.

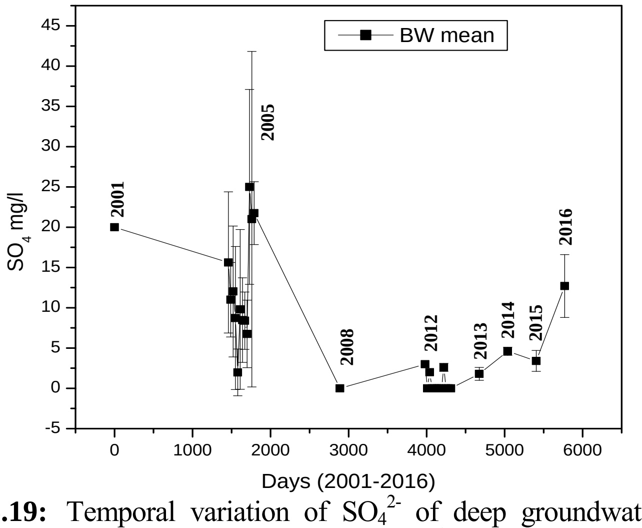


Figure 6.19: Temporal variation of SO_4^{2-} of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016

6.2.11 Redox Potential (Eh)

Reduction potential is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. The transfer of electrons between chemical species determines the reduction potential of an aqueous solution. From the post tsunami studies of 2005, the monthly variation of Eh of BW strata is obtained. In March, July and August 2005, oxidising environment is observed whereas in all other months, reducing environment is prevalent in BW strata with mean ($\bar{x} \pm \sigma$) of $^{-}$25 ±20mV (Figure 6.20). In 2008, the mean ($\bar{x} \pm \sigma$) Eh of BW strata is $^{-}$42±10mV. In all months of year 2012, reducing environment is observed in BW strata with a mean ($\bar{x} \pm \sigma$) of $^{-}$28±22. The results of the subsequent years analysis reveal mean ($\bar{x} \pm \sigma$) Eh -29±9 (2013), -15±12 (2014), -33 ±11 (2015) and -34±15mV (2016). Thus the data generated over the last 16 years reveal that the Eh of BW strata show the presence of a reducing environment in deep groundwater sources of the study area.

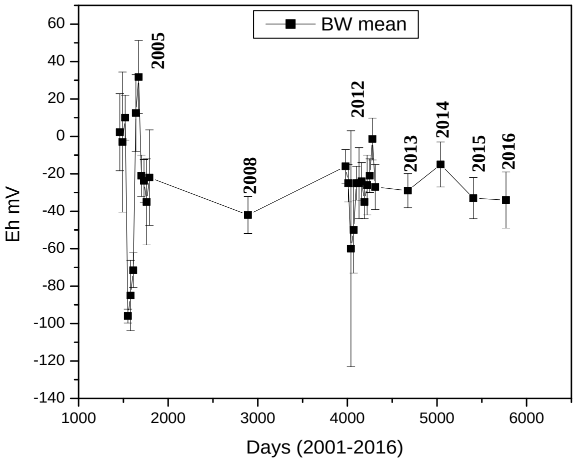


Figure 6.20: Temporal variation of Eh of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016

6.2.12 Alkalinity (AL)

The alkalinity of water is a measure of its capacity to neutralize acids. The alkalinity of natural water is due to the presence of bicarbonate, carbonate and hydroxide compounds of calcium, magnesium, sodium and potassium. Borates, phosphates and silicates also contribute to alkalinity. The determination of alkalinity provides an idea of the nature of salt present.

In 2001, the alkalinity of the sampled bore well (BW) is only 4.3mg/l (Figure 6.21). From the post tsunami studies of 2005, the monthly variation of alkalinity of BW strata is obtained. The annual mean ($\overline{x} \pm \sigma$) alkalinity is 230 ±30 with a confidence interval of 211-249. Alkalinity variation is similar to bicarbonate variation. In 2008, the mean value of Alkalinity of BW strata is 23±13.In 2012, the alkalinity range is 170-226mg/l which is very much similar to 2005 variation. The results of the subsequent years analysis reveal mean ($\overline{x} \pm \sigma$) 256±47(2013), 209±57 (2014), 150 ±75 (2015) and 174±83mg/l (2016). Thus, the data generated over the last 16 years reveal that the alkalinity of BW strata show higher than standard limit of 200mg/l in certain periods.

If the alkalinity is greater than hardness it indicates the presence of basic salts-sodium and potassium in addition to those of calcium and magnesium.

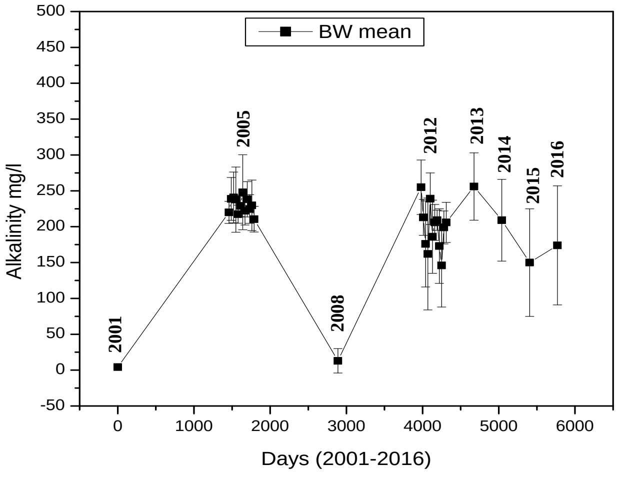
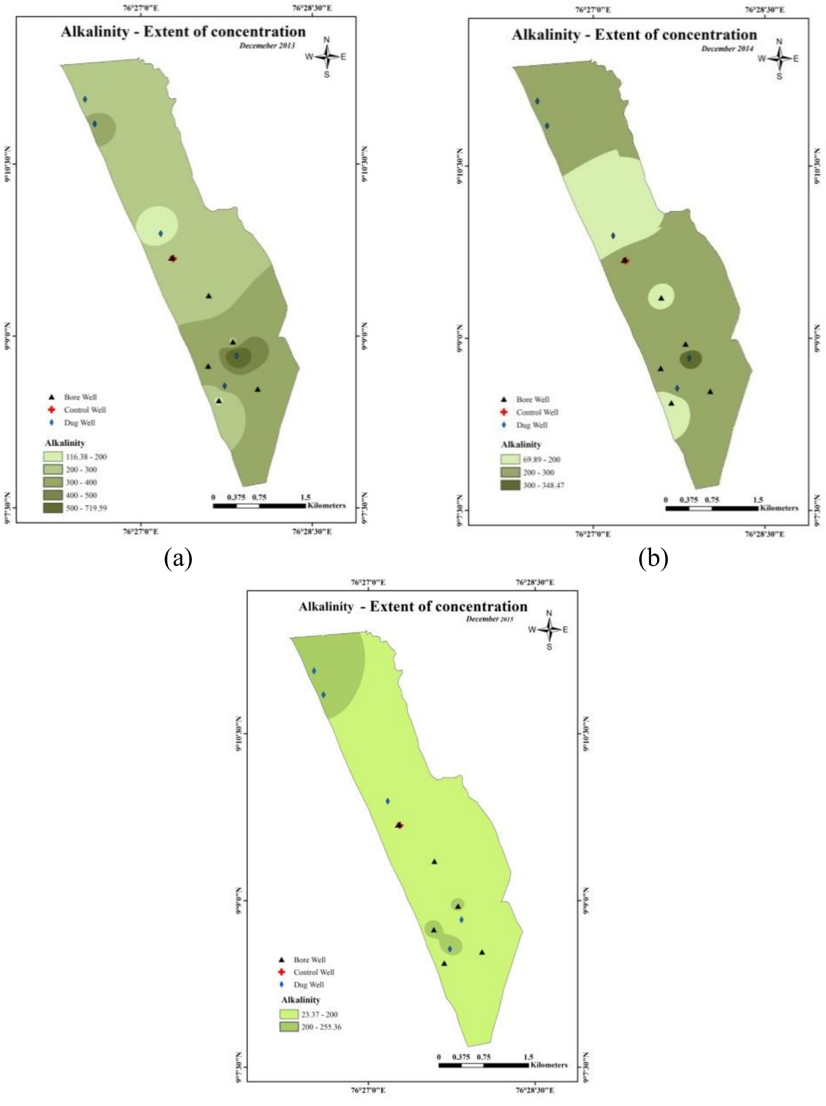


Figure 6.21: Temporal variation of alkalinity of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016

The spatial variation map for alkalinity of the study area is presented in Figure 6.22. In 2013, slightly higher alkalinity in lower part. In 2014, only the central small area show low alkalinity and rest of the area show 200-300mg/l range. In 2015, lowering of alkalinity and major area below 200mg/l.



(a) (b)

(c)

Figure 6.22: Spatial distribution map for alkalinity of the study area Arattupuzha coast, Alappuzha, Kerala, during December a) 2013 b) 2014 and c) 2015.

6.2.13 Dissolved Oxygen (DO)

Oxygen is dissolved in most waters in varying concentrations. Solubility of oxygen depends on temperature, pressure and salinity of water. It is essential to the life of fish and other aquatic organisms. The concentration of dissolved oxygen decreases with depth. For the deep groundwater sources DO data is available from 2005. The post tsunami study data show an average DO of 4.1±2.4mg/l with a CI of 2.5-4.7 at 95% confidence level in the year 2005 (Figure 6.23). In 2008, the mean ($\bar{x} \pm \sigma$) DO is 5.7±2.9mg/l. The monthly study of 2012, shows an annual mean ($\bar{x} \pm \sigma$) DO 4.7±1.6 with a CI of 3.7-5.7 at 95% confidence level. The results of the subsequent years analysis reveal mean ($\bar{x} \pm \sigma$) DO 6.0±1.8mg/l (2013), 6.0±2.5mg/l (2014), 5.9±2.0mg/l (2015) and 6.7±0.5mg/l (2016). So in the present study period an improvement in DO of deep groundwater is observed.

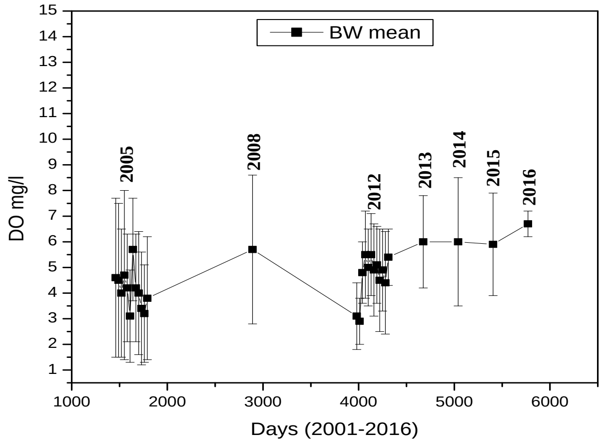
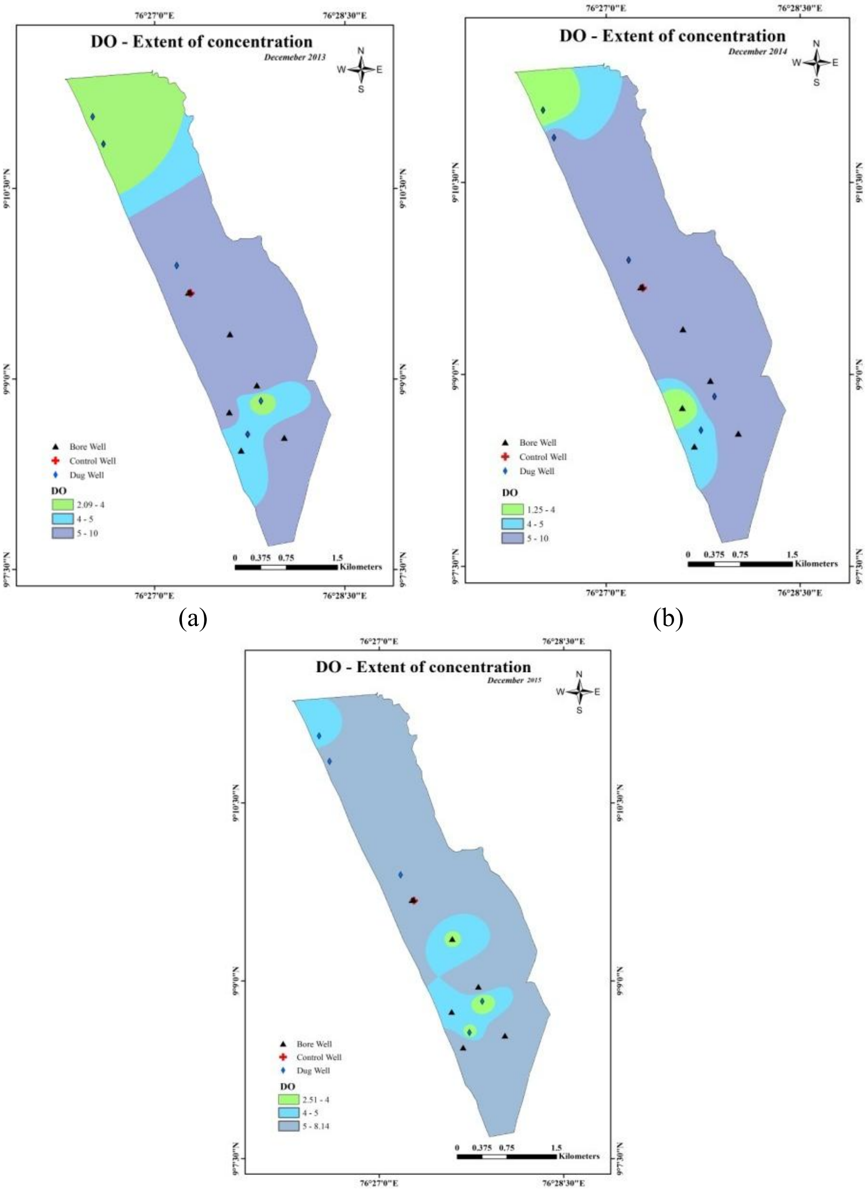


Figure 6.23: Temporal variation of DO of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016

The spatial variation map for DO of the study area is presented in Figure 6.24. In 2013 major area show DO higher than 5mg/l and there is an upper small region lower than 4mg/l DO. In 2014, also more area show higher than 5mg/l DO. In 2015, again improvement in DO and almost whole region having DO higher than 5mg/l is observed.



(a) (b)

(c)

Figure 6.24: Spatial distribution map for DO of the study area Arattupuzha coast, Alappuzha, Kerala, during December a) 2013 b) 2014 and c) 2015.

6.2.14 Biochemical Oxygen Demand (BOD)

From the post tsunami studies of 2005, the monthly variation of BOD of BW strata is obtained. The annual mean ($\overline{x} \pm \sigma$) BOD is 9.9 ±6.5 mg/l with a confidence interval of 5.7-14.1(Figure 6.25). In 2008, the mean ($\overline{x} \pm \sigma$) BOD of BW strata is 9±5mg/l. The results of 2012 study shows that the annual mean ($\overline{x} \pm \sigma$) BOD is 3.8±1.7 with a CI 2.7-4.9 at 95% confidence level. The results of the subsequent years analysis reveal mean ($\overline{x} \pm \sigma$) BOD 2.9±0.9 (2013), 4.7±2.1 (2014) and 1.6±1.6mg/l (2015). Compared to post tsunami year BOD shows a decline in the present study period.

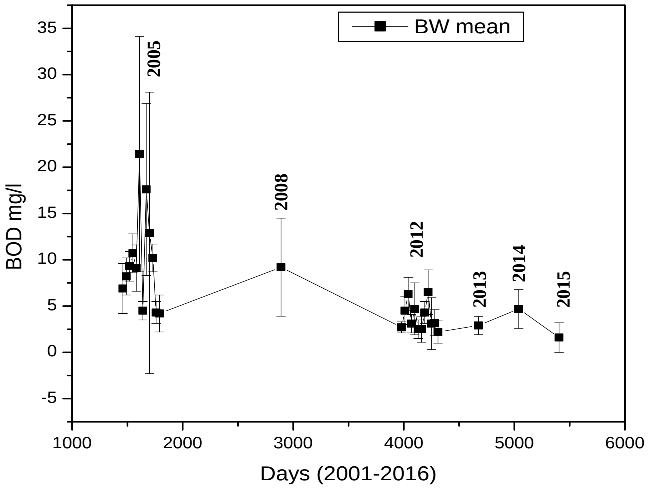


Figure 6.25: Temporal variation of BOD of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016

6.2.15 Phosphate (PO_4^{3-})

Phosphate in large quantities in fresh waters indicates pollution, through sewage and industrial wastes. It promotes growth of nuisance microorganisms. In the present study area, from the post tsunami studies of 2005, the monthly variation of phosphate of BW strata is obtained. The annual mean ($\overline{x} \pm \sigma$) is

0.04±0.07 mg/l (Figure 6.26). In 2008, the mean ($\bar{x} \pm \sigma$) phosphate of BW strata is 0.08±0.09mg/l. The results of 2012 study shows that the annual mean ($\bar{x} \pm \sigma$) phosphate is 0.1mg/l. The results of the subsequent years analysis reveal that the mean in 2016 is 0.05±0.01mg/l. So very small concentration of phosphate is observed in few stations of the study area.

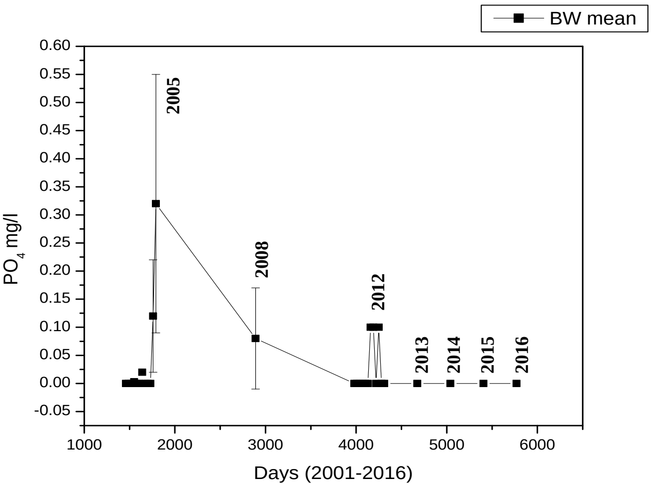


Figure 6.26: Temporal variation of PO_4^{3-} of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016

6.2.16 Nitrate (NO_3^-)

The presence of nitrate in water indicates organic pollution. Significant source of nitrate are chemical fertilizers, domestic effluents, industrial discharge etc. Excessive concentration in drinking water is considered hazardous for infants because in their intestinal track, nitrates are reduced to nitrites which may cause methaemoglobinaemia. In the present study area in 2005, nitrate is 0.6±0.4mg/l and in 2008, the nitrate concentration in BW strata is 0.4±0.6mg/l. The 2014 analysis shows that the mean ($\bar{x} \pm \sigma$) nitrate is 1.7 ±0.9mg/l, in 2015 it is 1.1±0.4mg/l and in 2016 it is 3.5±4.3mg/l (Figure 6.27). The increasing trend of nitrate suggests anthropogenic influence.

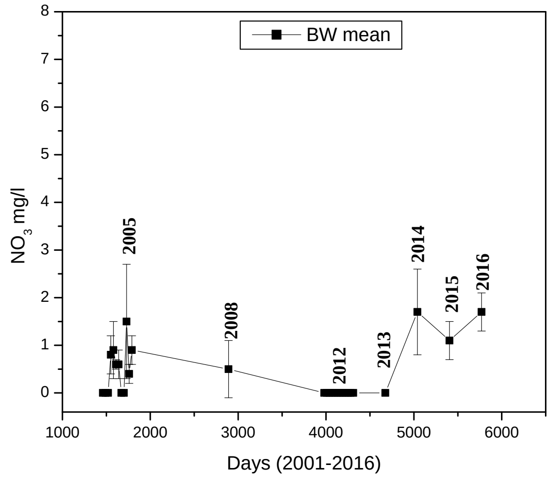


Figure 6.27: Temporal variation of NO_3^- of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016

6.2.17 Iron (Fe)

In the present study area the iron concentration of BW strata in 2005 is 0.06 ±0.08mg/l (Figure 6.28).

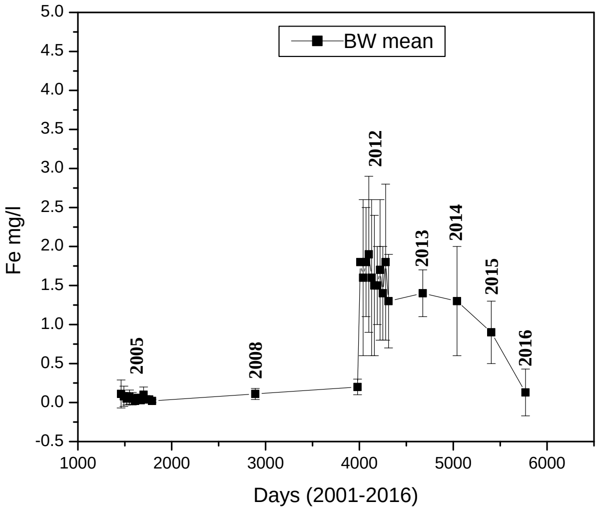


Figure 6.28: Temporal variation of Fe of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016

In 2008, the iron concentration is 0.1±0.07mg/l. The annual mean ($\bar{x} \pm \sigma$) of 2012 analysis is 1.5±0.8mg/l. The results of the subsequent years analysis reveal mean 1.4±0.3 (2013), 1.4±0.7 (2014), 509±0.4 (2015) and 0.1±0.3 (2016)mg/l. In 2012 onwards higher concentration of iron than the permissible limit of 0.3mg/l are observed in certain bore wells. The lateritic soil at depth causes the increase in the concentration of iron.

6.2.18 Total Dissolved Solids (TDS)

TDS data of the present study area shows 182mg/l in 2001 and in 2005 annual mean ($\bar{x} \pm \sigma$), TDS is 384±135mg/l. Data available from 2012 analysis give annual mean ($\bar{x} \pm \sigma$) TDS of BW strata 299±86 mg/l with a CI of 245-353 at 95% confidence level. The results of the subsequent years analysis reveal mean ($\bar{x} \pm \sigma$) TDS 96±115 (2013), 212±5.1 (2014), 149±103 (2015) and 229±64 mg/l (2016). Thus the TDS of BW strata is within the permissible limit of 500mg/l throughout the sampling period.

