HYDROCHEMICAL CHARACTERIZATION AND WATER QUALITY ASSESSMENT OF SPRING AND WELL WATER SOURCES OF TWO RIVER BASINS OF SOUTHERN WESTERN GHATS, KERALA, INDIA

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DECLARATION

I hereby declare that the thesis entitled, "**Hydrochemical characterization and water quality assessment of spring and well water sources of two river basins of Southern Western Ghats, Kerala, India**" is an authentic record of research work carried out by me under the supervision and guidance of Dr. D Padmalal, Scientist F and Group Head, Natural Resources and Environmental Management, National Centre for Earth Science Studies (NCESS), Thiruvananthapuram, and Dr. Ammini Joseph, Professor, School of Environmental Studies, Cochin University of Science and Technology (CUSAT) in partial fulfillment of the requirements for the award of Ph.D. degree of Cochin University of Science and Technology under the School of Environmental Studies and that the work did not form part of any dissertation submitted for the award of any degree, diploma, associateship, or any other title or recognition from any University/Institution.

Kochi
February 2017

Hema C Nair

Certificate

This is to certify that this thesis entitled, **“Hydrochemical characterization and water quality assessment of spring and well water sources of two river basins of Southern Western Ghats, Kerala, India”** is a bonafide record of research carried out by **Ms. Hema C Nair** under our joint guidance and supervision in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy under the Faculty of Environmental Studies, Cochin University of Science and Technology and that no part thereof has been included for the award of any other degree. All the relevant corrections and modifications suggested by the audience during the pre-synopsis seminar and recommended by the Doctoral Committee of the candidate have been incorporated in the thesis.

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Hema C Nair

Contents

PREFACE

Through the wonders of nature, water – the life blood of the biotic world – takes different forms. Although nearly 72 percent of the earth's surface is covered by water, fresh water constitutes only a small part of it. Distribution of fresh water in the world is erratic – there is surplus at one place while deficit in another due to various reasons. Spatio-temporal variation in rainfall, regional/local differences in geology and geomorphology, etc., are some of the prominent reasons behind these observed disparities. In India, more than 90% of the rural and nearly 30% of the urban population depend on groundwater for meeting their drinking and domestic water requirements. Apart from this, nearly 60% of the water for irrigation also comes from groundwater sources. But it is unfortunate that a greater part of the Indian population still find it strenuous to meet the basic needs of water. A balance between demand and supply as well as between different sources of water is imperative to overcome the difficulties in fresh water requirements. There have been many initiatives in water quality monitoring but efforts towards improving its quality have yet to gather required momentum. Monitoring makes it easy to capture how land and water use impact the quality of water and help estimating the extent of pollution. Once these issues are addressed, evolving solutions to manage this vital resource would be the next logical step.

Groundwater has long been regarded as a pure form of water in comparison with surface water, because purification of water occurs in the soil column through anaerobic decomposition, filtration and ion exchange. This is one of the reasons for over dependence on groundwater, more specifically well water, in the country and elsewhere. Over exploitation of groundwater resources due to population growth, urbanization and ever increasing demands have resulted in lowering of water table and deterioration of water quality. The situation is rather alarming in Kerala, a state located in the south western part of India having high population density and low percapita land/natural resource availability. It has been reported that well water and other forms of groundwater sources like natural springs in Kerala contain a variety of harmful substances, the concentration of which increases with increased human activity. These point to the immediate need for more focused efforts to maintain the availability and quality of water within standard limits. Although microbial pathogens have been the main source of water contamination for most parts of Kerala in the past, chemical pollution from point and non-point sources have also emerged as an equally serious threat in recent years. Lack of adequate base line data on the quality and availability of drinking water is a major hurdle in strengthening the existing regulatory systems and/ or policies related to conservation and management of fresh water sources.

Taking this impending crisis into account, a detailed study has been carried out here to assess the water quality and drinking water potential of the groundwater resources (springs and wells) in two important river basins of Kerala – the Ithikkara and Kallada river basins, draining the southern Western Ghats, as an example. The outcome of the results of the study will provide insights for the management and wise utilization of drinking water sources of these two river basins in particular and similar river basins in the country in general.

The entire study is addressed in 7 chapters.