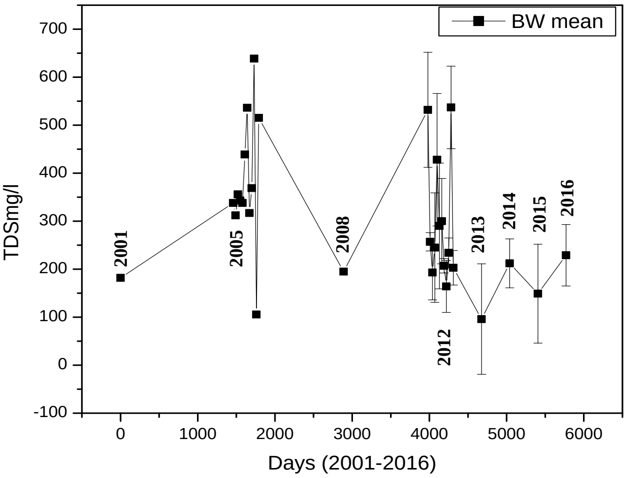
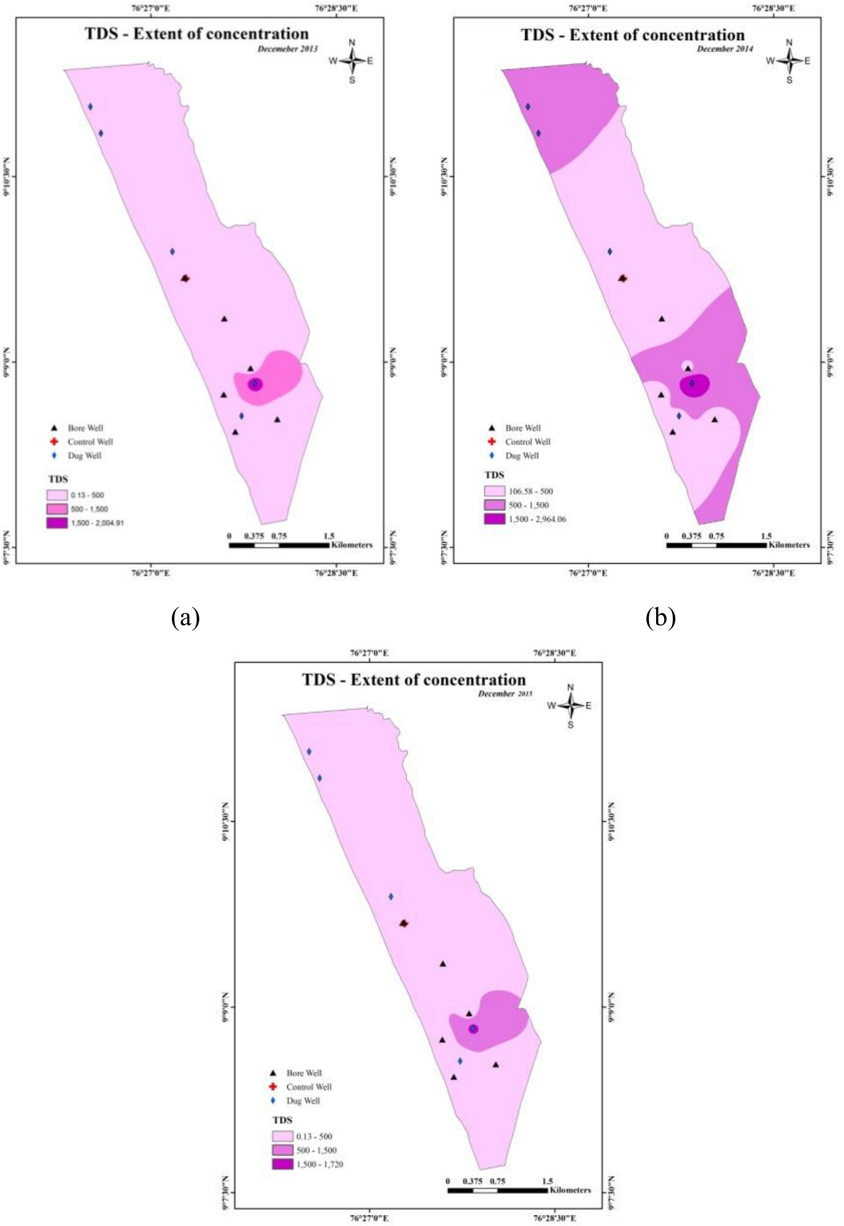


Figure 6.29: Temporal variation of TDS of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016



(a)

(b)

(c)

Figure 6.30: Spatial distribution map for TDS of the study area Arattupuzha coast, Alappuzha, Kerala, India during December a) 2013 b) 2014 and c) 2015.

The spatial variation map for TDS of the study area is presented in Figure 6.30. In 2013,except a small pocket of higher than 1500mg/l TDS, rest of the area show TDS lower than 500mg/l. Almost similar TDS distribution can be observed in the years 2014 and 2015.

6.3 Water Quality Index (WQI)

WQI calculated [13] for BW strata using the parameters pH, EC, TH, Ca, Mg, Na, K, HCO_3, Cl & SO_4 are given in Table 6.1. In 2001, the WQI of 101 suggest *very poor* quality of water (D Grade).

Table 6.1: Temporal variation of WQI, Water Quality & grade of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001-2016).

Year/Month	WQI	Water Quality	Grading
2001Apr	101	Very Poor	D
2005 Jan	59	Poor	C
2005 Feb	55	Poor	C
2005Mar	48	Good	B
2005Apr	42	Good	B
2005May	42	Good	B
2005Jun	39	Good	B
2005Jul	28	Good	B
2005Aug	16	Excellent	A
2005Sep	69	Poor	C
2005Oct	58	Poor	C
2005Nov	52	Poor	C
2005Dec	44	Good	B
2008Dec	30	Good	B
2012 Jan	32	Good	B
2012 Feb	36	Good	B
2012Mar	69	Poor	C
2012Apr	48	Good	B
2012May	42	Good	B
2012Jun	32	Good	B
2012Jul	38	Good	B
2012Aug	42	Good	B
2012Sep	36	Good	B
2012Oct	35	Good	B
2012Nov	24	Excellent	A
2012Dec	34	Good	B
2013Dec	38	Good	B
2014Dec	30	Good	B
2015Dec	30	Good	B
2016Dec	33	Good	B

Using the post tsunami data of 2005 WQI is calculated for each month. It's mean, 59 in January and 55 in February, show that the water is *poor* quality (C Grade). Thus the WQI calculation shows that, in BW strata the quality damage due to tsunami wave inundation is not as much as in DW water sources. From March 2005, onwards the quality become *good* and then to *poor* after September. In 2008, the WQI calculation using those 10 parameters give a value of 30 which suggest *good quality* water (B Grade).

In 2012, monthly variation as dicussed in Chapter 4 suggest *good water quality*. During 2013-2016 study the WQI of BW strata is near to 40 suggest *good quality*.Thus unlike DW strata, the water of BW strata maintain *good quality* over the study period.

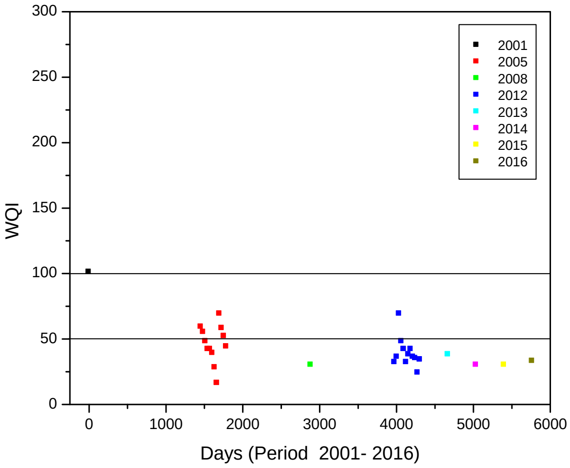


Figure 6.31: Temporal variation of Water Quality Index of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001-2016).

Figure 6.31 give the temporal variation of Water Quality Index of deep groundwater sources. Two cut off points, one at 50 below which water has *good quality* and another at 100 above which water is *unfit for human use* are shown. For BW strata all points mostly come below 75 except in 2001. WQI between 50 and 75 suggest *poor water quality but fit for human use*.

6.4 Sodium – Chloride Ratio

If the value of $Na/(Na+Cl)$ is higher than 0.5 and that of Na/Cl is higher than 1.0, it shows ion exchange (all concentrations in meq/l).

Table 6.2: Temporal variation of $\frac{Na}{Cl}$, $\frac{Na}{Na+Cl}$ & Inference of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001-2016).

Year/Month	$\frac{Na}{Cl}$	$\frac{Na}{Na+Cl}$	Inference
Apr 2001	0.5	0.4	Reverse ion exchange
Jan 2005	0.3	0.2	Reverse ion exchange
Feb 2005	0.2	0.1	Reverse ion exchange
Mar 2005	0.1	0.1	Reverse ion exchange
Apr 2005	0.1	0.1	Reverse ion exchange
May 2005	0.1	0.1	Reverse ion exchange
Jun 2005	1.1	0.5	Ion exchange
Jul 2005	1.6	0.5	Ion exchange
Aug 2005	0.8	0.4	Reverse ion exchange
Sep 2005	1.0	0.5	Ion exchange
Oct 2005	1.1	0.5	Ion exchange
Nov 2005	0.9	0.5	Reverse ion exchange
Dec 2005	1.1	0.5	Ion exchange
Dec 2008	7.1	0.9	Ion exchange
Jan 2012	2.8	0.7	Ion exchange
Feb 2012	2.3	0.7	Ion exchange
Mar 2012	2.5	0.7	Ion exchange
Apr 2012	2.4	0.6	Ion exchange
May 2012	1.1	0.5	Ion exchange
Jun 2012	3.3	0.7	Ion exchange
Jul 2012	3.2	0.7	Ion exchange
Aug 2012	2.8	0.7	Ion exchange
Sep 2012	2.8	0.7	Ion exchange
Oct 2012	3.4	0.7	Ion exchange
Nov 2012	3.2	0.7	Ion exchange
Dec 2012	3.4	0.7	Ion exchange
Dec 2013	3.1	0.7	Ion exchange
Dec 2014	2.4	0.6	Ion exchange
Dec 2015	2.1	0.7	Ion exchange
Dec 2016	2.1	0.7	Ion exchange

From Table 6.2, which shows mean of these ratios of BW strata, it is clear that in 2001 *reverse ion exchange* is occurring in deep groundwater sources of the study area. In the post tsunami year 2005, till May *reverse ion exchange* is the main process. This is due to the higher concentration of sodium in water. In June and July 2005, *ion exchange* is occurring. In August and November 2005, again *reverse ion exchange* occur. In 2008, 2012, 2013, 2014, 2015 & 2016 ion exchange is the main process occurring in BW strata.

Figure 6.32 give the temporal variation of Na/Cl ratio of bore well water sources. Except in 2001 and in the early months of 2005, the points come above 1, suggesting *ion exchange* as the main process.

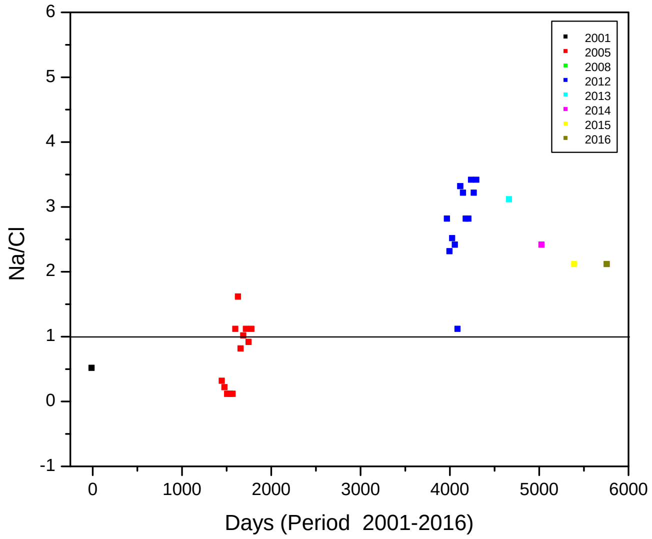


Figure 6.32: Temporal variation of Na/Cl ratio of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001-2016).

6.5 Irrigation Quality Evaluation

The chemical constituents of irrigation water can affect plant growth due to toxicity or deficiency, or indirectly by altering availability of nutrients. The suitability of the water for irrigation purposes is determined by the amount and type of dissolved ions present. The problems that result vary both in kind and degree, and are modified by soil, climate and crop, as well as by the skill and knowledge of a water user. The soil problems most commonly encountered and used as a basis to evaluate water quality are those related to salinity, water infiltration rate, toxicity and a group of other miscellaneous problems [14-20].

Salinity can have a flocculating effect on soils, causing fine particles to bind together into aggregates. Salinity of the soil solution has a positive effect on enhancing or stabilizing soil aggregation. At high levels, salinity has a negative and potentially lethal effect on plants. Sodium has the opposite effect on soils that salinity does. Soil dispersion is the primary physical process associated with high sodium concentrations. The effect of sodium-induced dispersion can have on the soil can be assigned to three main categories: reduction in infiltration, reduced hydraulic conductivity, and surface crusting. Each of these conditions makes it difficult for roots of plants to penetrate the soil, and to obtain adequate water and nutrients. Overall, these effects negatively impact plant yield and survival. Other ions such as calcium and magnesium do not have this effect.

6.5.1 Electrical Conductivity (EC) & Total Hardness (TH)

In all analysis, based on EC, the water of BW strata is either good or permissible for irrigation (Table 6.3). Considering TH as $CaCO_3$, water of

BW strata is *hard* in majority periods. Occasionally it change to *moderately hard* type. In January 2005, very hard nature is observed. Using alkalinity data, permanent hardness is determined. In 2001, *permanent hardness* is noted. In January, February and August 2005 also *permanent hardness* is prominent. After that, in 2012 October *permanent hardness* is present.

Table 6.3: Temporal variation of EC, TH, Alkalinity, Permanent hardness (PeH) and Inferences of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016

Year/Month	**ECµS/cm**	**Inference**	**TH mg/l as $CaCO_3$**	**Inference**	**Alkalinity mg/l**	**PeH**
Apr 2001	300	G	56.0	S	4.3	52
Jan 2005	520	G	318	VH	220	98
Feb 2005	480	G	277	H	239	39
Mar 2005	550	G	240	H	241	0
Apr 2005	530	G	225	H	238	**0**
May 2005	520	G	167	H	218	**0**
Jun 2005	680	G	179	H	229	**0**
Jul 2005	830	P	170	H	248	**0**
Aug 2005	490	G	137	MH	222	**0**
Sep 2005	570	G	260	H	238	22
Oct 2005	980	P	176	H	225	**0**
Nov 2005	160	E	164	H	230	**0**
Dec 2005	790	P	194	H	211	**0**
Dec 2008	300	G	107	MH	13.0	**0**
Jan 2012	250	G	165	H	255	**0**
Feb 2012	350	G	178	H	213	**0**
Mar 2012	260	G	159	H	176	**0**
Apr 2012	260	G	151	H	162	**0**
May 2012	420	G	175	H	239	**0**
Jun 2012	290	G	123	MH	186	**0**
Jul 2012	310	G	178	H	206	**0**
Aug 2012	380	G	174	H	209	**0**
Sep 2012	360	G	177	H	173	4.0
Oct 2012	400	G	182	H	146	36
Nov 2012	350	G	186	H	199	**0**
Dec 2012	360	G	164	H	206	**0**
Dec 2013	630	G	151	H	256	**0**
Dec 2014	440	G	173	H	209	**0**
Dec 2015	320	G	126	MH	150	**0**
Dec 2016	430	G	147	MH	174	**0**

6.5.2 Kelly's ratio (KR)

Kelly's ratio calculation of BW strata reveals that in all analysis, except in 2008, the KR value is less than 1.0 and so the water is *suitable* for irrigation (Table 6.4).

Figure 6.3 give the temporal variation of Kelly's ratio of bore well water sources. Except in 2008 all points come below 1.0, which suggest water is *suitable* for irrigation.

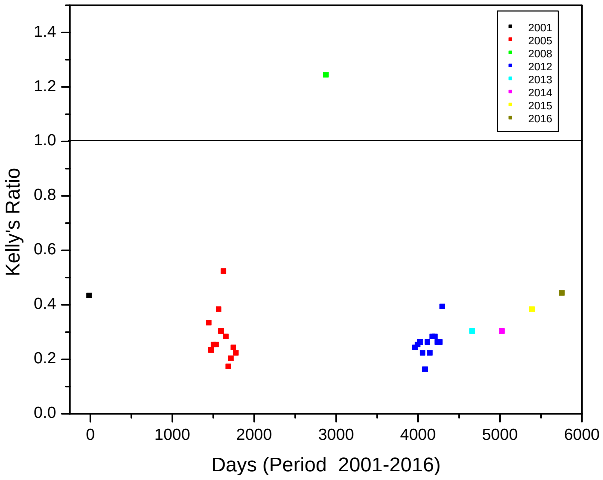


Figure 6.33: Temporal variation of Kelly's Ratio of deep groundwater Bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001-2016).

6.5.3 Magnesium adsorption ratio (MAR)

MAR higher than 50 is observed in some months of 2005, which shows the *unsuitability* of water for irrigation. In all other analysis, based on MAR the water is *suitable* for irrigation.

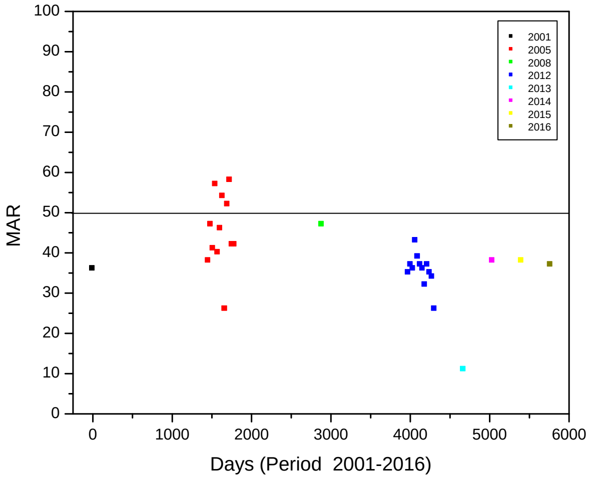


Figure 6.34: Temporal variation of magnesium adsorption ratio of Deep groundwater Bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001-2016).

6.5.4 Permeability Index (PI)

Water containing excessive amount of HCO_3^- and CO_3^{2-}, react with Ca^{2+} and Mg^{2+} in soil solution and will precipitate them as calcite and magnesite. This will increase sodium hazard and its related problems such as reducing soil permeability, soil aeration, high pH and inhibited root penetration.The effect of interactions among these parameters on water quality for irrigation purpose are evaluated by calculating RSC, PI etc. Considering PI, in 2001, the single bore well station shows 49. As it is less than 75%, water comes in class II which is *good* for irrigation. In 2005 study, PI vary from the lowest of 49 in January to the highest 94 in June. Since PI is higher than 25%, water comes in class I and class II, in both cases water is *good* for irrigation. In 2008 analysis, PI is 69 suggesting class II water which is *good* for irrigation. In 2012 study, PI of all the months suggest class I or class II water where water is *good* for irrigation. In 2013, mean PI is 82, in

2014 it is 70, in 2015 it is 97 and in 2016 it is 74. Thus in all the analysis of BW strata, the PI calculated is higher than 25% and so the water come in the class I or class II category which are *good* for irrigation.

Table 6.4: Temporal variation of Kelly's ratio (KR), magnesium adsorption ratio (MAR) & Permeability index (PI) of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016.

Year/Month	KR	Inference	MAR	Inference	PI	Inference
Apr 2001	0.43	S	36	S	49	Class II
Jan 2005	0.33	S	38	S	49	Class II
Feb 2005	0.23	S	47	S	53	Class II
Mar 2005	0.25	S	41	S	58	Class II
Apr 2005	0.25	S	57	US	60	Class II
May 2005	0.38	S	40	S	74	Class II
Jun 2005	0.30	S	46	S	94	Class I
Jul 2005	0.52	S	54	US	74	Class II
Aug 2005	0.28	S	26	S	86	Class I
Sep 2005	0.17	S	52	US	54	Class II
Oct 2005	0.20	S	58	US	67	Class II
Nov 2005	0.24	S	42	S	72	Class II
Dec 2005	0.22	S	42	S	61	Class II
Dec 2008	1.24	US	47	S	69	Class II
Jan 2012	0.24	S	35	S	76	Class I
Feb 2012	0.25	S	37	S	67	Class II
Mar 2012	0.26	S	36	S	69	Class II
Apr 2012	0.22	S	43	S	74	Class II
May 2012	0.16	S	39	S	65	Class II
Jun 2012	0.26	S	37	S	88	Class I
Jul 2012	0.22	S	36	S	63	Class II
Aug 2012	0.28	S	32	S	65	Class II
Sep 2012	0.28	S	37	S	71	Class II
Oct 2012	0.26	S	35	S	57	Class II
Nov 2012	0.26	S	34	S	63	Class II
Dec 2012	0.39	S	26	S	83	Class I
Dec 2013	0.30	S	11	S	82	Class I
Dec 2014	0.30	S	38	S	70	Class II
Dec 2015	0.38	S	38	S	97	Class I
Dec 2016	0.44	S	37	S	74	Class II

6.5.5 Sodium Adsorption Ratio (SAR)

SAR calculation is a classical method of irrigation quality evaluation. In 2001 SAR, of the bore well station is 0.64 which is very low and the water quality is *excellent*. In 2005 study the monthly variation of SAR is from 0.5-1.3, again considerably lower value suggests excellent water quality. In 2008, SAR increases to 2.5 due to the increased sodium concentration, but still water quality is *excellent*. In 2012 study, SAR varies from the lowest value of 0.43 in May to 0.87 in December, suggesting *excellent* water quality of bore well strata during 2012. In 2013, mean SAR is 0.74, in 2014 it is 0.78, in 2015 it is 0.67 and in 2016 it is 0.90, suggesting *excellent* quality in all the years. Here, in the present study, the BW stations in the study area show *excellent* quality throughout the study period since the SAR calculated is lower than 10. Compared to shallow groundwater sources SAR of bore wells indicate much lower values, mostly less than 1.

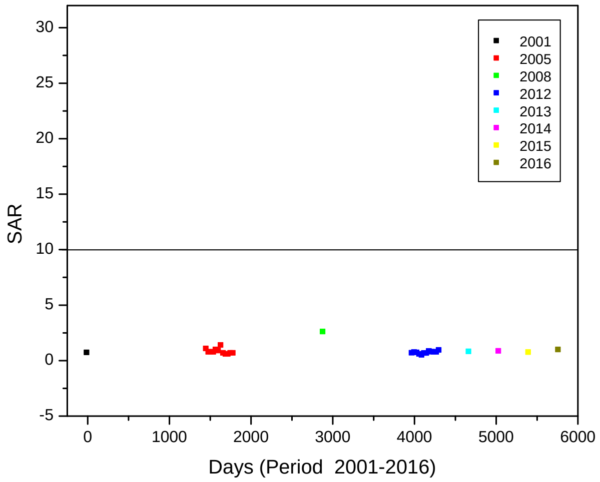


Figure 6.35: Temporal variation of sodium adsorption ratio (SAR) of deep groundwater bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001-2016).

Figure 6.35 give the temporal variation of sodium adsorption ratio (SAR) of bore well water sources, in all analysis SAR is below 10.

6.5.6 Residual sodium carbonate (RSC)

In 2001, residual sodium carbonate is -1.0 which is less than 1.25 and shows *good* water quality. In 2005, monthly study RSC increases from -1.9 in January to 1.0 in June and show *good* quality of water. RSC higher than 1.25 is observed in July (1.6), August (1.7) and November (1.3) 2005, which suggest *doubtful* water quality. The increased bicarbonate (HCO_3^-) concentration decreases the irrigational use of water. In 2008, RSC is -1.7 suggesting *good* quality. In 2012 study, from January to December RSC is less than 1.25 and deep groundwater quality is *good* in bore well stations.

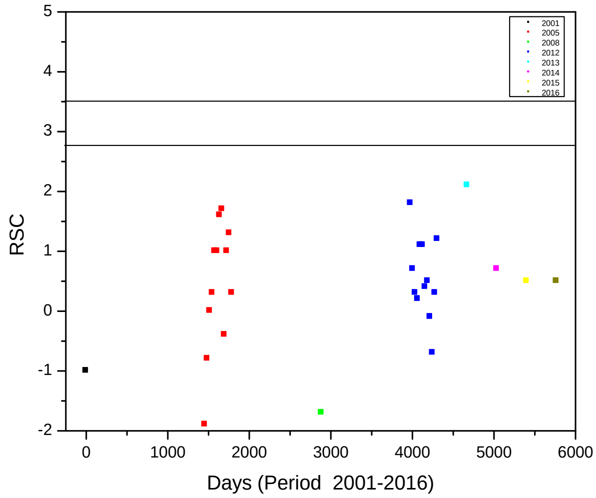


Figure 6.36: Temporal variation of residual sodium carbonate (RSC) of deep groundwater bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001-2016).

In 2013, RSC shows an increased value of 2.1 suggesting *doubtful* quality of water. This is due to the increased alkalinity which contributes higher concentration of bicarbonate. In 2014, there is a considerable decrease in RSC and it is 0.7 suggesting *good* quality. In 2015 and 2016 RSC again decreases and shows a constant value of 0.5 suggesting *good* irrigational quality based on residual sodium carbonate. Thus, over the study period RSC is less than 1.25 in majority samples suggesting *good* quality. In few occasions, it becomes higher than 1.25, which suggests *doubtful* quality, but never crosses the limit of 2.5, above which water quality become *unsuitable* for irrigation (Figure 6.36). In Thos periods, the water quality is *doubtful* for irrigation. In all other periods, water is *good* for irrigation

6.5.7 Sodium Percentage (Na%)

In 2001, the sodium percentage for the representative deep groundwater is 22 which suggest *good* water quality. In 2005, the post tsunami data of each month for bore wells shows a Na% variation from 13-26. Since, it is less than 40 water quality is *good*. Na % higher than 50 is observed in 2008, which describe the water quality as *permissible* range for irrigation. In 2012 study, sodium percentage is less than 20 in most of the months, except 22 in August, 21 in September and 26 in December 2012. Na% less than 20 suggest *excellent* water quality and up to 40 *good* water quality. In 2013, mean Na% of the different bore well stations is 22, in 2014 it is again 22, in 2015 it is 25 and in 2016 it is 28. So in the subsequent four years almost steady sodium percentage is observed. Thus based on Na% water of bore well strata shows *excellent* to *good* quality for irrigation over the study period of 16 years (Figure 6.37).

Table 6.5: Temporal variation of sodium adsorption ratio (SAR), Residual Sodium Carbonate (RSC) and Sodium Percentage (Na%) of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period 2001-2016

Year/Month	SAR	Inference	RSC	Inference	% Na	Inference
Apr 2001	0.64	E	-1.0	G	22	G
Jan 2005	1.0	E	-1.9	G	20	G
Feb 2005	0.7	E	-0.8	G	17	E
Mar 2005	0.7	E	0.0	G	18	E
Apr 2005	0.7	E	0.3	G	18	E
May 2005	0.9	E	1.0	G	25	G
Jun 2005	0.8	E	1.0	G	22	G
Jul 2005	1.3	E	1.6	D	26	G
Aug 2005	0.6	E	1.7	D	20	G
Sep 2005	0.5	E	-0.4	G	13	E
Oct 2005	0.5	E	1.0	G	16	E
Nov 2005	0.6	E	1.3	D	19	E
Dec 2005	0.6	E	0.3	G	17	E
Dec 2008	2.53	E	-1.7	G	53	P
Jan 2012	0.61	E	1.8	D	19	E
Feb 2012	0.67	E	0.7	G	19	E
Mar 2012	0.63	E	0.3	G	20	G
Apr 2012	0.51	E	0.2	G	17	E
May 2012	0.43	E	1.1	G	13	E
Jun 2012	0.58	E	1.1	G	20	G
Jul 2012	0.58	E	0.4	G	17	E
Aug 2012	0.76	E	0.5	G	22	G
Sep 2012	0.71	E	-0.1	G	21	G
Oct 2012	0.70	E	-0.7	G	20	G
Nov 2012	0.70	E	0.3	G	20	G
Dec 2012	0.87	E	1.2	G	26	G
Dec 2013	0.74	E	2.1	D	22	G
Dec 2014	0.78	E	0.7	G	22	G
Dec 2015	0.67	E	0.5	G	25	G
Dec 2016	0.90	E	0.5	G	28	G

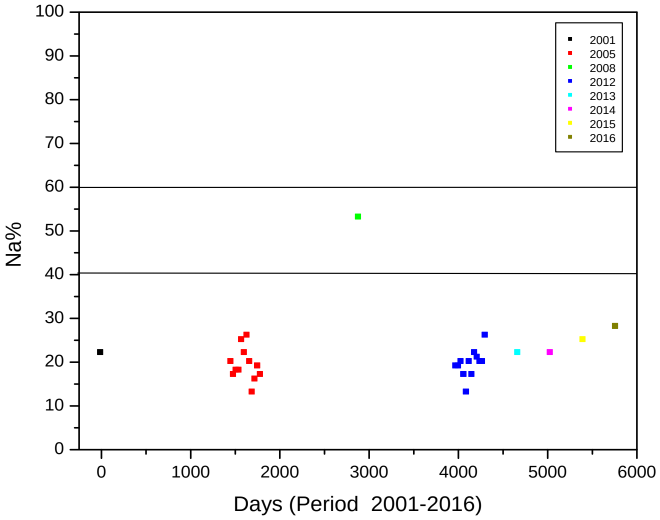


Figure 6.37: Temporal variation of sodium percentage (Na%) of deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India for the period (2001-2016).

6.6 Hill-Piper Trilinear Plot and Water Quality Evaluation

In the Piper diagram cations, expressed as percentages of total cations in milliequivalents per litre, plots as a single point on the left triangle and anions similarly expressed as percentages of total anions, appear as a single point in the right triangle. These two points are then projected into the central diamond-shaped area parallel to the upper edges of the central area. This single point is thus uniquely related to the total ionic distribution. The Piper Diagram also conveniently reveals similarities and differences among groundwater samples. Those samples with similar qualities will tend to plot together as groups.

Figure 6.38 give the Hill-Piper Trilinear diagram for the BW strata of the study area in the years 2001, 2005, 2008, 2012, 2013, 2014, 2015 & 2016.

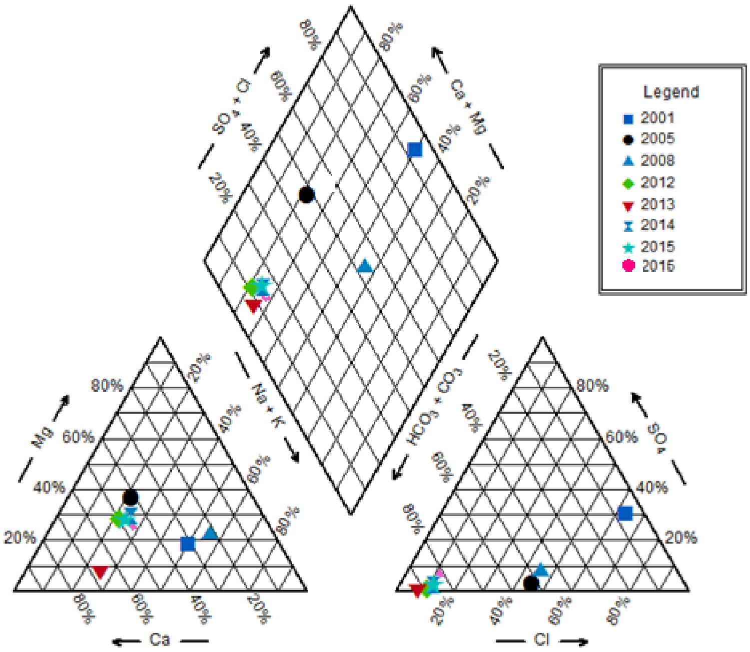


Figure 6.38: Hill-Piper Trilinear diagram for the deep groundwater bore well (BW) sources along the 26th December 2004, Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India in the years 2001, 2005, 2008, 2012, 2013, 2014, 2015 & 2016.

For BW strata, the piper plot obtained in 2001 shows the features, in the diamond area it is in the border line of saline region, in the cation triangle the point is in the border of Na+K region with 50% Na+K, 32% Ca & 18%Mg, in the anion triangle the point is clearly in the Cl region with 62% Cl, 35% SO_4^{2-} & 8% HCO_3^-. So the triangles suggest the prominence of Na+K cation and Cl^-anion and thus in the diamond area the point corresponding to 2001 show Na-K- Cl as the prominent hydrochemical facies. In 2005 the data point is shifted towards temporary hardness region. It shows the prominence of Ca+Mg cation and HCO_3^-anion. In the cation triangle the point is in no dominance area with 42% Ca, 38% Mg & 20% Na+K. In the anion triangle the point is close to HCO_3^- region with 52%

HCO_3, 45% Cl & 3% SO_4. So even if tsunami affected the coast in 2005, the prominent hydrochemical facies of bore well strata is Ca-Mg- HCO_3.In 2008 the point again move towards the saline region. In the cation triangle the point is clearly in Na+K region with 55% Na+K, 23% Ca &22% Mg. In the anion triangle the point is in no dominant area and close to zero SO_4 line with 48% HCO_3, 45% Cl & 7% SO_4. From the cation triangle it is clear that the shift is due to the prominence of Na+K cation. So in 2008 the prominent hydrochemical facies of bore well strata are Na-K- HCO_3 and Na-K-Cl. The points corresponding to the years 2012, 2013, 2014, 2015 & 2016 cluster in the temporary hardness region, suggesting the water is mainly Ca+Mg+ HCO_3^- type. In the cation triangle the point of 2013 lie differently from the rest of points which are close to the 2005 point, suggesting higher Ca concentration. Thus from cation triangle a composition of 67% Ca, 25% Na+K & 8% Mg can be inferred. In anion triangle as in the diamond area all points cluster in one point and it is almost in the HCO_3^- apex. So from the recent 5 year study Ca- HCO_3 is the prominent hydrochemical facies of bore well strata of the study area.

6.7 Overall Deep Groundwater Quality of the Region (2001-2016)

This chapter of the thesis elaborately discusses the temporal variation of groundwater quality of deep groundwater sources along the study area from year 2001 to 2016. The mean of various physico-chemical characteristics of deep groundwater sources are compared with the IS and WHO standards in Table 6.6.

Table 6.6: Physico-chemical characteristics of deep ground water sources of the study area during years 2001, 2005, 2008, 2012, 2013, 2014, 2015 & 2016

Strata	Data	pH	Eh	EC mS/cm	TH mg/l	Alkalinity mg/l	TDS mg/l	DO mg/l	BOD mg/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Fe mg/l	HCO$_3$ mg/l	Cl mg/l	SO$_4$ mg/l	PO$_4$ mg/l	NO$_3$ mg/l
BW2001	$\bar{x} \pm \sigma$	8.0	-	0.28	56		182	-	-	14	4.9	11	25	-	5.3	31	20	-	-
BW2005	$\bar{x} \pm \sigma$	7.6 ± 0.4	-25 ± 20	0.6 ± 0.2	209 ±67	230 ±30	384 ±135	4.1±2.4	9.9 ±6.5	44.7 ±18	23.6 ±12	23.5 ±16.5	6.4 ±1.5	0.06 ±0.08	280±36	162 ±146	12.5 ±10.6	0.04 ±0.07	0.6±0.4
	μ	7.6 ± 0.2	-25 ± 13	0.6 ± 0.1	209 ±42	230±19	384 ±86	4.1 ±1.6	9.9 ±4.2	44.7 ±11.5	23.6 ±7.7	23.5 ±10.5	6.4 ±0.9	0.06 ±0.05	280±23	162 ±93	12.5 ±6.8	0.04 ±0.05	0.6±0.3
	CI	7.4-7.8	38-12	0.5-0.7	167-251	211-249	298-470	2.5-4.7	5.7-14.1	33.2-56.2	15.9-31.3	13-34	5.5-7.3	0.01-0.11	257-303	69-255	5.7-19.3	0-0.09	0.3-0.9
BW2008	$\bar{x} \pm \sigma$	7.2± 0.05	-42± 10	0.3±0	107±15	23±13	195 ±0	5.7±2.9	9±5	22±3	12.5±4.2	60±7	7±0.8	0.1±0.07	27±15	14±3.5	3±1	0.08±0.09	0.4±0.6
	μ	7.2± 0.07	-42± 14	0.3±0	107±21	23±17	195 ±0	5.7± 4.0	9±7	22±4	12.5±5.8	60±10	7±1	0.1±0.09	27±21	14±5	3±1	0.08±0.1	0.4±0.8
	CI	7.13+7.27	56-28	0.3	86-128	6-50	195	1.7-9.7	2-16	18-26	6.7-18.3	50-70	6-8	0.01-0.19	6-48	9-19	2-4	0-0.18	0-1.2
BW2012	$\bar{x} \pm \sigma$	7.5± 0.24	-28± 22	0.33±0.04	168±41	198±45	299±86	4.7±1.6	3.8±1.7	43±11	16±6	19±6	6±1.4	1.5±0.8	241±58	16±13	2.5±0.5	0.1±0	-
	μ	7.5± .15	-28± 14	0.33±0.04	168±26	198±28	299±54	4.7±1	3.8±1.1	43±7	16±4	19±4	6±0.9	1.5±0.5	241±37	16±8	2.5±0.5	0.1±0	-
	CI	7.4-7.7	42-14	0.28-0.38	142-194	170-226	245-353	3.7-5.7	2.7-4.9	36-50	12-20	15-23	5.1-6.9	1.0-2.0	204-278	8-24	2.0-3.0	0.1	-
BW2013	$\bar{x} \pm \sigma$	7.5±0.2	-29± 9	0.6± 0.1	151±34	256±47	96±115	6.0±1.8	2.9±0.9	54±15	3.9±2.9	20.8±6.3	5.7±1.2	1.4±0.3	312±57	13.5±8.5	1.8±0.8	-	-
	μ	7.5± 0.1	-29±8	0.6±0.1	151±31	256±42	96±105	6.0±1.6	2.9±0.9	54±14	3.9±2.7	20.8±5.8	5.7±1.1	1.4±0.3	312±52	13.5±7.8	1.8±0.8	-	-
	CI	7.4-7.6	37-21	0.5-0.7	120-182	214-298	0-201	4.4-7.6	2.0-3.8	40-68	1.2-6.6	15.0-26.6	4.6-6.8	1.1-1.7	260-364	5.7-21.3	1.0-2.6	-	-
BW2014	$\bar{x} \pm \sigma$	7.2 ± 0. 2	-15 ±12	0.4 ±0.1	173 ±44	209 ±57	212 ±51	6.0 ±2.5	4.7 ±2.1	42 ±11	16.4 ±5.6	24 ±7.2	5.8 ±1.4	1.4 ±0.7	255 ±69	19 ±10	4.6 ±0.5	-	1.7 ±0.9
	μ	7.2 ± 0.2	-15 ±11	0.4 ±0.1	173 ±40	209 ±52	212 ±46	6.0 ±2.3	4.7 ±1.9	42 ±10	16.4 ±5.1	24 ±6.6	5.8 ±1.3	1.4 ±0.6	255 ±63	19 ±9.5	4.6 ±0.5	-	1.7 ±0.9
	CI	7.0-7.4	26-4	0.3-0.5	133-213	157-261	166-258	3.7-8.3	2.8-6.6	32-52	11.3-21.5	17.4-30.6	4.5-7.1	0.8-2.0	192-318	9.5-28.5	4.1-5.1	-	0.8-2.6
BW2015	$\bar{x} \pm \sigma$	7.4 ± 0.2	-33 ±11	0.3 ±0.2	126 ±72	150 ±75	149 ±103	5.9 ±2.0	1.6 ±1.6	32± 20	11±6.7	16.4±7.7	4.4±2.1	0.9±0.4	182±91	13.6±7.7	3.4±1.3	-	1.1±0.4
	μ	7.4 ± 0.2	-33 ±10	0.3 ±0.1	126 ±65	150 ±68	149 ±93	5.9 ±1.8	1.6 ±1.4	32±18	11±6.1	16.4±7	4.4±1.9	0.9±0.4	182±83	13.6±7.0	3.4±1.2	-	1.1±0.4
	CI	7.2-7.6	43-23	0.2-0.4	61-191	82-218	56-242	4.1-7.7	0.2-3.0	24-50	4.9-17.1	9.4-23.4	2.5-6.3	0.5-1.3	99-265	6.6-20.6	2.2-4.6	-	0.6-1.5
BW2016	$\bar{x} \pm \sigma$	7.5± 0.3	-34±15	0.4±0.2	147±60	174±83	229±64	6.7±0.5	-	38±17	13±5.2	23.7±4.5	4±2.3	0.1±0.3	213±101	20±8.2	12.6±3.8	0.05± 0.01	3.5±4.3
	μ	7.5± 0.3	-34± 16	0.4± 0.2	147±61	174±84	229±66	6.7±0.5	-	38±17	13±5.2	23.7±4.6	4±2.3	0.1±0.3	213±103	20±8.4	12.6±3.9	0.05± 0.01	3.5±4.4
	CI	7.2-7.8	50-18	0.2-0.6	86-208		163-295	6.2-7.2	-	21-55	7.8-18.2	19.1-28.3	1.7-6.3	0-0.4	110-316	11.6-28.4	8.7-16.5	0.04-0.06	0-7.9
BIS2012		6.5-8.5		-	200	200	500			75	30	-	-	0.3	-	250	200		50
WHO2011		6.5-8.5		1.5	-		500			75	50	200	12	0.3	500	250	250		50

Results of ANOVA tests conducted to check the various hypotheses, suggested in the introduction chapter, give the following results:

a) *Whether there is any significant difference in the mean values of the parameters in BW strata at different time periods (2001-2016)*

Table 6.7: ANOVA table for the comparison of mean values of the parameters in bore well (BW) strata at different time periods (2001-2016).

Source	ss	df	ms	F	p-value
Total	462785.42	79			
Years	28140.05	7	4020.0068	2.241	$p<0.05$
Parameters	321631.03	9	35736.7811	19.922	$p<0.05$
Residual	113014.34	63	1793.8785		

Inferences

1) Between years the mean value of the parameters differ significantly ($p<0.05$).The mean values of the parameters are significantly higher in 2005 followed by 2013. Significantly low mean values of the parameters are observed in 2001 ($p<0.05$).

2) Between parameters also depicted a significant difference ($p<0.001$). Significantly higher mean values are observed in HCO_3 followed by TH ($p<0.001$).

b) *Whether the water quality index for bore well strata differ significantly for the years 2013-2016*

Table 6.8: Anova table for the comparison of water quality index for bore well strata for the years 2013 to 2016.

Source	ss	df	ms	F	p-value
Total	5635.43	27			
Years	358.00	3	119.3333	0.484	$P>0.05$
Bore well	836.43	6	139.4056	0.565	$P>0.05$
Residual	4441.00	18	246.7222		

Inference

The average WQI do not differ significantly between years and between bore wells ($P>0.05$)

6.8 Conclusion

The long term variation of water quality parameters of deep groundwater sources of the study area is discussed in this chapter. Tsunami inundation of 2004 December in the coastal segment affected the quality of deep groundwater sources, to a lesser extend compared to shallow groundwater sources. For the last 5 years, a major variation in water quality is not observed for bore well (BW) strata. WQI calculation suggest good quality of BW water. Sodium-chloride ratio suggest mainly ion exchange in BW strata. Irrigational quality study based on EC suggest good quality, hardness suggest hard to *moderately* hard nature, KR, MAR, PI, SAR, RSC & %Na suggest water is mostly *suitable* for irrigation. Hill-Piper Trilinear Diagram show Na-K- Cl as the prominent hydrochemical facies in 2001, Ca-Mg-HCO_3 in 2005, Na-K- HCO_3 and Na-K-Cl in 2008 and Ca-Mg- HCO_3^- in the present study period (2012, 2013, 2014, 2015,& 2016). The study is useful for evaluating the change in deep groundwater quality and also for future reference.

Results of ANOVA test conducted to check whether there is any significant difference between mean values of the parameters in BW strata at different time periods suggest that the parameters differ significantly. The mean values of the parameters are significantly higher in 2005 followed by 2013. Significantly low mean values of the parameters are observed in 2001. The average WQI of BW strata do not differ significantly between years and between stations.

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Chapter 7

SUMMARY AND CONCLUSION

7.1 Introduction

The study presented in the precceding chapters descriptively discussed groundwater chemistry of shallow and deep groundwater sources of Arattupuzha coast, Alappuzha, Kerala, India – one of the devastated coastal areas of Kerala by the 26th December 2004 Indian Ocean Tsunami. This coastal segment is elaborately studied with respect to groundwater quality for a period 2001-2016. Accordingly pages of this bound thesis through respective sections exhaustively and critically discussed the water quality parameters and their interpretations for the three strata, control well (CW), dug well (DW) and bore well (BW) in each month of year 2012 and in the subsequent years 2013,2014,2015& 2016. Also overall water quality for a period 2001-2016.

Objectives

The main objective of groundwater monitoring study is to evaluate compositions and quality of groundwaters on a regional scale as well as create a primary data bank on different chemical constituents of ground water. The various objectives of the present study may be listed as follows;

(1) To establish the temporal groundwater quality profile of Arattupuzha coastal segment of Kerala in Alappuzha district intermittently for a period 2001-2016. (2) To study the variation of the ground water quality profile of the study area with respect to depth profile of ground water sources classified as dug wells (DW) of average depth 2m and bore wells of average depth 25-100m. (3) To study the groundwater chemistry and monthly variation of major groundwater quality parameters of shallow and deep groundwater sources of the study area during year 2012. (4) To evaluate the drinking water suitability of various sources by comparing with BIS &WHO standards and also to classify them using designated best use (DBU) suggested by central pollution control board (CPCB), Government of India. (5) To analyse the trace element content of shallow and deep groundwater sources. (6) To evaluate the statistical relationship between the water quality parameters using Pearson correlation matrix. (7) To compute the monthly water quality index of each groundwater source by giving adequate weightage to significant water quality parameters. (8) To evaluate ionic ratios (sodium-chloride) and to study the major processes occurring in the study region. (9) To plot ionic ratios in Gibb's plot to study the major processes controlling the groundwater quality of the study area. (10) To study in detail the irrigational quality of various groundwater sources by using the parameters sodium adsorption ratio (SAR), sodium percentage (Na %), magnesium adsorption ratio (MAR), residual sodium carbonate (RSC), permeability index (PI) and Kelly's ratio (KR). (11) To classify water based on irrigation suitability by using graphical plots such as USSL and WILCOX diagrams. (12) To plot Hill-Piper Trilinear diagrams to understand the hydrogeochemical facies of the study area. (13) To evaluate saturation indices for studying industrial utility of various groundwater

sources. (14) To study the groundwater quality parameters and to evaluate other interpretation parameters of the groundwater sources in the years 2013, 2014, 2015 & 2016. (15) To suggest recommendations for management of groundwater quality problems.