Chapter 1 deals with a detailed discussion on groundwater and its changes over the years. A brief write up on the groundwater scenario in India with specific attention to Kerala, description about the different forms of groundwater, especially springs and wells, classification of springs, spring occurrence, human interest in springs and facts about springs and wells in Kerala are also given, apart from the objectives and scope of the study. Chapter 2 presents the geo-environmental setting of the study area. The details of location, population, topography, slope, geomorphology, geology, hydrogeology, soil, climate, stream network, drainage density, lineament density, irrigation, agriculture, land use, flora and fauna, economic minerals and environmental issues are also detailed in the chapter. The materials used and the different methodologies adopted for the generation of data base for the study is dealt in chapter 3. This chapter describes the various procedures adopted for the sampling of springs and well waters, the analytical, graphical and statistical methods employed for the estimation and interpretation of data. The methodology followed for the delineation of groundwater potential zones is also included.

Chapter 4 covers the hydrochemistry of spring waters. The highlights of previous studies carried out on spring waters are given in the chapter followed by presentation of the results of physico-chemical parameters, trace elements and bacteriological analysis. A detailed discussion on hydrochemical process, ion exchange process and influence of terrain and geologic factors on hydrochemistry is made in this chapter. The hydrochemical characteristics of well water samples are dealt in detail in chapter 5. The results of physico-chemical parameters, bacteriological analysis, discussion on hydrochemical processes, major ion chemistry, hydrochemical facies, saturation indices estimation and the study on water mineral equilibrium with respect to well water samples is included in this section. Chapter 6 deals with a detailed assessment of water quality as well as water potential of springs and wells in the study area. Drinking water suitability and irrigation water suitability of springs and well waters are also showcased in this chapter, in addition to delineating the groundwater potential zones of the study area using GIS and Remote Sensing methods. The summary, conclusions and recommendations drawn from the study are given in chapter 7.

The references cited are given at the end of the thesis.

Chapter - 1

INTRODUCTION

1.1 Introduction

Water is a vital natural resource, the availability of which is utmost essential for the existence of life on earth. It is also essential for sustenance of agricultural productivity, environmental purity, industrial growth, power generation and many other natural and man-made processes (UNECE, 1995). However, expanding population coupled with urbanization, industrialization and skewed agricultural developments have resulted in marked impact on the quantity and quality of water resources. Fresh water is distributed in nature in different environmental systems like rivers, lakes, glaciers, groundwater etc. According to the United States Geological Survey (USGS, 1984), 84.9% of fresh water is locked up as ice in polar glaciers. Groundwater accounts for about 14.16% of fresh water while, lakes and reservoirs together contains about 0.55% and, soil moisture and atmospheric vapour hold about 0.33% of fresh water.

Out of the total, only a small fraction of fresh water flows through rivers and streams. Unscientific and unplanned fresh water use and distribution lead to a wide range of water related problems, including conflicts over access and quality, competition between urban, rural and environmental uses, human health problems and constraints on economic development. Reports show that a total of

22 countries, including India, currently have renewable water supplies less than 1000 m^3/person/year (Goyal, 2014). Agriculture is the largest water user and over 30% of the world's food production comes from irrigated lands. Industrial water use is estimated to the tune of 24%. World-wide house hold consumption of water is estimated to be 8% which include water used for drinking, bathing, cooking, sanitation, and gardening (Omran *et al.,* 2014).

India has a potential groundwater reserve of 431423 million m^3. There are about 1500 glaciers in the Himalayan region with an estimated volume of 1400 km^3 water (Subramanian, 2000). About 2.8 million km^2 of Indian Territory is reported to be groundwater worthy and about 30% of it is used for sustaining the existing water supply networks. The annual utilizable surface and groundwater resources of India come to about 690 km^3/ year and 396 km^3/ year, respectively (Kumar *et al.,* 2005). Although there are plenty of fresh water resources in India, many regions of the country experience drinking water scarcity due to vast disparity existing in the availability of water. About 70% of the population depends directly on agriculture and about 28% of the country's Gross National Product (GNP) is also from these primary sectors, which in turn depend significantly on the surface water resources. The World Resources Institute, a US based R & D organization estimated that the demand for water in India will grow to almost 1500 billion cubic meter by 2030, driven by domestic demand for rice, wheat and sugar (Shiao *et al.,* 2015). The current water supply of India is estimated to be 740 billion cubic meter. Many of the river basins are expected to face acute water shortage by the year 2030, if corrective measures are not taken without much delay. The situation of groundwater is also expected to be bleak as the resource is markedly depleting both in quality and quantity.