Hypotheses to be tested are,

(1) Whether there is any significant difference between mean values of various parameters in control well (CW) stratum at different months of 2012. (2) Whether there is any significant difference between the values of various parameters of dug well (DW) strata in April, 2012. (3) Whether there is any significant difference between the values of various parameters of dug well (DW) strata in July 2012. (4) Whether there is any significant difference between the values of various parameters of dug well (DW) strata in December 2012. (5) Whether there is any significant difference between mean values of various parameters of dug well (DW) strata in each month of year 2012. (6) Whether there is any significant difference between mean values of various parameters of dug well (DW) and control well (CW) strata in each month of year 2012. (7) Whether there is any significant difference between mean values of water quality index of dug well (DW) strata in each month of year 2012. (8) Whether there is any significant difference between water quality index of control well (CW) and dug well (DW) strata in year 2012. (9) Whether there is any significant difference between water quality parameters between control well (CW) and bore well (BW) for the months of 2012. (10) Whether there is any significant difference between water quality index for different bore well stations for the months of 2012. (11) Whether there is any significant difference in the mean values of the parameters in dug well (DW) strata at different time periods (2001-2016).

(11) Whether the water quality index for dug well (DW) strata differ significantly for the years 2013-2016. (12) Whether the water quality index for dug well (DW) strata differ significantly in the months of 2005 for 5 stations DW1, DW2, DW3, DW4, DW5. (13) Whether there is any significant difference in the mean values of the parameters in bore well (BW) strata at different time periods (2001-2016). (14) Whether the water quality index for bore well (BW) strata differ significantly for the years 2013-2016. (15) Whether there is any significant difference in the mean of the water quality parameters between dug well (DW) and bore well (BW) strata. (16) Whether mean water quality index of dug well (DW) and bore well (BW) strata differ significantly over the last 16 years.

To test the hypothesis, the collected data for the study are subjected to statistical analysis using Two-Factor and three factor ANOVA. Whereever treatment effects are found to be significant, least significant difference (LSD) at 5% level are calculated to identify the significant treatment component. The results concerning each chapter are discussed in the respective chapters.

The study focused on the groundwater chemistry of shallow and deep groundwater sources along an ecologically sensitive coastal segment, Arattupuzha village in Alappuzha district, Kerala, India. The coastal erosion in this stretch is one of the recurring natural hazards. As an area of high population density, the economically backward fishermen of the region feel a lack of availability of quality fresh water. This region is environmentally sensitive area and research studies and reports are available with respect to impact of Tsunami for the year 2005. Sampling at these stations started in January 2012 and continued in each month till December 2012. In the subsequent years, 2013, 2014, 2015 & 2016, sampling and analysis were done towards the end of the year. Post-tsunami study data of year 2005 and those available for year 2001, help in generating a database intermittently for a period 2001-2016 along the study area. The study is planned to continue for the years to come. So the present work is an evaluation of groundwater quality with respect pre and post tsunami situation.

With well planned field trips in every month of 2012 (Jan –Dec, 2012) and December of the subsequent years (2013, 2014, 2015 & 2016), selected station of the above strata singled out for the study was sampled in prominence. The locations chosen for the study, the sampling sites earmarked for each location and their respective serial numbers were well specified as a part of robust protocol followed. White plastic cans of three-liter capacity were used as sample containers. They were labeled with the name of the sampling site, the respective serial number and date. BOD bottles also subjected to the same preliminaries of sampling in line with the plastic containers. In the field diary, the day and date of sampling sites and their respective serial numbers were entered well before the sampling trip was embarked upon. At the site, the time of sampling and the temperature of the sample taken were individually recorded.

Chemical analysis of water generates the fundamental data essential for the determination of groundwater quality. Major constituents are measured in milligrams per litre and trace constituents in microgram per litre. Water quality standards for domestic, agricultural and industrial use published by various agencies are used for evaluating the water quality of the present study area. Presentation of results in graphical forms help studying temporal and spatial variation of constituents. Results of chemical analysis are statistically evaluated by correlation study which help to identify relationship among parameters. Water Quality Index (WQI) calculated using WHO standards help in easily identifying the quality of water. The ratios of sodium and chloride concentrations are particularly important because they give suggestions regarding the groundwater processes like ion exchange and reverse ion exchange. Hill-Piper Trilinear diagrams are particularly useful to infer hydrogeochemical facies. Gibb's plot is another diagrammatical method to evaluate the prominent hydrogeochemical processes occurring in the study area. Different parameters used for irrigational quality evaluation are sodium adsorption ratio (SAR), sodium percentage (Na %), magnesium adsorption ratio (MAR), residual sodium carbonate (RSC), permeability index (PI) and Kelly's ratio (KR). USSL and WILCOX diagrams are graphical plots to classify water samples based on irrigation suitability. Saturation indices calculation help in evaluating the industrial use of water.

7.2 Major Findings and Inferences

Major findings and inferences sprout out of this study are given in the respective chapters in a highly descriptive approach. The geochemistry of shallow and deep groundwater sources are discussed in separate chapters along with proper interpretations. For year 2012 of present study, monthly water quality evaluations and other interpretations are done and in the subsequent years it is done in the month of December.

7.2.1 Water quality parameters and statistical relations

Considering 2012 study, annual mean of major physico-chemical characteristics of control well (CW), dug well (DW) and bore well (BW) of the study area are given in Table 7.1. From TOC analysis, it is clear that major components present in both DW and BW strata are inorganic in nature. So present study focused on inorganic hydrogeochemistry. pH shows slight alkaline nature mostly for the sources. There is not much variation in pH and throughout the year it is within standard range of 6.5-8.5. Since pH is below 8.5, the alkalinity is mainly due to the presence of bicarbonate. Total alkalinity is mostly lower than 200mg/l in both DW and BW strata except periodically in some DW stations. EC differ significantly between DW and BW. After September 2012, there is a hike in the EC of DW strata, which is an indication of sea water intrusion in dug wells near the sea. As regards to EC, the water of those wells become unsuitable for domestic purposes because the EC exceed the standard limit of 1.5mS/cm. The degree of sea water contamination, defined by sea water- fresh water interface, depends on the height of the fresh water column over the mean sea level. So the DW stations show variation in EC over the year. But the control well and bore well keep pristine character throughout the year 2012. In all the strata redox potential is negative throughout the year which suggest reducing environment. DO is relatively low in the present study area as a result of higher BOD, which is a measure of the amount of oxygen required by aerobic bacteria and other microorganisms to stabilize decomposable organic matter.

Water is a great solvent for calcium and magnesium. So in the limestone rich present study area, water obtained from the wells are hard. Total Hardness as $CaCO_3$ of DW strata show higher values (282± 198mg/l) compared to BW (168±41mg/l), CW also show considerable hardness. An excess of total alkalinity over total hardness indicate the presence of bicarbonate of sodium. In DW stations total hardness is higher than alkalinity (equal to temporary hardness or carbonate hardness, CH), which suggest permanent hardness (non carbonate NCH) due to chlorides and sulphates of Ca and Mg. Considering *Vesilind* classification, shallow dug wells (DW) in the summer months of March and April, 2012 and in the months from September to December, 2012, show a water type *too hard for ordinary domestic use* (THODU), because the hardness is greater than 250mg/l. Compared to BW strata, DW strata show higher Ca, which occasionally exceed standard limit. Equilibria involving carbonates such as the calcite dissolution-precipitation and dissolved carbon dioxide species equilibria are the major factors limiting the solubility of calcium in most natural water. The cation-exchange behaviour of magnesium is similar to that of calcium. Both ions are strongly adsorbed by clay minerals and other surfaces having exchange sites. Mg shows much less concentration as the study area is not rich in minerals containing Mg. But sea intrusion result in high Mg in some DW stations.

Sodium is the prominent cation in DW strata whereas; calcium is prominent in BW strata. There are no important precipitation reactions for sodium and it is retained by adsorption on mineral having high cation-exchange capacities such as clays. But, the interaction between surface sites and monovalent ions is much weaker than the interactions with divalent ions. Cation exchange processes in freshwater systems tend to extract divalent ions from solution and to replace them with monovalent ions. Control well (CW) retains a steady lower sodium concentration throughout the year whereas high variation is observed in dug wells. Potassium shows much lower concentration compared to sodium and many sinks are available for potassium. Lateritic soil present in the study area at depth result in higher iron concentration in BW strata.

Table 7.1: Major physico-chemical characteristics of control well (CW), dug well (DW) and bore well (BW) of the study area, Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Sl. No	**Parameter**	**CW Mean $(\bar{x})\pm SD(\sigma)$**	**DW Mean $(\bar{x})\pm SD(\sigma)$**	**BW Mean $(\bar{x})\pm SD(\sigma)$**	**IS 10500 : 2012**	**WHO 2011**
1	Temperature °C	29.9±0.83	29.9±1.1	31.1±1.5	-	-
2	pH	7.8±0.3	7.8±0.4	7.5±0.24	6.5-8.5	6.5-8.5
3	EC (mS/cm)	0.34±0.04	1.2±1.4	0.33±0.04	-	1.5
4	Eh mV	-44±14	-50±22	$^{-}$27.95±22.2	-	-
5	DO (mg/l)	4.98± 1.15	4.83± 1.96	4.7±1.6	-	-
6	BOD (mg/l)	4.23± 1.9	5.9± 3.5	3.8±1.7	-	-
7	TA(mg/l)as$CaCO_3$	211± 27	199± 80	198±45	200	-
8	TH(mg/l)as $CaCO_3$	196± 18	282± 198	168±41	300	100
9	TDS(mg/l)	280± 125	1210± 1491	299±86	500	500
10	Ca (mg/l)	67± 12	69± 47	43±11	75	75
11	Mg (mg/l)	7± 5	28± 29	16±6	30	50
12	Na (mg/l)	14±3	107± 127	19±6	-	-
13	K (mg/l)	2.1± 2	12.9± 8.7	6±1.4	-	-
14	Fe (mg/l)	-	0.08±0.14	1.5±0.8	0.3	0.1
15	HCO_3^- (mg/l)	258± 34	242± 98	241±58	-	-
16	Cl^- (mg/l)	16± 7	311± 484	16±13	250	250
17	SO_4^{2-} (mg/l)	4.8± 2.5	27± 24	2.5±0.5	200	250
18	PO_4^{3-} (mg/l)	0.09± 0.05	0.19±0.14	0.1±0	-	-
19	NO_3^- (mg/l)	-	1.6±0.7	1.1±0.4	45	50

The higher concentration of HCO_3^- in BW water points to the dominance of mineral dissolution. In deep aquifers, rock weathering is the source of major constituents in water. Chloride concentration is very low in CW but high variation is observed in dug wells and among the stations also high variation is observed as evidenced by the high standard deviations. Other anions, such as sulphate, nitrate and phosphate are present only in very low concentrations.TDS of DW strata exceed the permissible limit due to the higher concentration of dissolved material in water. Trace element determination by ICP-MS method in the present study area reveal that the elements are not present in harmful level.

From Pearson's correlation study, in CW and DW significant correlations are observed some of them are; (1) Electrical Conductivity (EC) to TH, Ca, Na, K and Cl^-; (2) TH to Ca; (3) Na to Cl^-. In BW strata pH is directly correlated to Iron.

7.2.2 Comparison of water quality parameters between DW and BW strata

Three factor ANOVA test is conducted to check whether there is any significant difference in the mean values of the water quality parameters between DW and BW strata in different months of year 2012 (Table 7.2).

Hypothesis: Whether there is any significant difference in the mean values of the water quality parameters between DW and BW strata.

Table 7.2: ANOVA table for the comparison of water quality parameters between bore well and dug well strata for the different months of year 2012

Source	**ss**	**df**	**ms**	**F**	**p-value**
Total	22355027.46	383			
Strata	836700.73	1	836700.73	24.357	$p<0.001$
Months	219586.46	11	19962.41	0.891	$p>0.05$
Parameters	13285453.34	15	885696.89	39.348	$p<0.001$
Residual	8013286.93	356	22509.23		

Inferences are summarized in this study as (1) There is significant difference in the mean value of the parameters between strata ($p<0.001$). Strata DW registered significantly higher mean value of the parameters than BW. (2) Parameters also showed a significant difference between them ($p<0.001$).The mean values of the parameters Cl, TH, HCO_3 and TDS are significantly higher than the rest. Between Cl, TH and HCO_3 the difference is not significant ($p>0.05$). TDS is highly significant among all the parameters under study registering the highest value compared to other parameters. (3) Between months the variation is not significantly different ($p>0.05$).

7.2.3 Summary of Hydrogeochemistry studied (2001-2016)

From the intermittent study during the period 2001-2016, it is observed that for dug well strata (DW), pH is within the standard limit of 6.5-8.5 although in some months the pH is close to 8.5 (Table 7.3). EC of dug well strata exceed the standard limit in 2005 and 2013. Total Hardness (TH) of DW strata infers *soft water* only in 2001 and in all other period *hard* nature is observed. Ca of DW strata is higher than standard limit of 75mg/l in the post tsunami year, 2005 and towards the end of year 2012. Na concentration of DW strata is much higher than the standard limit of 200mg/l in the post tsunami year 2005. Last 5 years data indicates the increased sodium level in number of stations than the conditions existed in 2001. Increased bicarbonate level suggests the prominence of rock weathering in the region in the post tsunamic period. Cl^-concentration of DW strata show much higher than standard limit of 250mgl in early months of 2005. After that geologically some reduction of the Cl^- occurs, in the coastal area. SO_4^{2-} concentration of DW strata of the region is within the standard limit of 200mg/l. After 26th December 2004 Indian Ocean Tsunami, SO_4^{2-} is considerebly reduced, though the wave inundation enhanced the SO_4^{2-} of the ground water.

Table 7.3: Mean values of various parameters in dug well (DW) strata of the study area, Arattupuzha coast, Alappuzha, Kerala, India at different time periods (year 2001 to year 2016)

Year / Parameter	**2001**	**2005**	**2008**	**2012**	**2013**	**2014**	**2015**	**2016**	**IS :2012**	**WHO 2011**
pH	7.5	7.9	7.3	7.8	7.9	7.8	7.7	8.2	6.5-8.5	6.5-8.5
EC mS/cm	0.37	2.97	0.6	1.2	1.7	1.5	0.89	1.3	-	1.5
TH mg/l	71	465	120	282	252	266.7	210.7	253	300	100
Ca mg/l	20.7	95.4	25	69.4	80.2	65.9	46.7	61	75	75
Mg mg/l	4.75	55.1	14	27.7	12.5	24.8	22.9	25	30	50
Na mg/l	39	458.1	106	109	119.2	141.1	58.3	143	-	-
K mg/l	6.3	22	11	12.8	14.2	12	7.3	13	-	-
HCO_3 mg/l	42.7	318.2	31.7	242.2	411.3	283.7	226.9	269	-	-
SO_4 mg/l	20.6	63	19	24.3	13.5	28.7	12.7	21	200	250
Cl mg/l	63	1570	97	310.6	186.1	259.4	170.9	166	250	250

Results of ANOVA test conducted to check whether there is any significant difference in the mean values of the parameters in DW strata at different time periods (2001-2016) suggests that there is significant difference between years and in 2005 the mean value of the parameters are significantly higher compared to other years. The parameters also showed a significant difference.TH, HCO_3 and Cl are significantly higher than the rest.

Table 7.4: Mean values of various parameters in bore well (BW) strata of the study area, Arattupuzha coast, Alappuzha, Kerala, India at different time periods (year 2001 to year 2016)

Year/ Parameter	2001	2005	2008	2012	2013	2014	2015	2016	IS :2012	WHO 2011
pH	8.0	7.6	7.2	7.5	7.5	7.2	7.4	7.5	6.5-8.5	6.5-8.5
EC mS/cm	0.28	0.59	0.3	0.33	0.63	0.44	0.32	0.4	-	1.5
TH mg/l	56	209	107	168.7	151	173	126	147	300	100
Ca mg/l	14	44.7	22	43.15	53.9	42.1	32	38	75	75
Mg mg/l	4.9	23.6	13	14.8	3.9	16.4	11.1	13	30	50
Na mg/l	11	23.5	60	18.4	20.8	23.8	16.4	24	-	-
K mg/l	25	6.42	7	5.9	5.7	5.8	4.4	4	-	-
HCO_3 mg/l	5.3	337.3	28.0	240.2	312	255.3	182.3	213	-	-
SO_4 mg/l	20	12.5	3	0.7	1.8	4.6	3.4	13	200	250
Cl mg/l	31	162	14	15.9	13.5	18.5	13.6	20	250	250

From the intermittent study during the period 2001-2016, for bore well strata (BW), it is observed that, pH goes to slightly acidic range in certain periods and the presence of iron has an influence on pH. EC of BW strata is within the standard limit of 1.5mS/cm and it is much lower compared to DW strata. Ground water is harder than surface water since it is rich in carbonic acid and dissolved oxygen, which have a high solubilising potential towards rocks containing calcite, gypsum and dolomite. Ca of BW strata is within the standard limit of 75mg/l. Magnesium is generally found in lesser concentration in natural waters than calcium. A slight increase from

30mg/l is observed in some months of 2005. Na, K and $HCO3^-$ of BW strata are within the standard limit. Cl^- of BW strata show higher than standard limit of 250mg/l in early months of 2005. SO_4^{2-} level of BW strata is much smaller than standard limit of 200mg/l.

Results of ANOVA test conducted to check whether there is any significant difference between mean values of the parameters in BW strata at different time periods suggest that the parameters differ significantly. The mean values of the parameters are significantly higher in 2005 followed by 2013. Significantly low mean values of the parameters are observed in 2001.

7.2.4 Water quality index

Considering 2012 study, for CW strata the annual mean of WQI is 38±10 and it vary from 31 to 45 (Table 7.5). As evidenced from parameter wise discussion sections, the water of CW strata keep *good* quality throughout the year.

For DW strata, WQI shows that, in most of the months the water quality ranges from *good* (G) to *unfit for drinking purpose* (UDP) category. Results of ANOVA test suggest that mean WQI of various months of year 2012 for DW strata do not differ significantly. Among different stations WQI is significantly higher in DW2 compared to others. Comparison of water quality index for control well and dug well strata for the year 2012 suggest that the mean WQI of dug well is significantly higher than that of control well in 2012, almost double. This study confirm the pristine nature of control well compared to other shallow dug well groundwater sources.

Table 7.5: Variation of water quality index (WQI) and water quality of control well (CW), dug well (DW) and bore well (BW) of the study area, Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Year (2012)	**CW**		**DW**		**BW**	
	WQI	**Water Quality**	**WQI**	**Water Quality**	**WQI**	**Water Quality**
Jan	49	G	35-97	G-VP	24.8-36.8	G
Feb	44	G	24-128	E-UDP	29.9-41.7	G
Mar	55	P	60-138	P-UDP	61.4-77.2	P
Apr	51	G	49-119	G-UDP	28.9-65.1	G-P
May	45	G	43-93	G-VP	27.6-59.8	G-P
Jun	33	G	36-102	G-UDP	26.7-38.9	G
Jul	31	G	31-95	G-VP	31.8-41.8	G
Aug	32	G	32-106	G-UDP	36.4-46.2	G
Sep	33	G	36-112	G-UDP	32.6-41.4	G
Oct	30	G	41-139	G-UDP	30.4-40.2	G
Nov	21	E	31-127	G-UDP	16.7-29.3	E-G
Dec	35	G	36-126	G-UDP	27.2-43.4	G
$\bar{x} \pm \sigma$	38±10		77±39		39 ±8.9	
μ	38±7		77±25		39 ±5.7	
CI	31-45	G	52-102	P- UDP	33.3-44.7	G

In BW strata, except in the summer months WQI suggest *good* quality water. Results of ANOVA test suggest that there is significant difference between bore wells with respect to WQI and it differ significantly between months with significantly higher in March 2012.

Considering the WQI variation over year, comparison of Water quality index (WQI) of DW strata of years 2013-2016 using ANOVA test showed significant difference. WQI in 2013, 2014 and 2016 are significantly higher than that of 2015. WQI also differ significantly between dug wells. Dug wells DW1, DW3, DW4, DW5 and DW6 registered significantly lower WQI compared to DW2. Comparing WQI in different months of post tsunami year and between stations suggest high significant difference. January and February experienced significantly higher WQI, the highest in the month of January. Between Dug wells also there is highly significant difference with respect to WQI. The average WQI of BW strata do not differ significantly between years and between stations.

7.2.5 Comparison of water quality index of DW and BW strata over the last 16 years

Hypothesis: Whether mean water quality index of DW and BW strata differ significantly over the last 16 years

Table 7.6: ANOVA table for the comparison of mean water quality index of bore well and dug well strata for the last 16 years

Source	**ss**	**df**	**ms**	**F**	**p-value**
Total	14259.94	15			
Years	3756.44	7	536.6339	0.551	p>0.05
DW& BW	3690.56	1	3690.5625	3.792	p>0.05
Residual	6812.94	7	973.2768		

Inferences are summarized in this study as there is no significant difference in water quality index between years and between strata ($p>0.05$).

7.2.6 Hydrogeochemical Processes: Ionic ratio, Gibbs plot, Piper Diagrams

From the study of year 2012, ionic ratios $Na/Na+Cl$ and Na/Cl calculated for CW suggests that *ion exchange* is the major process occurring. In *ion exchange* process Ca & Mg in water replaces Na in clays. Since Ca & Mg are removed from water, this process is also called *natural softening*. In *reverse ion exchange*, the opposite changes occur and it is observed when highly saline waters come in contact with calcium rich clays. Ion exchange is observed if $Na/Na+Cl > 0.5$ and if $Na/Cl > 1.0$.

In DW strata during the months March, April and May 2012 *reverse ion exchange* is observed. The annual mean of *Na/(Na+Cl)* is 0.5±0.2 and that of Na/Cl is 1.2±0.7. In BW strata *ion exchange* is occurring in all months of year 2012. That is *Na/Na+Cl* is higher than 0.5 and that of *Na/Cl* is higher than 1.0 in all months.

From sodium-chloride ratio, it is confirmed that *ion exchange* is prominent in the groundwater studied under DW strata. But salinity leads to *reverse ion exchange* occasionally. It is seen that in groundwater studied under BW strata *ion exchange* is the major process.

From Gibb's plots for anion ratio and cation ratio of shallow groundwater sources, the major processes occurring in these stations are rock weathering and evaporation. Rock weathering is the major process controlling deep groundwater composition.