The water related environmental issues will be critical in the densely populated states of India like Kerala (Chakrapani, 2014). Apart from high population density and rapid economic development, factors such as high per capita water consumption at a rate of 160 lpcd against national average of 135 lpcd, higher personal hygiene and poor water resource development have collectively brought in marked problems in the demand and supply of water in the state. The problem may worsen in future as the state is already in the grip of water scarcity during summer season. The climate change effects complicate the situation further. All these point to the imminent need for finding new and/or alternate sources of freshwater for domestic and drinking purposes. Also, there is an impending need to monitor the quality and availability of the existing sources of groundwater in the state. Considering all these, an attempt has been made in this investigation to study the water quality, potential and hydrochemical characterization of spring and well water sources in two important river basins of Southern Western Ghats - the Ithikkara and Kallada river basins (Fig. 1.1).

1.2 Groundwater

The water existing underneath the earth's surface is called sub surface water. The sub surface water is of two kinds - soil water and groundwater. The zone in which soil water occurs is called the unsaturated zone or vadose zone or zone of aeration; whereas, the zone in which groundwater (water found in voids and spaces of soil, sand and rocks) occurs is the saturated zone. The volume of fresh water stored in soils and aquifers are about 40 times higher than the total amount of water in lakes, rivers and reservoirs throughout the world (USGS, 1984). Groundwater comprises an important section of the total water systems for human consumption. Groundwater is the major source of water for domestic purposes in urban and rural India. It is an important source for agricultural and industrial sectors. The active role of groundwater in nature is its ability to interact with the surrounding and the systematized spatial distribution of its flow (Toth, 1999). In nature, groundwater attains its quality through

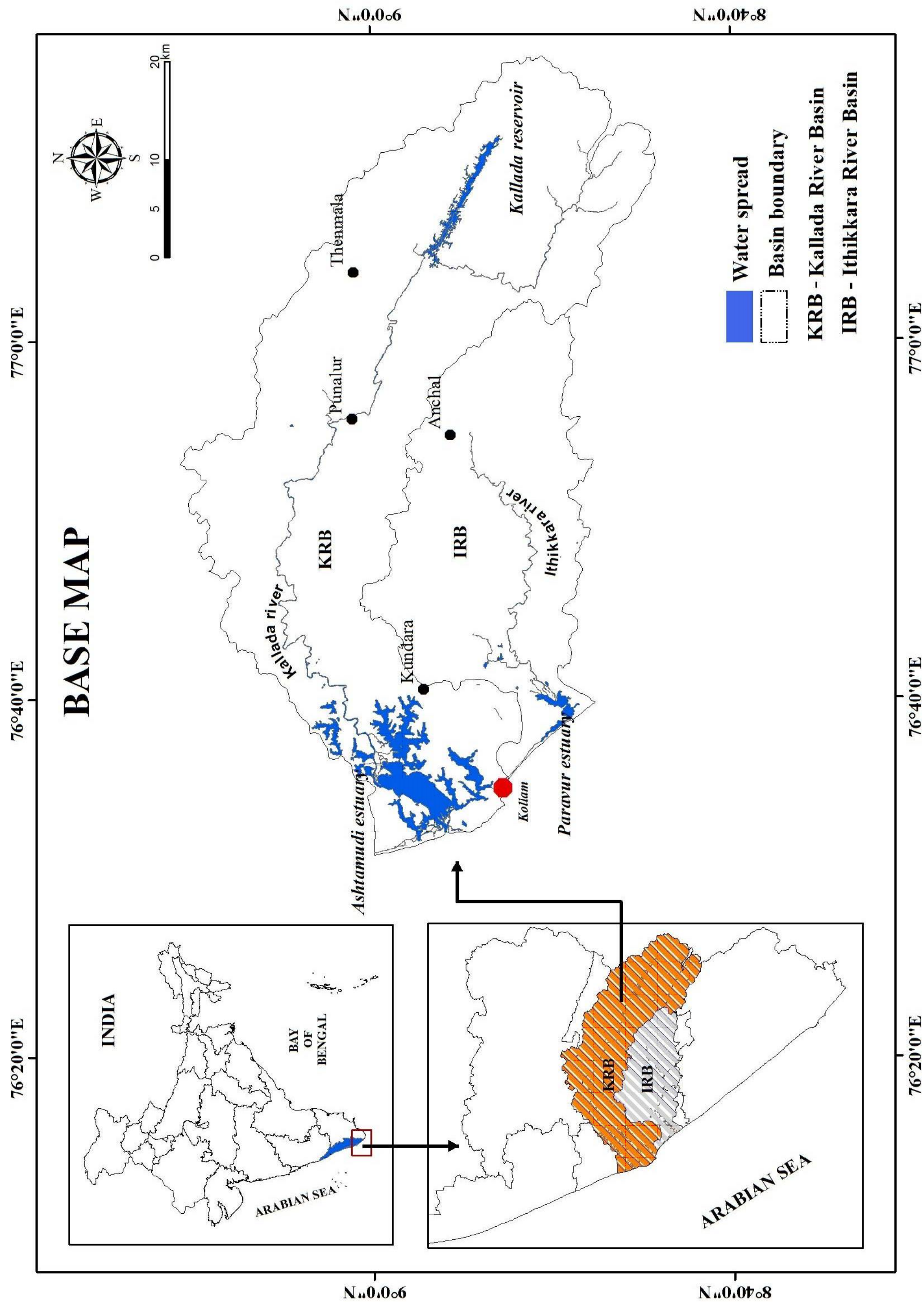


Fig. 1.1 Location of the area selected for the present study.

the interaction of the recharge water with the host rocks in the zones of aeration and saturation. The term water quality has an extremely broad spectrum of meanings. It must be considered relative to the proposed use of water. Water quality problems stem basically from factors such as natural hydrology of a river basin and development and use of land and water resources by human beings. Depending on the inter relation of these two factors, a host of quality problems can occur. Each river basin is unique and it must be subjected to intensive and individual water quality assessment to provide a proper basis for judicious management of the land and water resources. The water quality parameters to be studied are critically dependent on the type of water and the objectives of the study.

Variations in water quality are caused by changes (increase or decrease) in the quantity of inputs into a water body, which may be natural or man-made and cyclic or random. The variability differs between rivers, lakes and underground waters. Underground water has a lower variability than that of rivers or lakes. The rate of water quality changes depends upon the depth of sampling, water volume in the aquifer and the hydraulic conductivity. Variations are often seasonal with a time lag according to the rate of percolation. But direct injection into boreholes or saline intrusion from subterranean sources takes effect more rapidly. Major water quality issues are water scarcity, oxygen depletion, pollution due to urbanization, non- point source pollution, eutrophication, salinity, natural contaminants related to local geology, pathogenic pollution and ecological health.

1.3 Changes in groundwater system

Demographic drivers, science and technology innovations, policy, law and finance are in one way or the other related to changes in groundwater systems. Demographic drivers include population growth, mobility and urbanization. Population growth leads to increasing demand for water and food and to bigger loads of waste and wastewater being discharged into the environment. Expanding urbanization and shifts in land use patterns complicate these pressures further. The same is true for the socio-economic drivers to a large extent. They reflect people's demands and behavior with respect to groundwater.

Intensive groundwater exploitation may be triggered by positive expectations on the economic profitability of groundwater, and by socio-economic conditions that allow the exploitation of this resource. Higher levels of social and economic development enable societies to adapt more easily to changing conditions and to pay more attention to sustainability. Science and technological innovations are the other drivers that have put their mark on the utilization and status of many groundwater systems. For example, aquifer exploration and improved technologies for drilling and pumping have contributed significantly to generating greater benefits from groundwater. But at the same time, the resulting intensive pumping has often increased stress on groundwater systems. Science, assisted by technical innovations in fields such as water use, water treatment and water-reuse helps to define ways of controlling unintended negative impacts.

Policy, law and finance form important drivers of planned change, in the context of groundwater resources development and management. There are two categories of physical drivers. The first is climate variability and climate change. They affect aquifers in arid and semi-arid regions. Minor variations in climatic conditions can have a pronounced influence on groundwater in three important ways: (1) change in the rate of groundwater renewal, (2) change in the availability of alternative sources of fresh water and (3) change in water demand. Climate change is also expected to contribute to sea level rise, which in turn will affect aquifers in low-lying coastal zones, where a large percentage of the world's population lives. The second category of physical driver is natural and anthropogenic hazards. This is quite different from other categories of drivers in the sense that hazards are strongly probabilistic and usually cause a sudden change rather than a trend over time. The different type of land use changes that may lead to changes in groundwater quality is given in Table 1.1.

Table 1.1 Land use change - a potential threat to groundwater quality.