Hill Piper Trilinear plot prepared with the hydrochemical results of groundwater collected from CW during each month of year 2012 clearly illustrates that the water is Ca–Mg–HCO_3 type. All the points cluster in the region of Temporary Hardness. That is the water rich in cations Ca^{2+} and Mg^{2+} and anion HCO_3^-. The rock type of the area is mainly calcite type. For DW strata during each month of year 2012 a mixed nature of different hydrochemical facies mainly (i) Ca–Mg–HCO_3 (Temporay Hardness), (ii) Ca-Mg-Cl-SO_4 (Permanent Hardness) and (iii) Na– K–Cl (Saline) is observed. Piper plot for BW strata in each month of year 2012 cluster in the area of Temporary Hardness. The water is Ca–Mg–HCO_3 type. The prominent cation is calcium and prominent anion is bicarbonate.

Over the years study of DW strata suggest Na-Cl facies in the years 2001, 2005 & 2008. In the present study period (2012, 2013, 2014, 2015 & 2016), points come in no dominant area between temporary hardness and saline regions. For BW strata, Hill-Piper Trilinear Diagram show Na-K- Cl as the prominent hydrochemical facies in 2001, Ca-Mg- HCO_3 in 2005, Na-K- HCO_3 and Na-K-Cl in 2008 and Ca-Mg- HCO_3^- in the month of December of years 2012, 2013, 2014, 2015,& 2016.

7.2.7 Irrigation Quality Study

The electrical conductivity (EC), total hardness (TH) and total dissolved solids (TDS) are three important parameters which determine irrigation quality. Control well keeps almost steady EC throughout the year 2012. In all the months the EC is below 750 µS/cm and water is *good* for irrigation. TH of CW water is in the range 150-300mg/l, which shows that the water is *hard*. TDS are much lower than 1000mg/l. So no salinity is observed in CW or throughout the year CW water is in the *fresh* category. Based on Kelly’s Ratio, Magnesium Adsorption Ratio (MAR), Permeability Index (PI) and Sodium Adsorption Ratio (SAR) control well water is *good* for irrigation. Residual Sodium Carbonate (RSC) for CW strata shows the *good* quality in all months except January 2012. The Na% for CW strata is less than 20 in all months which shows the *excellent* quality of CW water for irrigation throughout the year.

In the case of DW strata Kelly’s ratio calculated is less than 1.0 till July 2012, which shows that the water of shallow ground water sources are *suitable* for irrigation till July 2012. From August to December 2012, the upper limit of KR is higher than 1.0. In September and October 2012 , the upper limit is 2.4, which shows the *unsuitability* of water for irrigation in some of the stations. The annual mean KR is 0.8±0.6. The ratio is less than 1.0 for BW strata throughout the year which suggest that the water is suitable for irrigation throughout the year (Table 7.7).

Considering MAR, for DW strata only in January water of all stations are *suitable* for irrigation. From February to December the range of MAR crosses the suitability limit 50 and hence all well waters are *not suitable* for irrigation. Excess Mg present due to salt water intrusion damages the quality. The MAR calculated for BW strata is less than 50% in all months except April 2012. This suggest the *suitability* of BW water for irrigation in majority period based on MAR.

PI calculated for DW strata show value greater than 25% in all months and hence water is good for irrigation based on PI value throughout the year. In the case of BW strata of the study area the annual mean of PI is 70.2±16.7 and the water is *good* for irrigation throughout the year 2012.

In the case of DW & BW strata the SAR value is less than 10 throughout the year. So based on SAR the water of both strata maintain *excellent* quality in the whole year 2012.

If RSC is higher than 2.5 the water is considered *unsuitable* for irrigation. In the case of DW strata in all the months except September and December 2012, the upper limit in the range of RSC is higher than 1.25 but lower than 2.5 indicating that the water quality ranges from *good* to *doubtful* category. In the case of BW, in the months May, June and December 2012 the water quality vary from *good* to *doubtful* range. In all other months the water shows *good* quality. The annual mean of RSC is (DW) -0.75±4 and (BW) 0.57±0.62.

Table 7.7: Irrigation quality parameters of control well (CW), dug well (DW) and bore well (BW) of the study area, Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Parameter	**CW mean (2012 annual)**	**Water Quality**	**DW mean (2012 annual)**	**Water Quality**	**BW mean (2012 annual)**	**Water Quality**
KR $KR = Na^+ / \left(Ca^{2+} + Mg^{2+}\right)$	0.16±0.03 (0.13-0.19)	S	0.8±0.6 (0.2-1.4)	S-US	0.26±0.08 (0.18-0.34)	S
MAR $MAR = Mg^{2+} \text{ x } 100 / \left(Ca^{2+} + Mg^{2+}\right)$	15±10 (5-25)	S	35±19.6 (15.4-54.6)	S-US	35.4±12.1 (23.3-47.5)	S
PI $PI = [Na^+ + \left(HCO_3\right)^{1/2}] \text{ x } 100 / [\ Ca^{2+} + Mg^{2+} + Na^+]$	59±5 (54-64)	G	73±13 (60-83)	G	70.2±16.7 (53.5-86.9)	G
SAR $SAR = Na^+ / [(Ca^{2+} + Mg^{2+}) / 2]^{1/2}$	0.44±0.08 (0.36-0.52)	E	2.5±2.2 (0.3-4.7)	E	0.65 ±0.18 (0.47-0.83)	E
RSC $RSC = (CO_3^{2-} + HCO_3^-) - \left(Ca^{2+} + Mg^{2+}\right)$	0.27±0.6 (-0.33-0.87)	G	-0.75±4 (-4.75-3.25)	G-US	0.57±0.62 (-0.05-1.19)	G
Na% $Na\% = Na^+ \text{ x } 100 / \left(Ca^{2+} + Mg^{2+} + Na^+ + K^+\right)$	14.4±2.6 (11.8-17.0)	E	40±17 (23-57)	G-P	22.9±4.76 (18.1-27.7)	E-G

E-Excellent G-good D-Doubtful S-Suitable US- Unsuitable

In the case of DW strata Na% comes in the *good* to *permissible* category from January to July 2012 and after that *good* to *doubtful* category. For BW water Sodium Percentage calculation reveals *excellent* to *good* quality. The Na % is lower than 40 in all months and its mean is (DW) 40±17 and (BW) 22.9±4.76.

USSL diagram show the *moderate* water quality of DW and Wilcox diagram also suggest mainly *good* to *permissible* category for DW strata. For BW strata from USSL diagram in all months water comes in C1S1and C2S1 regions showing *low to medium* salinity hazard and *low sodium* or alkali hazard and water is *good* for irrigation. From Wilcox Diagram BWwater belongs to *excellent* to *good* category in all months.

7.2.8 Saturation indices

As regards to corrosive nature of water, aggressive and scale formation evaluation based on saturation indices is one of the key factors for groundwater quality. The results of the year 2012 study for different strata based on Aggressiveness Index (AI), Langlier Saturation Index (LSI) & Ryznar Stability Index (RSI) are summarized in Table 7.8.

Aggressiveness index (AI) higher than 12 for control well (CW) suggests that the water is *non-aggressive* in all months except in February 2012. In February 2012 AI is 11.8, which is less than 12 and so the water shows *moderately aggressive* nature. From the LSI water character vary from *slightly scale forming and corrosive* (SSFC) to *scale forming but non corrosive* (SFNC). In February 2012 the value is little lower than 0 ($^{-}0.04$) which shows that water is in the category *slightly corrosive but non scale forming*. From RSI study, CW strata in most of the months come between 6 and 7 which indicate the water has *little scale or corrosion* (LSC) nature. In the months February, April and July 2012 the RSI is in the range 7.0-7.5 which shows *corrosion significant* (CS) nature of water. Thus slight corrosive and scale forming tendencies of control well are observed, throughout the year of study.

AI calculated for DW strata suggests that the quality of water ranges from Moderately aggressive (MA) to Non-aggressive (NA) in all months and BW strata suggest that, the water is Moderately Aggressive. However, in the months March, April, August and December 2012 the tendency of water ranges from Moderately Aggressive (MA) to Non Aggressive (NA). The annual mean of AI for DW is 12.2±0.4 and for BW is 11.8±0.4.

The mean value of LSI for DW is 0.4±0.4 which suggest the variation in quality from *slightly scale forming and corrosive* (SSFC) to *scale forming* *but non corrosive* (SFNC). For BW strata LSI calculation show the tendency of water is mainly in the range slightly corrosive but non scale forming (SCNSF) to *slightly scale forming and corrosive* (SSFC). The annual mean of LSI is $^{-}$0.04±0.4.

The annual mean of RSI is 7.1±0.7 for DW which suggest the variation in tendency from *little scale or corrosion* (LSC) to *corrosion significant* (CS). The annual mean of RSI for BW is 7.6±0.6 which suggest that the tendency of water vary from *corrosion significant* (CS) to *heavy corrosion* (HC). Thus, as regards to saturation indices of the region's water, shallow well water is slightly scale forming and deep well water is slightly corrosive.

Thermodynamic corrosion of iron and copper pipes cannot be eliminated. Corrosion control is accomplished by chemical treatment of the water or electrochemical treatment of pipes. Chemical controls include adjustment of water pH, removal of dissolved oxygen, adjustment of calcium content etc.

Table 7.8 Corrosion indices, Aggressiveness index(AI), Langelier Saturation Index (LSI), Ryznar Stability index (RSI)of control well (CW), dug well (DW) and bore well (BW) of the study area, Arattupuzha coast, Alappuzha, Kerala, India during year 2012.

Parameter	**CW mean (2012 annual)**	**Water Tendency**	**DW mean (2012 annual)**	**Water Tendency**	**BW mean (2012 annual)**	**Water Tendency**
AI AI = pH + log (AH)	12.3±0.3 (12-12.6)	NA	12.2±0.4 (11.8-12.6)	MA-NA	11.8±0.4 (11.4-12.2)	MA-NA
LSI LSI = pH - pHs	0.48±0.3 (0.18-0.78)	SSFC - SFNC	0.4±0.4 (0-0.8)	SSFC-SFNC	$^{-}$0.04±0.4 ($^{-}$0.04-0.44)	SCNSF-SSFC
RSI RSI = 2pHs – pH	6.8±0.4 (6.4-7.2)	LSC-CS	7.1±0.7 (6.4-7.8)	LSC- CS	7.6±0.6 (7-8.2)	CS-HC

MA-moderately aggressive NA-nonaggressive SCNSF- slightly corrosive but non scale forming SSFC- slightly scale forming and corrosive SC- serious corrosion SFNC -Scale forming but non corrosive CS-corrosion significant HC- heavy corrosion LSC- little scale or corrosion

7.3 Water quality problems and remedial measures suggested

Parameters observed in higher than permissible levels in the study area, their effects and remedial measures are suggested in this section.

pH higher than standard limit of 8.5 are observed in some stations which can be treated by alum coagulation followed by flocculation, sedimentation and filtration.

High hardness is observed in the dug well and bore well water sources. Its natural source is limestone present in the area, which are dissolved by percolating rainwater (made acidic by dissolved carbon dioxide). Hardness has no known adverse effects on health. However, some evidence has been given to indicate its role in heart disease. It is undesirable due to the formation of scales in boilers and other heat exchange equipment. Hard water is also unsuitable for domestic use in washing, cleaning and laundering and it clog the skin pores due to deposition and hence result in scaling of skin and hair loss. Excess chloride level is observed in some stations. As a coastal area, it can be attributed to saline water mixing which is confirmed by the high sodium level and high electrical conductivity in those stations. High chloride content has deleterious effects on metallic pipes and structures as well as on agricultural crops. It can also corrode concrete by extracting calcium in the form of calcite. The problem of high TH, EC & Cl can be overcome by lime soda process or Ion exchange (Zeolite) process or demineralization. The remedial measures for problems of high salinity are desalination, eletrodialysis, or reverse osmosis.

As the lithology of the area contain laterite, higher iron content is observed in deep groundwaters. Iron may also occur in water as a result of corrosion of pipes, pumps, etc. The harmful effects are discoloration of water, bitter, metallic, astringent taste, brown colour deposition on utensils and clothes during washing or cooking. A dose of 1500 mg/L has a poisoning effect on a child, it can damage the blood tissues. Iron causes digestive disorders, skin diseases and dental problems. High iron content can be treated by aeration or chemical oxidation followed by filtration or zeolite ion exchange.

Irrigation quality damage is observed in DW strata. In monsoon season rainfall periodically leaches out salts accumulated in the root zone during the previous season. Accumulation of sodium on soil can be reduced by applying appropriate quantities of gypsum. The adverse effects of the high salinity of irrigation water on the crops can be minimized by irrigating them frequently. More frequent irrigations maintain higher soil water contents in the upper parts of the root zone while reducing the concentration of soluble salts. Proper choice of crops can result in good returns even when using high salinity water.

This study focused on the hydrogeochemistry of shallow and deep groundwater sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Arattupuzha, Alappuzha, Kerala, India. Present study of last 5 years (2012-2016), added to the previous years data (2001, 2005, 2008) help in studying a long term variation of groundwater quality based on different criteria. Thus this study is useful for evaluating the change and also for future references. Systematic assessments of groundwater quality along the coastal area provide useful data for the formulation of viable policy for the management of groundwater sources of the coastal zone.

7.4 Future scope of the study

The study of the Arattupuzha coastal area, Kerala, India is planned to continue for the years to come with respect to total environmental quality of air, soil and water. Biodiversity of the study area is yet to be investigated. Being it is one of the most significant regions of the country due to vast beach sand deposits, saline intrusion, sensitive to coastal hazards, densely populated, prone to severe coastal erosion, temporal and spatial evaluation is most vital for environmental research. Study of hydrogeochemistry of prominent rare earths in the groundwater is one of the thrust area yet to be explored form the future scope of this research study.

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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), (in press)

[2] George, R. T., Achari, V. S, Geochemistry of Ground Water along a Tsunami Affected Coastal Area: Arattupuzha Coast, Kerala, Proceedings of the International Conference, MATCON, Department of Applied Chemistry, CUSAT January 14-16, (2016) 370-373

[3] Achari, V. S., George, R. T., Deepa, P., Ambili, M. S., Study of Temporal and Spatial variation of Groundwater quality along a Coastal stretch of Alappuzha district, Kerala, India: Post Tsunami study, Academy of Chemistry Teachers (JACT, ISSN No.2395-6801), Thiruvananthapuram, Kerala, Reg No:774/91 (2017) (in press)

[4] Achari, V. S., George, R. T., A comparative study of ground water quality of Arattupuzha Coast, Alappuzha during the years 2005-2012. Abstract in the International conference on water: From pollution to purification (ICW 2015) January 23-26, (2015), Kottayam, India. pp 50.

[5] Achari, V. S., George, R. T., Tsunami Impact on Groundwater Quality: A Case Study from Kerala, India Article, Proceedings of the 24th Swadeshi Science Congress - A National Seminar [Volume 1; Chief Editor – Dr. R. Jayaprakash] organized by Swadeshi Science Movement – Kerala and Thunchath Ezhuthachan Malayalam University, Thirur, Malappuram District, Kerala on 6-8 November 2014, ISBN 978-81-928129-2-2, pp 334- 339.

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Hydrogeochemistry of groundwater along a tsunami devastated coastal segment of Kerala: Arattupuzha Village, Alappuzha, India

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Water quality parameters exceed the permissible standard limit set by IS 2012, WHO 2011 and USEPA 2014 in many instances of sources studied. GIS study shows the spatial variation of parameters. Pearson's Correlation matrix study suggest that electrical conductivity of water is correlated with TH, Ca, Na, K and Cl. There are noticeable decline in quality with regards to WQI. Sodium – Chloride ratio shows that reverse ion exchange occur in the region. Hill-Piper Trilinear plots reveal mixed nature of different hydrochemical facies, mainly (i) Ca–Mg–HCO_3 (Temporary Hardness), (ii) Ca-Mg-Cl-SO_4 (Permanent Hardness) and (iii) Na– K–Cl (Saline) in shallow dug wells. Deep bore wells, the water is Ca–Mg–HCO_3 type. Some of the sources are having saline water, corrosive and scale forming.

[**Keywords:** Tsunami, Groundwater Quality, Pearson Correlation, Water Quality Index(WQI), Sodium-Chloride ratio, Saturation Indices, Hydrogeochemical facies]

Introduction

Study of ground water rest on an understanding of the subsurface water chemistry and fresh water availability in a region is important as a post disaster impact study[1]. In India groundwater is an important water resource for domestic and agriculture uses in both rural and urban areas[2, 3]. The need to assess the ground water quality is becoming increasingly important in a local perspective[4]. Primary standards and treatment techniques protect public health by limiting the levels of contaminants in drinking water and is possible through unfailing research initiatives region wise. Several publications are available reporting the ground water quality in India[5-10] and water conservation initiatives are planned based on the data available. India has about 7517km long coastline and a complete groundwater quality profile of these regions comprising physico-chemical and biological parameters over a period of 12 months is rare. Present study is focused on a coastal segment of Kerala-Arattupuzha in Alappuzha district[11]. This district has a flat unbroken coastline of 82km length which constitutes 13.9 percent of the total coast of the State of Kerala. Water level data determined by ground water department for the period since 1987 shows declining trend[12]. This indicates that extensive groundwater extraction is taking place over the years and the recharge during monsoon season is not enough to compensate. Coastal erosion is one of the grave natural hazards affecting the Alappuzha district and extensive coastal erosion is taking place in the present study area. This area is devastated by 26th December 2004 Indian Ocean Tsunami[13,14] and has many significant features resulted by rich mineral sand deposits.

Materials and Methods

Study Area

The present study area (coastal region of Arattupuzha village, Alappuzha, Kerala, India) lies between 9°7'41" & 9°11'26"N latitudes and 76°26'25" & 76°28'23"E longitudes. This region has been severely affected by 26th December 2004 Indian Ocean Tsunami. Evaluation of groundwater quality with respect to pre and post tsunami situation is elaborately done in this study (Figure 1).

The sand and silt is the lithological feature of the study area. A major part of the district forms part of the coastal plains. General elevation of the area is less than 6 m above mean sea level. Soils have low content of organic matter and of low fertility level. Geomorphology of the area includes beach, mudflat, coastal plains and water body (Figure 2a). Beach ridges are suggestive of marine regression. Beach is very narrow and straight. Absence of extensive tidal plain and the intensive coastal erosion may be indicative of neo-tectonic activity. Land use of the area includes agricultural field, mixed vegetation, built up and water body (Figure 2b).

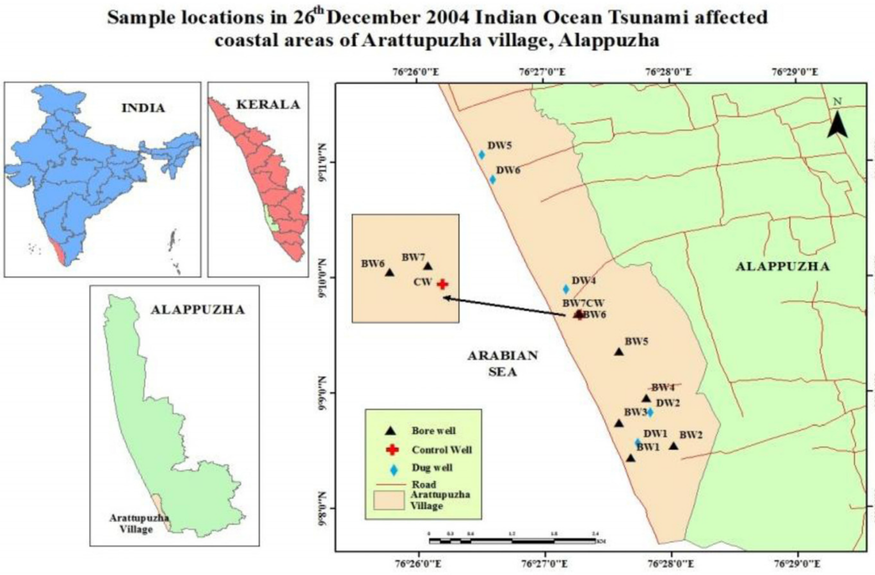
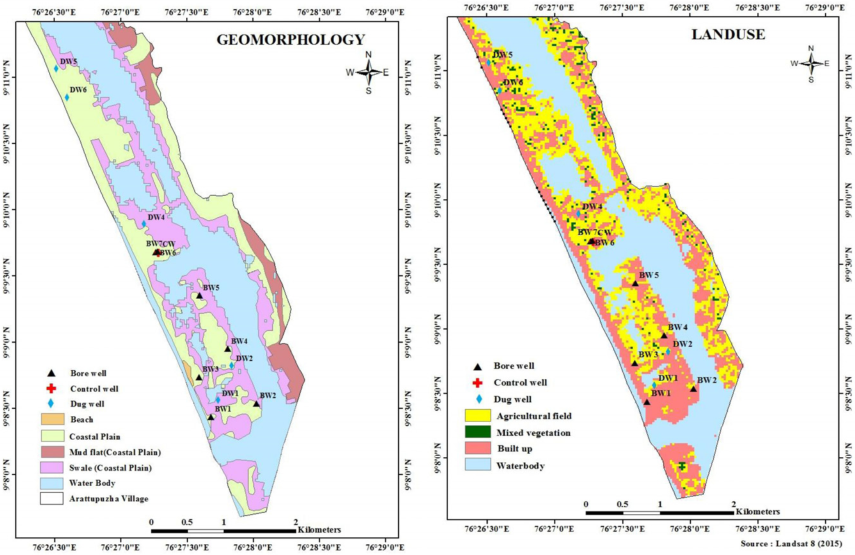


Fig. 1 - Location map of the study area, Arattupuzha coast, Alappuzha, Kerala, India



(a) (a)

Fig. 2 - a) Geomorphology and b) Land use pattern of the study area, Arattupuzha coast, Alappuzha, Kerala, India.

Groundwater samples are collected every month from 6 shallow open dug wells and 7 deep bore wells from January 2012 to December 2012 (Figure 1). During sample collection (handling and preservation) and analysis standard procedures recommended by the American Public Health Association (APHA)[15] are followed. The suitability of groundwater for domestic purposes are evaluated by comparing the water quality parameters with those of the Indian standards IS 2012, World Health Organisation (WHO 2011)[16] and US Environmental Protection Agency (USEPA 2014) guideline values for drinking water. Spatial analysis of various physico-chemical parameters was carried out using the ArcGIS 10 software. In order to interpolate the data spatially and to estimate values between measurements, an inverse distance weighed (IDW) algorithm was used. Pearson Correlation[17-19] study is done to understand the relationship between different parameters. Water Quality Index (WQI)[20-22] of the different water sources were evaluated by weighted arithmetic index method using the parameters pH, EC, Total Dissolved Solids (TDS), Total Hardness (TH), Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-,Cl^- & SO_4^{2-}. To study the possibility of major processes such as ion exchange or reverse ion exchange ratios *Na/(Na+Cl)* and *Na/Cl* are determined . *If Na/Na+Cl* > 0.5 and if *Na/Cl* > 1.0, ion exchange is observed. To assess the irrigation quality[23-25] of the water samples collected 6 parameters are calculated using the concentrations of various ions obtained from chemical analysis after converting to milliequivalents per litre (meq/L). They are Sodium Adsorption Ratio (SAR), Sodium Percentage (Na%), Magnesium Adsorption Ratio (MAR), Residual Sodium Carbonate (RSC), Permeability Index (PI) and Kelly's ratio (KR). USSL and WILCOX diagrams are graphical plots to classify water samples based on irrigation suitability. Analytical values obtained for the groundwater samples are plotted on Hill-Piper Trilinear diagram to understand the hydrochemical regime of the study area. These diagrams clearly explain the variations of cation and anion concentration in the study area. The diamond-shaped field of piper diagram is divided into four classes. The study presented in this paper comprises hydrogeochemistry of the region based on groundwater quality of 6 dugwells and 7 bore wells sampled and analysed from January to December 2012.