Land use	Activities potential to groundwater pollution
Residential	Unsewered sanitation Land and stream discharge of sewage Sewage oxidation ponds Sewer leakage, solid waste disposal, landfill Road and urban run- off, aerial fall out
Industrial and commercial	Process water, effluent lagoon Land and stream discharge of effluent Tank and pipeline leakage and accidental spills Well disposal of effluent Aerial fall out Land fill disposal and solid waste and hazardous wastes Poor house keeping Spillage and leakages during handling of material
Mining	Mine drainage discharge Process water, sludge lagoons Solid mine tailings Oilfield spillage at group gathering stations
Rural	Cultivation with agro chemicals Irrigation with waste water Soil salinization Live stock rearing
Coastal areas	Salt water intrusion

(Source: CPCB, 2007)

1.3.1 Groundwater – The Indian Scenario

India possesses a great variety and diversity of climate. Climatic conditions govern to a great extent the availability of water resources in the country. The Himalayan rivers of India are snow fed rivers and thus are much vulnerable to climate change. India with an area of 3.29 million square kilometers receives an annual rainfall of about 4000 cubic kilometers (CGWB, 2011). Rainfall is governed by south-west and north-east monsoons. Shallow cyclonic depressions, violent local storms, cool humid winds from the sea etc., also result in additional rainfall in the country.

Indian rainfall shows great temporal and spatial variations on distributions. About 80 - 90% of the total rainfall occurs during four monsoon months. The basin-wise average annual flow in Indian river systems, as estimated by the National Commission for Integrated Water Resources Development, is 1953 km^3. The utilizable annual surface water of the country is 690 km^3. The annual groundwater recharge from precipitation in India is about 342.43 km^3, which is 8.6% of total annual precipitation. The annual potential groundwater recharge augmentation from canal irrigation system is about 89.46 km^3. Thus, the total replenishable groundwater resource of the country has been estimated to be 431.89 km^3. After allotting 15% of this quantity for drinking, and 6 km^3 for industrial purposes, the remaining can be utilized for irrigation purposes. Hence the available groundwater resource for irrigation amounts to about 361 km^3, of which utilizable quantity (90%) is only 325 km^3 (Kumar *et al.,* 2005). India is one of the major users of groundwater in the world, i.e. to the tune of about 230 km^3 of groundwater per year. About 60% of irrigated agriculture and 85% of drinking water demands are relied upon groundwater. Groundwater in India is a vital resource. An increasing number of aquifers in our country face unsound levels of exploitation. If the present scenario continues, in about 20 years, 60% of all India's aquifers will be in critical condition (World Bank, 2010). This will have serious repercussions on the sustainability of agricultural food security, in the long run.

The problem of groundwater pollution in several parts of the country has become so acute that urgent steps for detailed identification and abatement are to be taken up to protect groundwater resources. Indiscriminate use of fertilizers causes leaching of very high concentrations of potassium and nitrate into groundwater at several places in the states of Punjab, Haryana and Uttar Pradesh. Groundwater pollution from industrial sources has reached alarming levels in many states. High levels of hexavalent chromium at Ludhiana and Faridabad, lead near Khetri in Rajasthan, nickel in Coimbatore, cadmium in Kanpur and parts of Delhi are some of the manifestations of heavy metal pollution. Arsenic concentration in groundwater has been reported in levels excessive to permissible limit of 0.05 mg/L in West Bengal (Kumar *et al.,* 2009).

1.3.2 Groundwater - The Kerala Scenario

Kerala, the Gods own country, has 44 rivers, many lakes and wetlands, in addition to productive aquifer system. But there is a marked disparity in the distribution and availability of fresh waters in the state. The disparity is getting widened day by day due to natural and anthropogenic causes. The state has surplus water during 6 months and scarcity during the remaining months. Groundwater extraction for all purposes is mainly from the phreatic aquifers in the state. In recent years, in addition to open wells, both bore wells and tube wells have become popular and catering to the drinking water needs in many districts. Groundwater is also an important source of water for irrigation and industrial uses especially in the districts like Palakkad and Kollam. As per the latest estimation of groundwater resources of in Kerala carried out jointly by Central Ground Water Board (CGWB) and the Kerala State Groundwater Department, the net annual groundwater resource availability in the state is of the order of 6.07 billion cubic metre (BCM) as of March 2011. The gross groundwater draft (extraction) for all uses, as computed from the data collected during the 4th Minor Irrigation Census of Government of Kerala is 2.84 BCM. The domestic and the industrial draft account for 54% of the total draft, whereas irrigation draft comes to about 46%.

Kerala has the maximum density of open wells in the world, but a major portion of the wells do not yield sufficient water during summer (Jessiamma, 2005). Salinity propagates not only to the downstream reaches of rivers but also into the groundwater aquifers of the thickly populated coastal belt. The major groundwater quality problems reported in Kerala are excess salinity, iron, fluoride, hardness and coliforms. The causes of contamination can be attributed to sea water intrusion, domestic sewage and runoff of waste water from industrial and agricultural areas. The water quality problems in the coastal areas are attributed mainly to the presence of excess chloride. In the midland region, concentration of iron and chloride are found to be on the higher side in bore wells. Abnormal values of pH and electrical conductivity are also noticed in a few wells. About 50% of the wells are contaminated by coliforms. The highland zone mostly yields good quality water (Megha *et al.,* 2015).

About two decades ago, groundwater exploitations were restricted to unconfined aquifers through dug wells. The people in the state at that time had enough knowledge to construct wells in valleys and nearby areas. The water table conditions had then enabled water flow in the drainages even during summer season. At present, the introduction of new technology and high-speed rigs has resulted in unabated utilization of the limited groundwater resources. About 88% of the total geographical area of the state is dominated by crystalline rocks that are lacking primary porosity as well as inadequate groundwater prospects (Shaji, 2015). In the alluvial formations which have multiple aquifer systems, quality is sometimes a restraint in the best possible development of available resources. The occurrence and accessibility of groundwater in Kerala show a discrepancy from place to place. The population explosion, urbanization and industrialization are some of the important factors that aggravated the use of groundwater resources over the last few decades.

The over extraction of groundwater in the state has created many destructive effects such as continuous lowering of water levels in both pre-monsoon and post-monsoon seasons, diminution of yield of wells, drinking water scarcity in summer months and earth subsidence. The analysis of decadal water level trend (1996 – 2005) indicates that 13% of monitoring wells of CGWB are showing declining trend of more than 0.1 m/year during pre-monsoon season. The corresponding values in post-monsoon season cross 30% (CGWB, 2009). The water level decline during post-monsoon period is attributed to changes in base flow, high groundwater development for a variety of uses and also alteration in land use pattern.

1.4 Springs and wells

1.4.1 Springs

Spring is a natural phenomenon of a concentrated discharge of groundwater at or above the ground surface as a current of flowing water (Todd, 1980). In arid regions they are less in number. But in many humid regions springs are frequent. Springs are caused by a number of principal and minor factors or by combinations of these factors. The source of water and rock structure which brings it into the surface are the prime factors for the formation of springs. Temperature, dissolved salts, contained gases, rate and amount of flow, form and position of the spring opening are all characteristics of springs, which vary among springs of the same origin.

1.4.2 Classification of springs

A unique characteristic of springs is that they form a three-way zone of interaction between groundwater, surface water and terrestrial ecosystems. The positioning of springs at these three-way zones of interaction has led to inevitable conflicts between human resource use within ecosystems and the natural ecosystem integrity of springs (Sada, 2005). Human activities can have significant effects on the parent aquifer, the spring and the connectivity between the spring and other aquatic habitats (Smith, 2002). Overall, spring habitats, and the biological diversity they support can be regarded as a natural environmental template that is overlain by varying levels of human impact. Conservation of spring systems will generally depend on two factors: (1) maintenance of groundwater quantity and quality and (2) minimization/mitigation of anthropogenic disturbances to the springs themselves and their associated habitats (Knott and Jasinska, 1998).

Spring differs from a seepage (or seep) with respect to its flow characteristics. Seepages are slow movement of water to the ground surface. And, most often the seepage water comes out not only from any deepest opening, but from pores in the ground. The amount of water yielded by most seeps is small. A series of seeps and springs may occur along a line, which is then called a spring line. The springs and seeps rise under pressure transmitted through the water as it lies as a continuous body in the voids of the rock. Groundwater takes soluble substances from the rocks through which it flows.

Springs can be divided according to its temperature into thermal and non-thermal springs. Thermal springs are usually called hot springs or warm springs depending on the degree of temperature. The term cold springs is also used to refer the non-thermal springs which may usually have temperatures equal to or below normal atmospheric temperature. 'Boiling' springs usually have a sandy bottom, through which water emerges with some force. The sand is constantly getting agitated and appears that it is boiling. The emission of gas or vapour with the water makes bubbling springs.

Perennial or permanent springs flow throughout the year. Some springs flow only at night because of a very delicate hydro- meteorological setting.

Periodic springs are not closely related to the fluctuations in rainfall and flow at full strength for long or short periods, depending on the existence of open cavities. Intermittent or temporary springs flow only during or after rain. Geysers are hot springs which emit a stream of mingled steam and hot water. The springs occurring along the sea coast are ebbing and flowing springs. The expulsion of air from cracks and pores of the rock results blowing or breathing springs. In arid climates, mound and knoll springs occur. The water emerges at or near the top of a mound which has been built up by the accumulation of wind-blown sand and dust in the belt of vegetation surrounding the spring. Pool springs have large, deep orifices filled with clear water (Bryan, 1919).