Results and Discussion

Analytical results for the general parameters such as Temperature, pH, Electrical Conductivity (EC), Redox Potential (E^h), Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), Total Alkalinity (TA), Total Hardness (TH), Total Dissolved Solids (TDS); cations such as Calcium (Ca), Magnesium (Mg), Sodium (Na^+), Potassium (K^+), Iron (Fe) and anions such as Bicarbonate (HCO_3^-), Chloride (Cl^-), Sulphate (SO_4^{2-}), Phosphate (PO_4^{3-}), Nitrate (NO_3^-) for shallow Dug Wells (DW) and deep Bore Wells (BW) are compared with the standards (WHO 2011& USEPA 2014) in Table:1. In the case of shallow dug wells mean of 6 stations and in the case of bore wells mean of 7 stations in each month of year 2012 are averaged to determine the annual mean and standard deviation. From the analysis of Total Carbon (TC), Total Inorganic Carbon (TIC) and Total Organic Carbon (TOC), it is clear that major components present in both DW and BW strata are inorganic.

pH shows slight alkaline in nature mostly for the sources. The 2012 annual mean pH of DW strata in the study area is 7.8±0.4 and that of BW strata is 7.5±0.24. There is not much variation in pH and throughout the year it is within standard range of 6.5-8.5. Since pH is below 8.5, the alkalinity is mainly due to the presence of bicarbonate. EC of groundwater with respect to DW strata during year 2012 is 1.2±1.4 mS/cm with confidence interval (CI) of 0.3-2.1 mS/cm at 95% significant level. After September 2012 there is a hike in the EC, which is an indication of sea water intrusion in dug wells near to the sea. As regards to EC determined, the water of those wells become unsuitable for domestic uses because the EC exceed the standard limit of 1.5 mS/cm. The degree of sea water contamination, defined by sea water- fresh water interface, depends on the height of the fresh water column over the mean sea level. So the DW stations show variation in EC over the year. Annual mean of EC of BW strata during year 2012 is 0.33±0.04mS/cm. From the spatial distribution map of EC for the month of December 2012 (Figure: 3a), very high profile for DW strata can be clearly seen.

The redox potential (Eh) is a numerical index of the intensity of oxidizing or reducing conditions within a system[26]. In the present study, redox potential is negative throughout the year this indicates reducing environment. Oxygen is supplied to ground water through recharge and by movement of air through unsaturated material above the water table. This oxygen reacts with oxidizable material encountered along the flow path of the water. Photosynthesizing biota enhances the DO, whereas organic matter decomposition depletes. DO is relatively low in most of the groundwater sources represented the study area, which may be due to the presence of high BOD of water. BOD is not a measure of some specific pollutant, but rather a measure of the amount of oxygen required by aerobic bacteria and other microorganisms to stabilize decomposable organic matter. BOD is very high; means there exists instances of organic pollution.

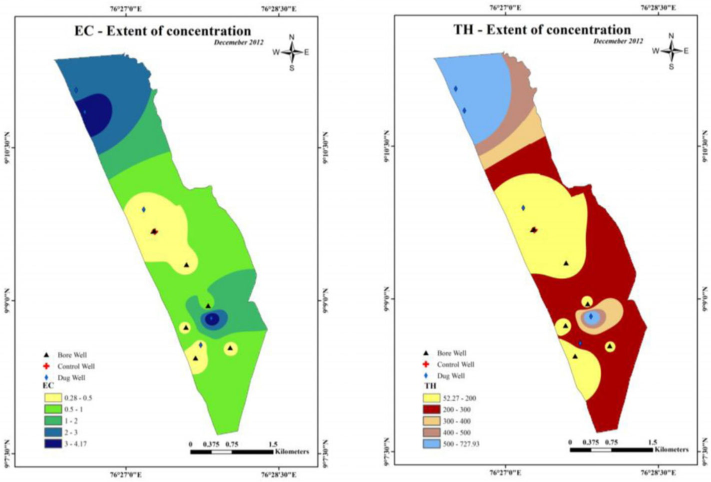
Total Alkalinity is an important characteristic of natural water which is defined as a capacity function because it is imparted by several solute species and is evaluated by acid titration. The principal solutes that constitute alkalinity are imparted to natural water during its movement through the hydrologic cycle. Alkalinity reflects the history of the water, as an imprint left by its hydrogeochemical transitions. Most natural waters contain substantial amounts of dissolved carbon dioxide species, which are the principal source of alkalinity. Total alkalinity is lower than 200mg/l in both DW and BW strata.

Hardness is mainly contributed by the multivalent cations mainly Ca^{2+} & Mg^{2+}. Other ions include $Fe^{3+}$and Fe^{2+}, Mn^{2+}, Sr^{2+}, Al^{3+} etc. Water as it moves through soil and rock, it dissolves small amounts of naturally-occurring minerals and carries them into the groundwater supply. Water is a great solvent for calcium and magnesium, so if the minerals of these ions are present in the soil around a well, the water obtained from the well will be hard. Total hardness as $CaCO_3$ of DW show higher values (282±198) compared to BW(168±41), but it is within the permissible limit of IS & WHO. Vesilind[27] classified waters with TH higher than 250mg/l as Too Hard for ordinary domestic use. From the spatial distribution map of TH in December 2012 (Figure: 3b), values lower than 300mg/l is observed in major part of the study area.

Hardness is a property of water that is not of much health concern, but it can be a nuisance. Hard water can cause mineral build-up in plumbing fixtures, water heaters, and also poor performance of soaps and detergents.

Table 1 Important water quality parameters of dug well (DW) and Bore well(BW) water sources in the study area, Arattupuzha coast, Alappuzha, Kerala, India during 2012 are compared with the standards IS 2012,WHO 2011& USEPA 2014

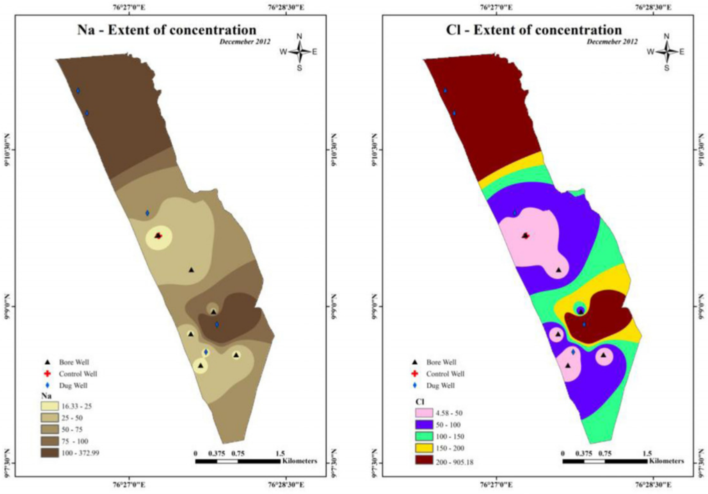
Sl. No.	Parameter	DW: mean $(\bar{x})\pm SD(\sigma)$	BW: mean $(\bar{x})\pm SD(\sigma)$	IS 10500 :2012 Permissible	WHO 2011	USEPA 2014
1	Temperature °C	29.9±1.1	31.1±1.5	-	-	-
2	pH	7.8±0.4	7.5±0.24	6.5-8.5	6.5-8.5	6.5-8.5
3	EC (mS/cm)	1.2±1.4	0.33±0.04	-	1.5	-
4	Eh mV	$^{-}50\pm22$	$^{-}27.95\pm22.2$	-	-	-
5	DO (mg/l)	4.83± 1.96	4.7±1.6	-	-	-
6	BOD (mg/l)	5.9± 3.5	3.8±1.7	-	-	-
7	TA(mg/l)as$CaCO_3$	199± 80	198±45	600	-	-
8	TH(mg/l)as $CaCO_3$	282± 198	168±41	600	100	-
9	TDS(mg/l)	1210± 1491	299±86	2000	500	500
10	Ca (mg/l)	69± 47	43±11	200	75	-
11	Mg (mg/l)	28± 29	16±6	100	50	-
12	Na (mg/l)	107± 127	19±6	-	-	-
13	K (mg/l)	12.9± 8.7	6±1.4	-	-	-
14	Fe (mg/l)	0.08±0.14	1.5±0.8	0.3	0.1	0.3
15	HCO_3^- (mg/l)	242± 98	241±58	-	-	-
16	Cl^- (mg/l)	311± 484	16±13	1000	250	250
17	SO_4^{2-} (mg/l)	27± 24	2.5±0.5	400	250	250
18	PO_4^{3-} (mg/l)	0.19±0.14	0.1±0	-	-	-
19	NO_3^- (mg/l)	1.6±0.7	1.1±0.4	45	50	10
20	Li (µg/l)	5.6±3.5	2.4±2.0	-	-	-
21	Rb(µg/l)	13.2±7.2	10±3.9	-	-	-
22	Cs (µg/l)	0.23±0.12	0.16±0.05	-	-	-
23	Sr (µg/l)	593±340	533±348	-	-	-
24	Ba (µg/l)	23±9	56±29	700	700	2000
25	V (µg/l)	2.52±1.32	0.28±0.15	-	-	-
26	Cr (µg/l)	0.35±0.1	0.29±0.07	50	50	100
27	Mn (µg/l)	4.65±3.66	25.09±14.42	300	400	50
28	Co (µg/l)	0.1±0.0	0.1±0.0	-	-	-
29	Ni (µg/l)	0.9±0.37	4.03±1.64	20	70	-
30	Cu (µg/l)	4.07±2.68	2.5±1.42	1500	2000	1000
31	Zn (µg/l)	4.48±2.19	13.91±11.93	15000	-	5000
32	Ag (µg/l)	0.3±0.25	0.2±0.06	100	-	100
33	Cd (µg/l)	0.1±0.0	0.1±0.0	3	-	5
34	Al (µg/l)	25.1±17.2	28.4±20.5	200	100	50-200
35	Ga (µg/l)	4.3±1.4	13.9±5.3	-	-	-
36	In (µg/l)	ND	0.1±0.0	-	-	-
37	Pb (µg/l)	0.6±0.6	0.6±0.4	10	10	15
38	As (µg/l)	1.3±1.0	0.17±0.06	50	10	10
39	Bi (µg/l)	0.1±0.0	0.18±0.09	-	-	-
40	Se (µg/l)	4.1±0.2	4.4±0.3	10	40	50
41	TIC (mg/l)	33±16	28.8±10.9	-	-	-
42	TC (mg/l)	34±14	29.4±10.0	-	-	-
43	TOC (mg/l)	1.7±2.3	0.65±0.89	-	-	-



(a) (b)

Fig. 3 - Spatial distribution map for a) Electrical Conductivity (EC) & b) Total Hardness (TH) of the study area, Alappuzha, Arattupuzha coast, Kerala, India during December 2012.

From the Total Hardness (TH) and Alkalinity (TA) inferences can be drawn about the Temporary or Permanent Hardness of water. An excess of total alkalinity over total hardness indicate the presence of bicarbonate of sodium. Since, Total hardness is mostly higher than alkalinity (equal to temporary hardness or carbonate hardness, CH); in many stations, permanent hardness (non carbonate NCH) is observed [ie; TH = CH + NCH]. TDS of DW strata exceed the permissible limit in many occasions. The cations calcium and magnesium are the major contributors of hardness. Equilibria involving carbonates such as the calcite dissolution-precipitation and dissolved carbon dioxide species equilibria are the major factors limiting the solubility of calcium in most natural water. The cation-exchange behaviour of magnesium is similar to that of calcium. Both ions are strongly adsorbed by clay minerals and other surfaces having exchange sites.



(a) (b)

Fig. 4 - Spatial distribution map for a) Sodium & b) Chloride of the study area, Arattupuzha coast, Alappuzha, Kerala, India during December 2012.

Sodium is the prominent cation in DW strata whereas, calcium is prominent in BW strata. Bicarbonate and chloride are the prominent anions in both. Sodium ions are not strongly hydrated in natural conditions. There are no important precipitation reactions that can maintain low sodium concentrations in water, in the way that carbonate precipitation controls calcium concentrations. Sodium is retained by adsorption on mineral having high cation-exchange capacities such as clays. But, the interaction between surface sites and monovalent ions is much weaker than the interactions with divalent ions. Cation exchange processes in freshwater systems tend to extract divalent ions from solution and to replace them with monovalent ions. The annual mean Na concentration of DW strata during year 2012 is 107± 127 and for BW strata it is only 19±6. The spatial variation map for (a) Na & (b) Cl^- of the study area is presented in Figure 4. Higher concentrations of Na & Cl are observed in the same areas where EC shows higher values. Thus, sea water intrusion can be confirmed in those areas during December 2012.

In BW strata, the only prominent ion having comparable concentration to DW strata is bicarbonate. The higher concentration of HCO_3^- in the water points to the dominance of mineral dissolution. In deep aquifers, rock weathering is the source of major constituents in water. Annual mean Iron concentration of BW strata during year 2012 is 1.5±0.8. Lateritic soil present in the study area at depth is the reason for the higher iron concentration in BW strata. Other anions, such as sulphate, nitrate and phosphate are present only in very low concentrations.

Minor and trace constituents are those substances that always or nearly occur in concentrations less than 1.0 mg/l. Human activities have had a particularly strong influence on the occurrence of many of the minor constituents of water. Trace element determined by ICP-MS method in the present study area revealed that any of the analysed elements are not present in harmful level.

Pearson Correlation study

On studying the Pearson's correlation matrix for DW (Table 2), it is clear that no significant correlation is observed between pH and other parameters. Analysis of the correlation coefficient suggest that Electrical Conductivity (EC) of drinking water is an important parameter and it is significantly correlated with TH (r = 0.98), Ca (r = 0.97), Na (r = 0.81), K (r = 0.89) and Cl (r = 0.92). It indicates that EC increases with increase in each of these parameters. Strong positive correlation exist between TH and Ca (r = 0.99). Significant correlation is also present between TH and Cl (r = 0.91), Na and Cl (r = 0.81) and K and Cl (r = 0.91) .

Pearson's correlation matrix for BW (Table 3) shows that pH is directly correlated to iron (r = 0.80). Thus the chemical behaviour of iron and its solubility in water depend on the pH. From the matrix we can see that pH doesn't show any other significant correlation. EC show slight positive correlation to TH and Ca and a slight negative correlation to Fe (r = $^{-}$0.55). TDS show slight positive correlation to bicarbonate (r = 0.64). TH show significant positive correlation to Ca (r = 0.89) and Mg (r = 0.74). No other significant correlations are observed in the Pearson correlation matrix for BW strata.

Table 2 Pearson Correlation matrix for Dug Well strata of Arattupuzha coast, Alappuzha, Kerala, India during year 2012

	pH	**EC**	**TDS**	**TH**	**Ca**	**Mg**	**Na**	**K**	**Fe**	**HCO_3**	**Cl**	**SO_4**	**PO_4**	**DO**	**BOD**
pH	1.00														
EC	-0.62	1.00													
TDS	-0.56	0.69	1.00												
TH	-0.62	0.98	0.66	1.00											
Ca	-0.67	0.97	0.64	0.99	1.00										
Mg	-0.46	0.70	0.44	0.73	0.71	1.00									
Na	-0.57	0.81	0.60	0.84	0.84	0.56	1.00								
K	-0.44	0.89	0.73	0.89	0.85	0.68	0.64	1.00							
Fe	-0.34	0.38	0.29	0.42	0.44	0.15	0.28	0.36	1.00						
HCO_3	-0.10	0.08	0.12	0.11	0.11	0.17	-0.35	0.25	0.06	1.00					
Cl	-0.43	0.92	0.71	0.91	0.89	0.52	0.81	0.91	0.34	-0.05	1.00				
SO_4	-0.57	0.78	0.47	0.71	0.69	0.56	0.53	0.69	0.31	0.12	0.60	1.00			
PO_4	0.43	0.04	0.27	0.00	-0.05	-0.10	0.12	0.12	-0.04	-0.25	0.27	-0.21	1.00		
DO	0.12	-0.40	-0.20	-0.35	-0.34	-0.62	0.07	-0.40	-0.16	-0.58	-0.19	-0.26	0.00	1.00	
BOD	-0.51	0.73	0.72	0.74	0.72	0.63	0.75	0.69	-0.03	-0.14	0.78	0.32	0.30	-0.20	1.00

Table 3 Pearson Correlation matrix for Bore Well strata of Arattupuzha coast, Kerala, India during year 2012

	pH	**EC**	**TDS**	**TH**	**Ca**	**Mg**	**Na**	**K**	**Fe**	**HCO_3**	**Cl**	**SO_4**	**PO_4**	**DO**	**BOD**
pH	1.00														
EC	-0.47	1.00													
TDS	-0.48	0.04	1.00												
TH	-0.31	0.57	0.35	1.00											
Ca	-0.30	0.54	0.28	0.89	1.00										
Mg	-0.19	0.39	0.30	0.74	0.36	1.00									
Na	-0.11	-0.04	-0.44	0.08	0.25	-0.21	1.00								
K	-0.03	0.49	0.28	0.43	0.29	0.47	-0.73	1.00							
Fe	0.80	-0.55	-0.37	-0.38	-0.37	-0.23	-0.18	0.06	1.00						
HCO_3	-0.30	0.06	0.64	0.21	0.26	0.05	-0.29	0.09	-0.49	1.00					
Cl	0.10	0.44	-0.19	0.28	0.15	0.35	-0.07	0.16	-0.14	0.23	1.00				
SO_4	-0.03	0.10	-0.26	0.07	0.03	0.08	0.13	0.11	0.18	-0.41	0.36	1.00			
PO_4	-0.16	0.37	-0.20	0.52	0.57	0.23	0.37	0.08	-0.30	-0.19	0.28	0.56	1.00		
DO	0.26	0.03	-0.47	-0.41	-0.28	-0.41	-0.12	0.11	0.37	-0.55	-0.40	-0.22	-0.14	1.00	
BOD	-0.27	0.36	0.11	0.36	0.38	0.18	0.26	0.17	-0.14	-0.48	-0.25	0.41	0.47	0.01	1.00

Water quality Index (WQI)

The water quality data (Table 1) is used for the development of water quality indices (WQI). WQI has the capability to reduce the bulk of the information into a single value to express the data in a simplified and logical form. These indices are most important to communicate the information on designated water quality trends to the general public or to the policy makers for quality management. In the present study, weighted arithmetic water quality index method (Table 4) is used and the calculation steps are as follows

$WQI = \sum W_i Q_i / \sum W_i$
$W_i = 1/S_i$
S_i = standard permissible value of particular parameter (WHO)
$Q_i = (V_o - V_i) x100/(V_s - V_i)$
V_o = observed value or mean of the observed values of any parameter
V_i = ideal value of that particular parameter (=0 for all parameters except pH & DO)
V_s = standard permissible value of particular parameter

By using weighted arithmetic index method WQI of DW strata calculated in each month of year 2012 shows that, in most of the months the water quality ranges from Good (G) to unfit for drinking purpose (UDP) category (Table 5). There are some DWs which show high decline in quality based on certain parameters such as EC, Na, Cl etc. This is the reason for the poor quality water in those wells. For DW strata the 2012 annual mean value for WQI is 77±39 and the value vary from 52 to 102.

In BW strata, in January and February water show Good quality. In March WQI range from 61.4 to 77.2 which define poor quality water. This is due to the high pH in that month. In April and May, water quality ranges from good to poor category. After that in the monsoon season the WQI calculated is in the range 25-50 which suggest good quality. In November the water quality improves and it range from 16.7-29.3 which suggest the water is in Excellent (E) to Good (G) category.

Sodium – Chloride Ratio

In ion exchange process Ca & Mg in water replaces Na in clays. Since Ca & Mg are removed from water, this process is also called natural softening. In reverse ion exchange, the opposite change occurs and it is observed when highly saline waters come in contact with calcium rich clays. Ion exchange is observed if *Na/Na+Cl* > 0.5 and if Na*/Cl* > 1.0.

In DW strata during the months March, April and May reverse ion exchange is observed (Table 6). The annual mean value of *Na/(Na+Cl)* is 0.5±0.2 and that of Na/Cl is 1.2±0. In BW strata ion exchange is occurring in all months of year 2012.That is *Na/Na+Cl* is higher than 0.5 and that of *Na/Cl* is higher than 1.0 in all months.

Irrigation Quality Evaluation

Dissolved salts in groundwater accumulate in soils according to the intensity of irrigation practiced. It causes salt toxicity to plants; reduces the availability of water to plants due to high osmotic pressure of the soil solution. Salt deposition brings changes in soil structure and textural properties. High Cl^- content generally affect tissues and plant leaves. Different crops require different irrigation water qualities. Therefore, testing of irrigation water quality contribute to effective management and utilization of the groundwater resources. The irrigation quality parameters calculated are Sodium Adsorption Ratio (SAR), Sodium Percentage (Na %), Magnesium Adsorption Ratio (MAR), Residual Sodium Carbonate (RSC), Permeability Index (PI) and Kelly's ratio (KR). Concentrations of various ions obtained from chemical analysis are converted to milliequivalents per litre (meq/L). Annual mean of these parameters for dug well and bore well groundwater sources are given in Table 7.