Calcium carbonate and silica are the most common minerals of spring deposits. The waters which circulate in the ground are divided into two types: (i) shallow waters and (ii) deep-seated waters. The shallow waters are resulting mainly from precipitation at the surface and move through openings, due to gravitative pressure transmitted through a continuous body of water, lying in the pore spaces and fractures of the rocks, i.e., by hydrostatic head. Deep-seated waters have a complex origin. They are water derived by absorption from the surface, water entrapped in sedimentary rocks at the time of their deposition, and/or water expelled during the phase of crystallization of igneous rocks. Figure 1.2 illustrates springs due to deep-seated water. It is believed that these waters do not move because of hydrostatic head, i.e., they are not connected with any overlying body of water, but the flow is the result of other factors that operate deep within the earth (Bryan, 1919). A perennial spring mostly has a deep-seated origin. The minimum depth from which the water may emerge can roughly being estimated from the temperature of the water, on the assumption that there is 1° F for every 60 to 100 feet of increase in depth.

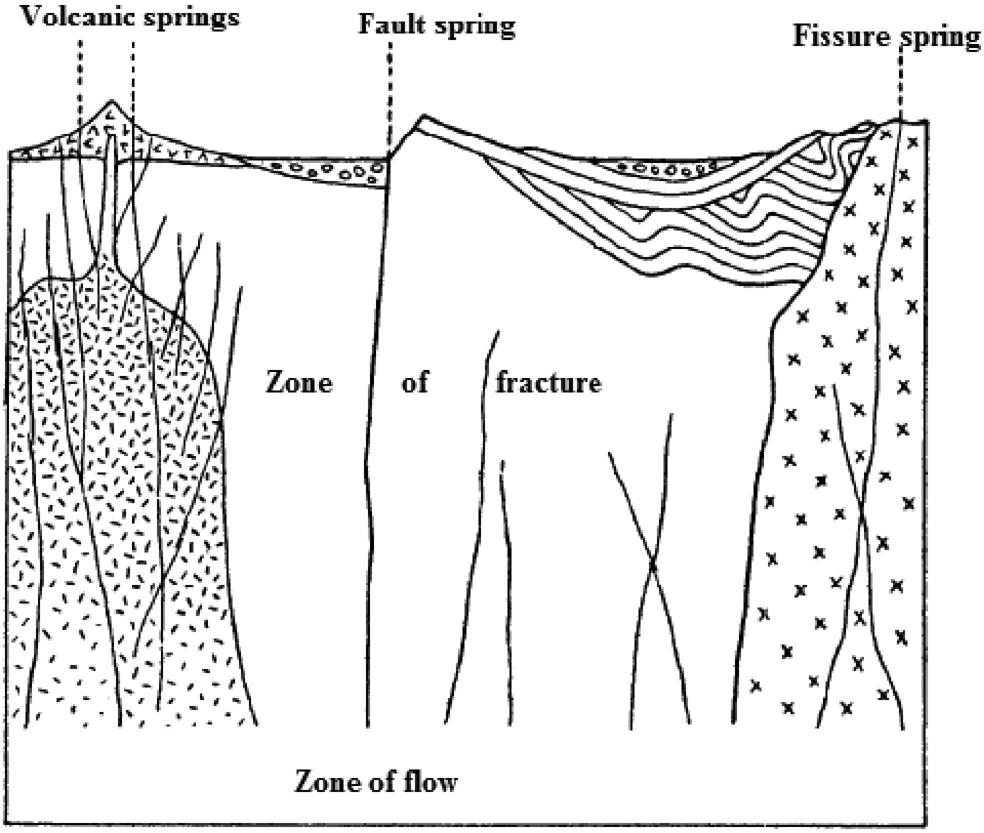


Fig. 1.2 Schematic diagram illustrating springs due to deep-seated water forcing.

Springs due to deep-seated water forcing: They are of two types, i) Volcanic springs and ii) Fissure springs

i) Volcanic springs: Associated with volcanism or volcanic rocks; water is commonly hot, highly mineralized and contain gases. Grade from gas vents to springs of normal temperature and are indistinguishable from those due to other causes.

ii) Fissure springs: Due to fractures extending into deeper parts of the crust; water is usually highly mineralized and is commonly warm or hot. They are of two types: (a) Fault springs (associated with recent faults of great magnitude) and (b) fissure springs (no direct structural evidence as to origin, but because of temperature and steady flow, believed to have deep origin).