Table. 4 Classification of ground water on the basis of Water Quality Index,WQI [28]

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

Table. 5 Monthly variation of WQI, Water Quality and Grading of Dug well (DW) & Bore well (BW)strata of Arattupuzha coast, Alappuzha, Kerala, India during year 2012

Year	DW			BW		
(2012)	WQI	Water Quality	Grading	WQI	Water Quality	Grading
Jan	35-97	G-VP	B-D	24.8-36.8	G	B
Feb	24-128	E-UDP	A-E	29.9-41.7	G	B
Mar	60-138	P-UDP	C-E	61.4-77.2	P	C
Apr	49-119	G-UDP	B-E	28.9-65.1	G-P	B-C
May	43-93	G-VP	B-D	27.6-59.8	G-P	B-C
Jun	36-102	G-UDP	B-E	26.7-38.9	G	B
Jul	31-95	G-VP	B-D	31.8-41.8	G	B
Aug	32-106	G-UDP	B-E	36.4-46.2	G	B
Sep	36-112	G-UDP	B-E	32.6-41.4	G	B
Oct	41-139	G-UDP	B-E	30.4-40.2	G	B
Nov	31-127	G-UDP	B-E	16.7-29.3	E-G	A-B
Dec	36-126	G-UDP	B-E	27.2-43.4	G	B
$\bar{x} \pm \sigma$	77±39			39 ±8.9		
μ	77±25			39 ±5.7		
CI	52-102	P- UDP	C-E	33.3-44.7	G	B

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

Table 6 Monthly variation of Na/(Na+Cl) ratio , Na/Cl ratio & probable inference of Dug well(DW) & Bore well(BW) strata of Arattupuzha coast, Alappuzha, Kerala, India during year 2012

Year (2012)	DW			BW		
	$\frac{Na}{Na+Cl}$	$\frac{Na}{Cl}$	Inference	$\frac{Na}{Na+Cl}$	$\frac{Na}{Cl}$	Inference
Jan	0.5 ±0.2	1.6 ±1.1	Ion exchange	0.7±0.1	2.8±1.6	Ion exchange
Feb	0.5 ±0.2	1.1 ±0.6	Ion exchange	0.7±0.1	2.3±1.3	Ion exchange
Mar	0.4 ±0.2	0.8 ±0.4	Reverse ion exchange	0.7±0.1	2.5±1.9	Ion exchange
Apr	0.4±0.1	0.8±0.3	Reverse ion exchange	0.6±0.1	2.4±2.2	Ion exchange
May	0.4±0.2	0.9±0.5	Reverse ion exchange	0.5±0.08	1.1±0.3	Ion exchange
Jun	0.5±0.2	0.9±0.5	Ion exchange	0.7±0.2	3.3±3.1	Ion exchange
Jul	0.5±0.2	1.2±0.7	Ion exchange	0.7±0.1	3.2±2.2	Ion exchange
Aug	0.6±0.1	1.9±0.6	Ion exchange	0.7±0.1	2.8±1.5	Ion exchange
Sep	0.6±0.1	1.5±0.7	Ion exchange	0.7±0.1	2.8±2.2	Ion exchange
Oct	0.6±0.1	1.5±0.8	Ion exchange	0.7±0.1	3.4±1.8	Ion exchange
Nov	0.5±0.2	1.1±0.7	Ion exchange	0.7±0.07	3.2±1.5	Ion exchange
Dec	0.5±0.2	1.3±0.8	Ion exchange	0.7±0.1	3.4±1.8	Ion exchange
$\bar{x} \pm \sigma$	0.5±0.2	1.2±0.7		0.68±0.12	2.76 ±1.9	
μ	0.5±0.1	1.2±0.4	Ion exchange	0.68±0.08	2.76 ±1.2	Ion exchange
CI	0.4-0.6	0.8-1.6		0.6 -0.76	1.56 -3.96	

Kelly's Ratio;

$KR=Na^{+}/ (Ca^{2+}+Mg^{2+})$

In the case of DW strata Kelly's Ratio calculated is less than 1.0 till July 2012 which shows that the water of shallow ground water sources are suitable for irrigation till July. From August to December 2012 the upper limit of KR value is higher than 1.0 and it is 2.4 in September and October 2012 which shows the unsuitability of water for irrigation in some of the stations. The annual mean of KR is 0.8±0.6. The ratio is less than 1.0 for BW strata throughout the year which suggest that the water is suitable for irrigation in all months.

Magnesium Adsorption Ratio;

$MAR=Mg^{2+}x100/ (Ca^{2+}+Mg^{2+})$

The MAR for DW strata in January 2012, is 39±11and the range is below 50, this too infers that water of all stations are suitable for irrigation. From February to December 2012, the range of MAR crosses the suitability limit 50 and hence all well waters are not suitable for irrigation. Excess Mg present due to salt water intrusion damages the irrigation quality. The MAR calculated for BW strata is less than 50% in all months except April 2012, which suggest the suitability of water for irrigation.

Permeability Index; $PI=[Na^{+}+(HCO_3)^{1/2}]x100/ [Ca^{2+}+Mg^{2+}+Na^{+}]$

PI calculated for DW strata shows greater than 25% in all months and hence water is good for irrigation based on PI throughout the year. In the case of BW strata of the study area the annual mean of PI is 70.2±16.7 and the water is good for irrigation throughout the year.

Sodium Adsorption Ratio,

$SAR=Na^{+}/[(Ca^{2+}+Mg^{2+})/2]^{1/2}$

In the case of DW & BW strata the SAR is less than 10 throughout the year. So based on SAR the water of both strata maintain Excellent quality in the whole year.

In U.S. Salinity diagram, Sodium Adsorption Ratio (SAR) are plotted against Electrical Conductivity (EC) along Y-axis and X-axis respectively to classify water sources. USSL diagram for DW strata (Figure 5a) illustrates that, in most of the months groundwater samples fall in the field of C3S1, indicating moderate water quality having medium to high salinity and low sodium. This shows, the groundwater of the study area – Arattupuzha coast, Alappuzha can be used for irrigation on almost all types of soil with little danger of exchangeable sodium. USSL diagram for BW (Figure 5b) shows the groundwater comes in C1S1 and C2S1 category showing low to medium salinity hazard and low sodium or alkali hazard.

Residual Sodium Carbonate,

$RSC = (CO_3^{2-} + HCO_3^{-}) – (Ca^{2+} + Mg^{2+})$

If RSC is higher than 2.5 the water is considered unsuitable for irrigation. In the case of DW strata in all the months except September and December 2012, the upper limit in the range of RSC is higher than 1.25 but lower than 2.5 indicating that the water quality ranges from Good to Doubtful category. In the case of BW, in the months May, June and December 2012, the water quality vary from good to doubtful range. In all other months the water shows good quality. The annual mean value of RSC is 0.57±0.62.

Sodium Percentage,

$Na\% = Na^{+} x 100/(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})$

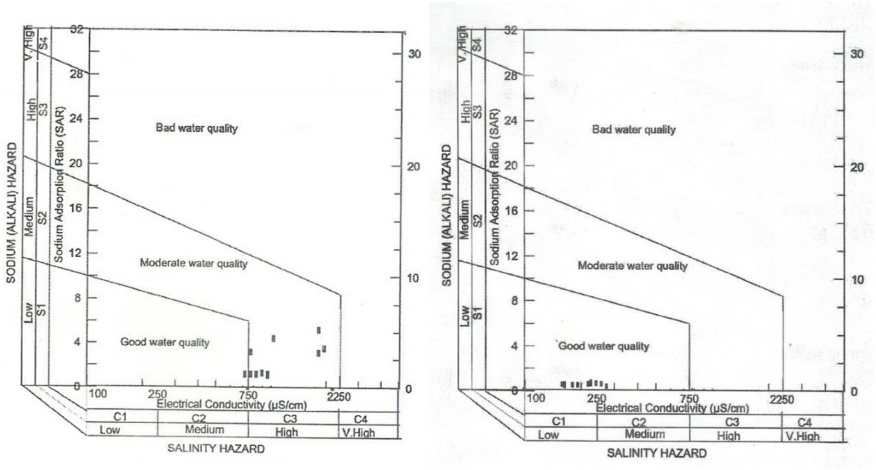
In the case of DW strata Na% value comes in the Good to Permissible category from January to July 2012, and after that Good to Doubtful category. Sodium Percentage calculation again reveals the excellent to good quality of BW water. The Na% is lower than 40 in all months and its mean is 22.9±4.76.

Calculated percent sodium for groundwater in the study area is plotted against electrical conductivity (EC) in Wilcox diagram. From Wilcox Diagram it is confirmed that water of DW strata (Figure 6a) comes in Good to Permissible category in most months and belongs to Doubtful to Unsuitable category in the months of October, November and December 2012. After October 2012, the increase in EC is the reason for the unsuitability of water for irrigation. In July 2012, the water is in Excellent to Good position because, monsoon season decreases the EC to 700µS/cm. For BW from Wilcox Diagram (Figure 6b) we can see that the water is Excellent (E) to Good (G) category in all months. So the points are clustered in that region.

Table 7 Assessment of irrigation water quality of Dug well (DW) & Bore well(BW) strata of Arattupuzha coast, Alappuzha, Kerala, India during year 2012

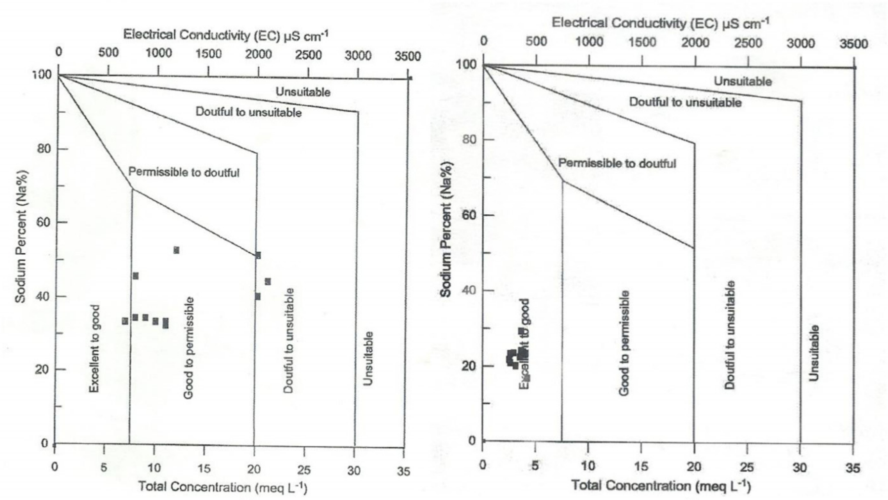
Parameter	Value	Water Quality	DW mean (2012 annual)	Water Quality	BW mean (2012 annual)	Water Quality
KR	<1	Suitable(S)	0.8±0.6		0.26±0.08	
(Kelly 1963)	>1	Unsuitable(US)	(0.2-1.4)	S-US	(0.18-0.34)	S
MAR	<50	Suitable(S)	35±19.6		35.4±12.1	
(Paliwal 1972)	>50	Unsuitable(US)	(15.4-54.6)	S-US	(23.3-47.5)	S
PI (Doneen1964)	>75%	Good(G)	73±13		70.2±16.7	
	25-75%	Good(G)	(60-83)	G	(53.5-86.9)	G
	<25%	Unsuitable(US)				
SAR (Todd1959; Richards 1954)	<10	Excellent(E)				
	10-18	Good(G)	2.5±2.2	E	0.65 ±0.18	E
	18-26	Doubtful(D)	(0.3-4.7)		(0.47-0.83)	
	>26	Unsuitable(US)				
RSC (Raghunath 1987)	<1.25	Good(G)	-0.75±4		0.57±0.62	
	1.25-2.50	Doubtful(D)	(-4.75-3.25)	G-US	(-0.05-1.19)	G
	>2.5	Unsuitable(US)				
%Na (Wilcox 1955)	<20	Excellent(E)				
	20-40	Good(G)	40±17	G-P	22.9±4.76	E-G
	40-60	Permissible(P)	(23-57)		(18.1-27.7)	
	60-80	Doubtful(D)				
	>80	Unsuitable(US)				

S- Suitable US- Unsuitable E-Excellent G-Good D-Doubtful



(a) (b)

Fig. 5 - USSL Diagram for a) Dug well(DW) & b)Bore well(BW) strata of Arattupuzha coast, Alappuzha, Kerala, India showing each month of year 2012.



(a) (b)

Fig. 6 - Wilcox Diagram for a) Dug well(DW) & b)Bore well(BW) strata of Arattupuzha coast, Alappuzha, Kerala, India showing each month of year 2012

Saturation Indices and Tendency of water

As regards to corrosive nature of water, aggressiveness and ease of scale formation based on saturation indices is regarded as one of the key factors. The corrosion of metallic and asbestos-cement distribution system can cause significant threat to human health. Selection of steel pipes that can best tolerate the water quality conditions for a specific use requires careful consideration of key indicators like pH, DO, H_2S, TDS, CO_2 and Cl^-. Using the results of hydrogeochemical analyses, these indicators can forecast the potential of ground water to cause corrosion. Corrosion indices are most useful to predict the corrosive behaviour or scale-formation of water. They are derived from chemical equilibrium equations for the $CaCO_{3(s)}$ system. Scaling is one of the most critical water quality issues in India[29]. Accordingly the respective indices are determined for the groundwater sources of the region studied.

Aggressiveness Index (AI)

This empirical indicator formula was developed for aggressiveness of water towards the corrosion of asbestos-cement pipes. AI calculated for DW strata suggest that the quality of water ranges from Moderately aggressive (MA) to Non-aggressive (NA) in all months and BW strata suggest that, the water is Moderately Aggressive. However, in the months March, April, August and December the tendency of water ranges from Moderately Aggressive (MA) to Non Aggressive (NA). The annual mean of AI for DW is 12.2±0.4 and for BW is 11.8±0.4 (Table 8).

Langlier Saturation Index (LSI) & Ryznar Stability Index (RSI)

Two indices commonly used in the water treatment industry to evaluate the aggressive nature of water are the Langelier Saturation Index (LSI or Saturation index) and the Ryznar Stability Index (RSI or Stability index). In both cases, these indices are based upon a calculated pH for saturation of calcium carbonate (pH_s). This pH_s is then used in conjunction with the actual pH of water to calculate the index as follows:

$$LSI = pH - pH_s$$

$$RSI = 2pH_s - pH$$

The mean of LSI for DW is 0.4±0.4, suggest the variation of quality (Table 8) from Slightly scale forming and corrosive (SSFC) to Scale forming but non corrosive (SFNC). For BW LSI calculation show the tendency of water is mainly in the range from Slightly corrosive but non scale forming (SCNSF) to Slightly scale forming and corrosive (SSFC). The annual mean of LSI is -0.04±0.4.

The annual mean of RSI is 7.1±0.7 for DW suggest the variation in tendency from Little scale or corrosion (LSC) to Corrosion significant (CS). Annual mean of RSI for BW is 7.6±0.6 indicate the tendency of water vary from Corrosion significant (CS) to Heavy corrosion (HC).Thus as regards to saturation indices of the region's water, shallow well water is slightly scale forming and deep well water is slightly corrosive.

Thermodynamic corrosion of iron and copper pipes cannot be eliminated. Corrosion control is accomplished by chemical treatment of the water or electrochemical treatment of pipes. Chemical controls include adjustment of water pH, removal of dissolved oxygen, adjustment of calcium content etc.

Table. 8 Variation of Aggressiveness index(AI), Langelier Saturation Index(LSI) & Ryznar Stability index(RSI) of Dug well (DW) & b)Bore well(BW) strata of Arattupuzha coast, Alappuzha, Kerala, India during year 2012

Para meter	Value	Water Tendency	DW mean (2012 annual)	Water Tendency	BW mean (2012 annual)	Water Tendency
AI	< 10.0	Highly aggressive (HA)	12.2±0.4		11.8±0.4	
	10.0-11.9	Moderately aggressive (MA)	(11.8-12.6)	MA-NA	(11.4-12.2)	MA-NA
	> 12.0	Non-aggressive (NA)				
LSI	< ˉ2	Intolerable corrosion (IC)				
	ˉ2 - ˉ0.5	Serious corrosion (SC)				
	ˉ0.5 - 0	Slightly corrosive but non scale forming (SCNSF)	0.4±0.4 (0-0.8)	SSFC- SFNC	ˉ0.04±0.4 (ˉ0.04-0.44)	SCNSF- SSFC
	0	Balanced but pitting (BP)				
	0 – 0.5	Slightly scale forming and corrosive (SSFC)				
	0.5 - 2	Scale forming but non corrosive (SFNC)				
RSI	4.0 – 5.0	Heavy scale (HS)				
	5.0 – 6.0	Light scale (LS)	7.1±0.7		7.6±0.6	
	6.0 – 7.0	Little scale or corrosion(LSC)	(6.4-7.8)	LSC- CS	(7-8.2)	CS-HC
	7.0 – 7.5	Corrosion significant(CS)				
	7.5 – 9.0	Heavy corrosion(HC)				

Piper Plot and Water Quality Evaluation

The composition of dominant ions is displayed graphically by several methods. A more concise presentation is followed in this study in the form of Hill-Piper diagrams (Piper 1944). In this analysis the relative concentrations of the major ions in percent (based on meq/L) are plotted on cation and anion triangles. Cation and anion fields are combined to show a single point in a diamond shaped field, from which inference is drawn on the basis of hydrochemical facies concept.

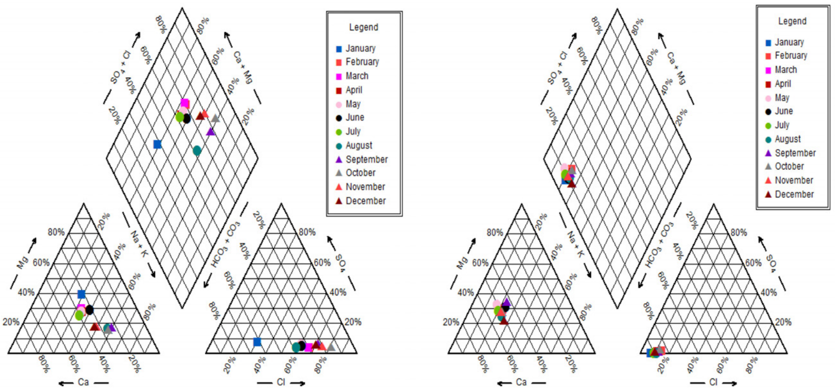


Fig. 7- Hill Piper Trilinear Diagram showing monthly water type of a) Dug well(DW) & b)Bore well(BW) strata of Arattupuzha coast, Alappuzha, Kerala, India showing each month of year 2012.

Hill Piper Trilinear plot prepared for the groundwaters collected from DWs during each month of year 2012 (Figure 7a) identify a mixed nature of different hydrochemical facies mainly(i) Ca-Mg-HCO_3 (Temporary Hardness), (ii) Ca-Mg-Cl-SO_4 (Permanent Hardness) and (iii) Na-K-Cl

(Saline). In January 2012, the prominent hydrochemical facies is Ca-Mg-HCO_3. Few groundwater of the coastal area show Na-K-Cl facies during the post monsoon period of September and October 2012. But these gradually get diluted to Ca-Mg-HCO_3 or Na-K-HCO_3 facies with the monsoon. The results suggest that mixed cation-HCO_3 is the dominant hydrochemical facies for the studied ground waters.

Hill-Piper plot for BW strata in each month (Figure 7b) cluster in the area of Temporary Hardness. The water is Ca-Mg-HCO_3 type. The prominent cation is calcium (Ca^{2+}) and prominent anion is bicarbonate (HCO_3^-).

Pretsunamic Groundwater Study of the Region

Gross composition of the ground water quality parameter of the Alappad – Arattupuzha region [14, 30-32] based on the data for the year 2001 shows: pH (7.5-7.7), EC (0.334-0.370) mS/cm, TH (55-81) mg/l as $CaCO_3$, Ca (14.2-23.8) mg/l, Mg (4.2-5.4) mg/l, Na (29-37) mg/l, K (7.5-12.5) mg/l, CO_3 (0.2-0.3) mg/l, HCO_3 (20.4-48.0) mg/l, SO_4 (15.1-25.7) mg/l, Cl (53.1-60.9) mg/l, F (0.077-0.083) mg/l. Total Hardness (TH) and concentration of cations; Ca, Mg, Na, K and anions; HCO_3^- and Cl^- show considerable increase over a decade.

The marked variation of the ground water quality of the region over the years is an indication of hydrogeochemistry that is prominent during the study. Post tsunamic water quality studies can bring about a reference finger print of groundwater quality of the coastal region. It is rejuvenated over a period and based on the primary results, variability of groundwater chemistry of the region in the years to come can be interpreted. In this regard, this paper is made an attempt to limelight some significant findings as a prologue to any future research works.

Conclusion

In the present study, hydrogeochemical analysis of shallow and deep ground water sources along Arattupuzha coast, Alappuzha, Kerala, India during year 2012. Study reveals that, some of the water quality parameters exceed the permissible standard limit set by BIS 2012, WHO 2011 and USEPA 2014. GIS shows the spatial variation of parameters- where ever Electrical Conductivity is prominent, Na^+ and Cl^- are high. Pearson's correlation matrix suggest that, in Dug well (DW) strata, electrical conductivity of water is an important parameter and it is significantly correlated with TH, Ca, Na, K and Cl.

Correlation matrix for Bore well (BW) strata suggests positive correlation of pH to Iron content. WQI calculation reveals that there are some DWs which show high decline in quality as revealed by its mean 77±39. WQI of BW strata suggest Good quality (G) and in November 2012, WQI from 17 to 29 suggest that the water is in Excellent to Good category (E-G).

From Sodium-Chloride ratio calculations it is inferred that occasionally reverse ion exchange occur in DW strata whereas ion exchange is prominent in BW strata. The irrigation quality parameters suggest the unsuitability mainly due to salinity in some shallow wells. USSL diagram show the moderate water quality of DW and Good water quality of BW. Wilcox diagram also suggest mainly good to permissible category for DW and excellent to good category for BW. Saturation Indices calculation suggest the slightly scale forming nature of shallow ground water (DW), and slightly corrosive nature of deep groundwater (BW) of the region.

The results of Hill-Piper study suggest that groundwater has mixed nature of different hydrochemical facies mainly (i) Ca-Mg-HCO_3 (Temporay Hardness), (ii) Ca-Mg-Cl-SO_4 (Permanent Hardness) and (iii) Na-K-Cl (Saline). Deep ground water of the region is Ca-Mg-HCO_3 type. Overall, the region's water exist as *mixed cation-HCO_3* as the dominant hydro chemical facies. Principal water type depicts rock–water interaction involving the dissolution of carbonates. Systematic assessment of groundwater quality along Arattupuzha coast, Alappuzha, Kerala, India- one of the most sensitive region prone to sea erosion, mineral sand mining issues and ecologically hazard (tsunami) affected coastal area, provide useful data for the formulation of viable policy for the management of coastal environment, economic engineering and protection of groundwater.

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Geochemistry of Ground Water along a Tsunami Affected Coastal Area: Arattupuzha Coast, Kerala

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ABSTRACT

The quality of ground water, based on various physico-chemical attributes, at selected 13 stations along Arattupuzha coast in Alappuzha district, Kerala was determined during each month of the year 2012 to assess their suitability for domestic and irrigation purposes. Post-tsunami studies of the coast in the year 2005, after the 2004 December Indian Ocean TsunamiIndian Ocean Tsunami, revealed that Arattupuzha coast was severely affected. The various physico-chemical parameters of ground water samples such as pH, Electrical Conductivity(EC), redox potential, Total alkalinity(TA), Total hardness(TH), Calcium (Ca), Magnesium(Mg), Dissolved Oxygen(DO), Biochemical Oxygen demand(BOD), Chloride(Cl^-), Sulphate(SO_4^{2-}),Phosphate(PO_4^{3-}), Iron(Fe) ,Fluoride(F^-), Nitrate(NO_3^-), Sodium(Na), Potassium(K) and Total Dissolved Solids(TDS) were analysed. The results were further evaluated in accordance with the physico-chemical, irrigation quality parameters and BIS. The Hill-Piper Trilinear plot is used to infer hydrogeochemical facies. After 8 years since Indian Ocean Tsunami and subsequent extensive inundation most of the above parameters attain within standard limits. In Arattupuzha coast ground water belongs to the Ca^{2+} -Mg^{2+}-HCO_3^- type.

KEYWORDS: *geochemistry, groundwater quality, hill-piper trilinear plot, irrigation quality*

INTRODUCTION

Availability of quality fresh water is one of the most critical issues of the 21st century. It has been estimated that the requirement of ground water in 2050 will be about more than 3 times the present level. Ground water is the important and dependable water resource, the chemistry of which is related to the lithology of the area [1]. Residence time the water is in contact with rock formations, the extend of precipitation, atmospheric emissions, soil quality and weathering have a direct influence on ground water quality of a region. Pollution sources such as mining, land clearance, saline intrusion, industrial and domestic effluent discharges deteriorate ground water quality [2]. In coastal plains of Kerala the alluvial deposits form the most potential phreatic aquifer.The phreatic ground water, which is the most dependable source for the settlers are continously subjected to contamination by extensive inundation. Present study area Arattupuzha Panchayat in Alappuzha district is a narrow strip of land lying between Kayamkulam lake and the Arabian sea having a length of 14 km and a breadth of only 50m at some places (Figure1).This region mostly devastated during 26 December Indian Ocean Tsunami caused widespread saline intrusion [3,4,5].In the present study of determining various physico- chemical parameters in each month of year2012, 13 ground water sources were selected along the Arattupuzha coast (Table1).

MATERIALS METHODS

The water samples collected in each month were analysed for the various parameters following standard procedures (APHA 2005). The results were evaluated in accordance with the physico-chemical, irrigation quality parameters and BIS standards. The Hill-Piper Trilinear plot have been made to study the prominance of ground water type.In this graphical method include 2 triangles, one for plotting cations and the other for plotting anions. The cation and anion fields are combined to show a single point in a diamond shaped field, from which inferences are drawn on the basis of hydrogeochemical facies concept [6].

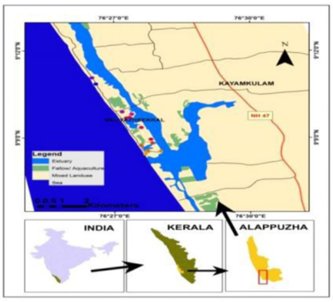

Figure1 Location Map of the study area

Table 1 Selected sampling stations along Arattupuzha coast

Sl.no	Station	Remarks	Location
1	Thara – house owner	Bore well BW1	09° 08' 26 N, 76° 27'41E
2	Valiyazheekal pump - jetty	Bore well BW2	09° 08' 32 N, 76° 28'01E
3	Valiyazheekal temple	Dug well DW1	09° 08' 33 N, 76° 27'43E
4	Prown shed	Bore well BW3	09° 08' 43 N, 76° 27'35E
5	Palliyara Sree Parvathy temple	Dug well DW2	09° 08' 49 N, 76° 27'49E
6	Yuvasakthi	Bore well BW4	09° 08' 56 N, 76° 27'48E
7	Baiju –house owner	Bore well BW5	09° 09' 21 N, 76° 27'35E
8	Kuriappaserry –pipe water	Bore well BW6	09° 09' 40 N, 76° 27'15E
9	Kuriappaserry temple	Dug well DW3	09° 09' 40 N, 76° 27'16E
10	Kuriappaserry pump house	Bore well BW7	09° 09' 40 N, 76° 27'16E
11	Panackal temple	Dug well DW4	09° 09' 53 N, 76° 27'10E
12	Bhaskaran vattachal – house owner	Dug well DW5	09° 10' 51 N, 76° 26'35E
13	Mohanan vattachal – house owner	Dug well DW6	09° 11' 03 N, 76° 26'30E

RESULTS AND DISCUSSION

Various physico-chemical parameters of ground water samples in Jan.2005 and Jan. 2012 showed much difference[7].Tsunami brought immense shift in the ground water quality due to inundation making pH more alkaline,with hardness, Na^+ and Cl^- contents high.The hike in all parameters just after tsunami decreased over 8 years and attained values within BIS limits. (Table 2).

Electrical Conductivity(EC), Total Hardness(TH),Total Dissolved Solids(TDS), Sodium Adsorption Ratio(SAR), Residual Sodium Carbonate(RSC) & % Na values suggest that throughout the year most of the ground water sources are suitable for irrigation purposes[8]. The Na^+ replacing adsorbed Ca^{2+}& Mg^{2+} in soil, is a hazard as it causes damage to the soil structure, making it compact and impervious. Reverse ion exchange is an indication of brine contamination. (Table 2).

The Hill-Piper Trilinear plot showed that due to tsunami inundation the dug well water was strongly saline (Na^+-K^+-Cl^--SO_4^{2-})type and persisted as such for the year 2005 [9]. Most of borewell waters are of Ca^{2+} -Mg^{2+}-HCO_3^- type in the year 2005 and may be due to the sources are well protected by casing and are mostly of mean depth of 250 feet. Hence they are not exposed to saline intrusion by tsunami waves. Inherently this ground water has a high quality profile as evidenced in their parameters(table2). In 2012 the dug well water changed to Ca^{2+} -Mg^{2+}-HCO_3^- type from the persisted saline type just after Tsunami. All the borewell waters in 2012 were remained to be Ca^{2+} -Mg^{2+}-HCO_3^- type.

Table 2 Various physico-chemical parameters of ground water samples in Jan.2005 and Jan. 2012 are compared with BIS values

Sl. no.	Category of parameters	Characteristics	Unit	2005January		2012January		BIS limit (1998)
				DW	BW	DW	BW	
1	General	Temperature	ºC	-	-	29±1.3	29.8±1.3	-
2		pH	-	7.9±0.2	7.7±0.4	7.7±0.4	7.3±0.2	6.5-8.5
3		Redox Potential Eh	mV	-	-	-33±18	-16±9	-
4		Electrical Conductivity EC	mS/cm	9±3	1.0±0.0	0.34±0.2	0.25±0.1	3
5		Alkalinity(as$CaCO_3$)	mg/l	229±58	220±15	218±85	255±38	600
6		Total Hardness(as $CaCO_3$)	mg/l	1002±432	318±132	160±58	165±32	600
7		Total Dissolved solids (TDS)	mg/l	-	-	504±145	533±119	2000
8	Major cations	Calcium	mg/l	230±88	81±45	42±16	43±9	200
9		Magnesium	mg/l	104±52	28±9	13±5.3	14±5	100
10		Sodium	mg/l	1296±1304	35±24	31±15.4	18±4.5	200
11		Potassium	mg/l	42±23	8±3	7.7±2.3	5.6±0.13	10
12		Iron	mg/l	0.04±0.01	0.11±0.19	-	0.64±0.17	-
13	Major anions	Bicarbonates	mg/l	279±58	268±15	266±85	311±38	-
14		Chlorides	mg/l	9849±4766	286±237	40±37	13±8.5	1000
15		Sulphates	mg/l	132±37	16±9	19±1.0	-	400
16		Phosphates	mg/l	0.63±1.4	-	0.39	-	0.3
17		Nitrates	mg/l	1.3±0.34	1.0±0.9	-	-	45

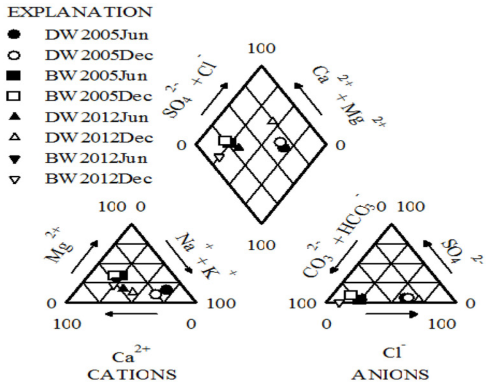

Figure 2 Hill-piper Trilinear plot fordug well(DW) and borewell(BW) samples during June and December of 2005 & 2012.

CONCLUSION

In the present study of evaluating various physico-chemical parameters Arattupuzha coast, Kerala are reported as a post tsunamic impact study, conducted in the year 2012.It is revealed that the quality of Tsunami affected dug wells improved much over the period of 8 years. Irrigational quality evaluation revealed that most of the samples fall in the good to permissible classes for irrigation purposes. Hill-Piper Trilinear Plot showed the prominence of Ca^{2+} -Mg^{2+}-HCO_3^- type water in the study area for all ground water sources from saline (Na^+-K^+-Cl^--SO_4^{2-}) for dug wells during year

2005.Being an ecologically and economically important, thickly populated coast which is prone to natural calamities, the ground water which is a rare commodity, of Arattupuzha coast need more attention. A long term study of ground water quality helps in deciding strategy and preventing the deterioration of quality in future.

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Study of Temporal and Spatial variation of Ground Water Quality along a Coastal stretch of Alappuzha District, Kerala, India: Post Tsunamic study

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ABSTRACT

Arattupuzha coast in Alappuzha is one of the tsunami affected coasts of India on 26th December 2004. In this study an attempt has been made to evaluate the temporal and spatial variation of important ground water quality parameters pH , Electrical Conductivity (EC), Total Dissolved Solids (TDS), Total Hardness (TH), Calcium, Magnesium, Sodium, Potassium, Bicarbonate, Chloride and Sulfate along the coastal strip of Alappuzha district by conducting sampling and analysis in each month of year 2012 and at the end of years 2013 & 2014.Comparison with WHO standards 2011 and BIS standards 2012 revealed that some of the sampling stations exceed the permissible limits in certain parameters. Comparative study of spatial distribution maps of water quality parameters generated using GIS revealed the temporal variation. Water Quality Index (WQI) calculated using these 11 parameters ranked good quality for dug well strata and excellent quality for bore well strata.

Keywords: Groundwater quality, Geographic Information System (GIS), Water Quality Index

INTRODUCTION:

Heavy ground water contamination was reported from Arattupuzha coast after the tsunami incident in 2004 December [1-3]. The present study was conducted with an objective to assess the current status of groundwater chemistry and water quality in the coastal area. Ground water composition is determined by atmospheric inputs, interaction of water with soil and rock and anthropogenic factors. The overexploitation of ground water in thickly populated coastal zones has detrimentally affected its quality and quantity and may result in negative water balance, triggering sea water intrusion.

The area selected for the present study (coastal area of Aartupuzha, Village) lies between North latitudes 9°7'41" & 9°11'26" and East longitudes 76°26'25" & 76°28'23" (Figure.1). The geomorphology of the area includes beach, mudflat, coastal plains and water body. The land use of the area includes agricultural field, mixed vegetation, built-up and water body. The area is a low lying coastal plain having a barrier island coast with a width about 50-200m and an elevation varying from 0 to1.5m above MSL. This coastal stretch is a permeable shoreline with a slanting plane. The slope of the area varies from 0^0 to 20.02^0. The soil texture of the area is sandy. The sand and silt is the litho logical feature of the study area. Fine to medium sands of Recent coastal alluvium mainly constitutes shallow phreatic aquifer and the thickness varies from a few metres to around 30m.

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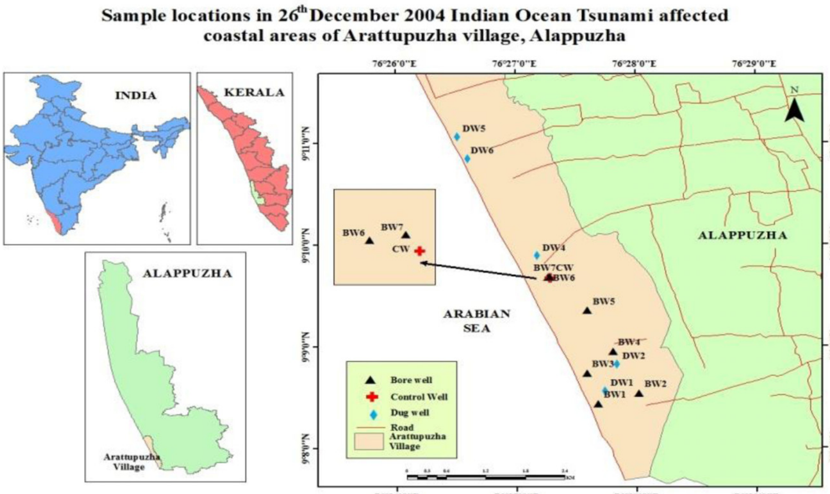

Figure.1: Location map of the study area

MATERIALS AND METHODS:

Ground water samples were collected from 13 stations (7 bore wells and 6 dug wells) during each month of year 2012 and at the end of subsequent years 2013&2014. The important ground water quality parameters were analysed following standard procedures suggested by the American Public Health Association (APHA). Using Geographic Information System (GIS) spatial distribution of various parameters along the study area were plotted. Hydro chemical analysis can give the quality of the isolated patches only, but GIS maps can give the concentration at unknown points by using Inverse Distance Weighed (IDW) algorithm. IDW is a method of interpolation that estimates cell values by averaging the values of sample data points in the neighbourhood of each processing cell. The closer a point is to the centre of the cell being estimated, the more influence or weight it has in the averaging process. Water Quality Index(WQI) of the different water sources were evaluated by weighted Arithmetic Index method using the parameters pH, EC, Total Dissolved Solids (TDS), Total Hardness (TH), Ca, Mg, Na, K, HCO_3^-, Cl^- & SO_4^{2-}.

RESULTS AND DISCUSSION:

The average values of the important ground water quality parameters are given in Table (1) for dug well (DW) and bore well (BW) strata and they are compared with WHO and BIS standards. pH of water shows slight alkaline nature. It is due to the prominence of Bicarbonate ions. It also suggested lower dissolved organic matter content .That is only methyl orange alkalinity is present in water[4].

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Table.1:Average values of the important Ground Water Quality parameters along the study area in various time periods

Parameter	April 2012		July 2012		December2012		December2013		December2014		WHO (2011)	BIS (2012)
	DW	BW	DW	BW	DW	BW	DW	BW	DW	BW		
pH	8.1	7.8	7.8	7.4	7.5	7.4	7.9	7.5	7.9	7.2	6.5-8.5	6.5-8.5
EC(mS/cm)	1.01	0.27	0.75	0.31	1.96	0.36	1.7	0.63	1.46	0.44	1.5	-
TDS (mg/l)	848	157	772	301	1345	113	536	96	832	212	500	500
TH (mg/l)	255	146	219	187	426	147	252	151	267	173	-	200
Ca (mg/L)	59	37	54.4	49	116	42	80	54	66	42	75	75
Mg (mg/L)	26.4	13	20	16	33	10	13	4	25	16	50	30
Na (mg/L)	56	15	47.8	18	177	23	119	21	141	24	200	-
K (mg/L)	13	6.2	10	6	16	6	14	6	12	6	12	-
HCO_3 (mg/L)	289	189	237	251	274	251	411	312	284	255	500	-
Cl (mg/L)	274	13.6	205	14	436	16	186	14	260	19	250	250
SO_4 (mg/L)	26	2	18	-	45	-	14	1.8	29	4.6	250	200

Electrical Conductivity (EC), which is useful for the rapid assessment of salinity of coastal well waters, shows higher than standard value in December 2012 for DW strata. In April (Pre monsoon) the average value was 1.01mS/cm which decreases to 0.75mS/cm in July due to monsoon dilution and then increases in the post monsoon period to a value of 1.96 mS/cm in December 2012. The value decreases in the subsequent years. In December 2013 average EC value decreases to 1.7 and in December 2014 the value again decreases to 1.46mS/cm .

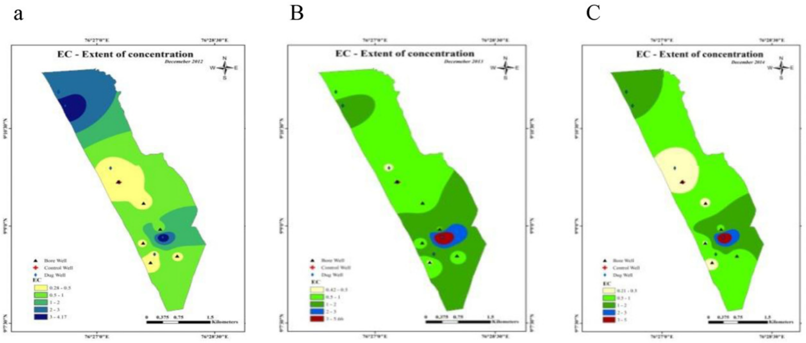

Figure.2: Spatial variation of Electrical Conductivity along the study area in a) 2012 December

Spatial distribution maps also shows that in the northern shallow dug well stations sea water intrusion result in high EC values in 2012 December (Figure.2). There is a station with high EC value in the southeast side (4.18mS/cm in Dec. 2012, 5.68 mS/cm in Dec.2013 and 5.02 mS/cm in Dec. 2014)

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which indicate salinity. It is confirmed by the high values of TDS for DW strata, 1345mg/l in Dec.2012, 536mg/l in Dec. 2013 and 832mg/l in Dec. 2014 all are higher than standard limit. Calcite weathering shows moderate TDS values (500mg/l) but sea water intrusion leads to TDS values greater than 500mg/l. Sodium (Na) and Chloride (Cl^-) concentrations have a direct influence on salinity.

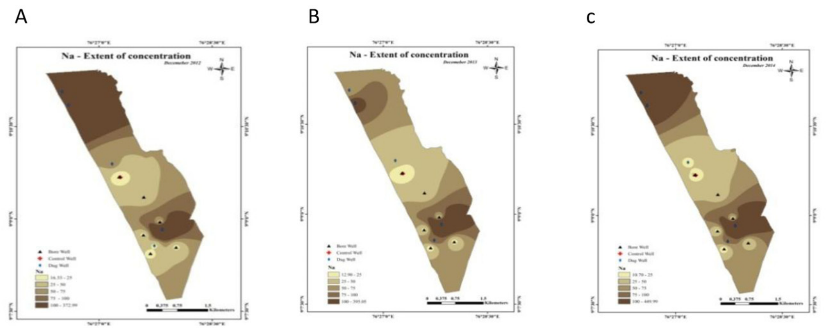

Figure.3: Spatial variation of Sodium (Na) along the study area in a) 2012 December b) 2013 December and c) 2014 December

The average sodium concentration in DW strata is 177mg/l in Dec. 2012, 119mg/l in Dec. 2013 and 141mg/l in Dec. 2014. Although the average values are within standard limit, some of the stations exhibit higher concentrations (Figure.3). Sodium concentration is always higher than potassium concentration because potassium is more readily removed from solution by plants and clay minerals than sodium. Ion exchange reactions also increase the sodium concentration.

The average concentration of Chloride in DW strata is 436mg/l in Dec.2012 and it decreases to 186mg/l in Dec. 2013and slightly increases to 260mg/l in Dec.2014. Primary source of Chloride in water is from sodium chloride directly from halite dissolution or indirectly from the ocean via rainfall. The higher concentration of Chloride ion is an index of pollution by salt water. These are observed in stations near to the sea (Figure.4). The higher concentration of chloride compared to sodium shows reverse natural softening.

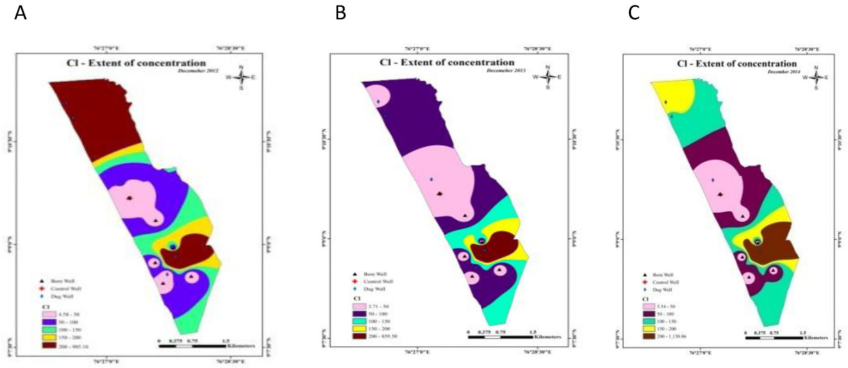

Figure.4: Spatial variation of Chloride (Cl^-) along the study area in a) 2012 December

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On comparing the values of Total Hardness and Total Alkalinity it is observed that, in most of the samples TH is lower than alkalinity which shows that all hardness is temporary. Hardness is the sum of the Ca and Mg concentrations expressed in terms of mg/l of $CaCO_3$. The average value of TH in DW strata is 426mg/l in Dec.2012 which is higher than standard limit and the value decreases to 252mg/l in Dec.2013 and 267mg/l in Dec.2014. Hardness is an important parameter for determining irrigation suitability of waters.

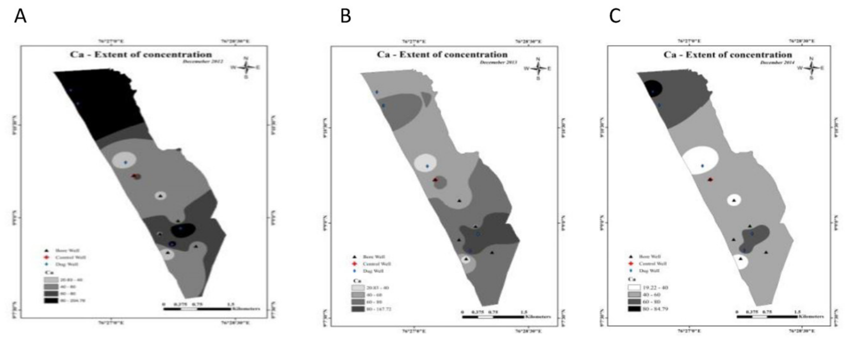

Figure.5: Spatial variation of Calcium (Ca) along the study area in a) 2012 December b) 2013 December and c) 2014 December

Calcium, which is a prominent cation in natural water, has an average concentration 116mg/l in Dec.2012 for DW strata. It decreases to 80mg/l in Dec.2013 and to 66mg/l in Dec.2014. The higher Calcium concentration compared to Magnesium show weathering of sedimentary rocks other than dolomite. Spatial variation of Calcium concentration also shows higher values in certain areas (Figure.5).

Bicarbonate is an important anion in natural ground water. Its average value in DW strata is 274mg/l in Dec.2012 and increases to 411mg/l in Dec.2013 and decreases to 284mg/l in Dec.2014.

In Bore well (BW) strata the only prominent ion is Bicarbonate. The average value is 251mg/l in Dec.2012, 312mg/l in Dec.2013 and 255mg/l in Dec.2014. The increased concentration of Bicarbonate ion in Bore well water sources points to the dominance of mineral dissolution. Anyway all the bore well stations maintain good quality throughout the study period.

Table.2: Water Quality of Dug well and Bore well strata based on Water Quality Index values(mean of 6 dug wells and 7 bore wells)

Strata	2012December		2013December		2014December	
	WQI	Water quality	WQI	Water quality	WQI	Water quality
DW	83	Good water	79	Good water	78	Good water
BW	34	Excellent water	38	Excellent water	30	Excellent water

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Water Quality Index (WQI) calculated using 11 parameters ranked good quality for dug well strata. Its average value is 83 in Dec.2012, 79 in Dec.2013 and 78 in Dec.2014. The average WQI values of BW strata are excellent quality for bore well strata (Table.2). In WQI the rating provide the composite influence of individual water quality parameters on the overall quality of water [8-10].

CONCLUSIONS:

A detailed study of the ground water quality of the coastal aquifers of Arattupuzha panchayath revealed that the major ground water quality parameters are within standard limit in most of the sampling stations except some shallow dug wells near the sea. The quality of water improved during the study period as revealed by Water Quality Index calculation.

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