Springs due to meteoric and occasionally other waters moving as groundwater under hydrostatic head are of 4 types : i) Depression springs, ii) Contact springs, iii) Artesian springs and iv) Springs in impervious rocks

i) Depression springs: Springs that emerges due to land surface truncation with respect to water table in porous rocks.

ii) Contact springs: Spring that emerges when porous rock overlies impervious rock.

iii) Artesian springs: Spring that emerges due to pervious bed between impervious materials.

iv) Springs in impervious rock: Spring that emerges due to more or less rounded channels in impervious rocks (known as Tabulator springs) or due to fractures consisting of joints, bedding planes, columnar joints, openings due to cleavage, fissility, schistosity, cross-bedding planes, and faults in impervious sedimentary, igneous, and metamorphic rocks (also known as Fracture springs).

1.4.3 Classification of springs by Tolman (1937) and Fetter (1980)

Geological heterogeneities can have a profound effect on ground water flow. For, deeper regional flow systems in areas of low relief, and also in karst terrains (where flow typically occurs in discrete channels), identification of the source area is more complicated and would usually require more detailed hydro geologic data. Hydrogeologists recognize a wide variety of spring types, and several physical classification schemes have been developed to describe the interaction between springs, the underlying ground water and the surrounding landscape. Table 1.2 shows the five categories of springs put forth by Tolman (1937).

Table 1.2 Classifications of springs by Tolman (1937).

Sl. No.	Types of Springs	Geologic material	Type of porosity	Setting
1	Depression springs	Unconsolidated sediments	Primary, intergranular	Occurs where water table intersects the land surface.
2	Contact springs	Unconsolidated sediments	Primary, intergranular	Occurs at or near base of underlying confining unit.
3	Fault/Fracture/ Joint springs	Bedrock	Secondary fractures	Occurs along joints, fractures or faults where they intersect the land surface.
4	Karst springs	Carbonate bedrock	Secondary solution channels	Occurs where solution channels developed in limestone and dolomite intersect the land surface.
5	Lava springs	Volcanic bedrock	Primary, flow tubes, interbeds and/or joints	Occurs where lava tubes, interbeds and cooling joints intersect the land surface.

Fetter (1980) also has given a five fold classification for springs which are described below:

i) Depression spring: Topographical depression intersects an unconfined aquifer.

ii) Contact spring : Permeable, water-bearing stratum overlies an impermeable stratum. Water discharges where the contact zone between the strata intersects the land surface.

iii) Fault spring: The faulted, impermeable rock stratum is located downslope of a ground water flow path.

iv) Sinkhole spring: The process of dissolution of carbonate rocks (karstification) lead to the development of sinkholes that intersect the water table.

v) Fracture spring: The fracture zone between two opposing rock strata provides a flow path for ground water to discharge.

1.4.4 Classification schemes of aquatic biologists

In addition to classifications proposed by hydrogeologists, attempts for classification of springs have also been put forth by aquatic biologists (Steinman, 1915; Zollhofer *et al.,* 2000). The most common and widely accepted classification was proposed by Steinman (1915) who developed a typology based on flow patterns:

Limnocrene: Spring discharges through the bed of a pond or lake.

Rheocrene : Spring discharges form a flowing stream.

Helocrene : Small springs (seepages) form a spring-fed marsh.

The classifications proposed by biologists tend to stress the role of springs as source of surface water habitats, whereas definitions put forward by hydrogeologists tend to focus on springs as the endpoint of groundwater flow paths.

1.4.5 Human interest in springs

Springs have apprehended the attention of scientists and philosophers for hundreds of years. Spring waters, particularly those from mineral and hot springs, have long been believed to possess therapeutic and medicinal value. However, no scientific evidence exists regarding their medicinal properties. On the contrary, water from hot springs often contain large amount of toxic dissolved materials, such as arsenic, that may have leached from underground layers of rocks (Chapelle *et al.,* 1997). Human usage and the resulting direct impacts are often critical in the health of springs and its adjoining ecosystems. Indirect human effects include changes in the quality and quantity of groundwater emerging out of springs.

1.4.6 Springs in the study area

The springs are generally confined to the highlands and coastal lowlands of the study area. Springs in the highlands, generally have water flowing through fractures and / or a narrow opening in the crystalline rocks or through the contact zones of unweathered rock with the weathered over burden. They generally fall in the category of fracture springs or contact springs. The fracture springs are genetically related to the Western Ghats evolution (up warping) and are generally aliened parallel to the fracture zones/lineament zones (Fig.1.3). The springs in the highlands play a vital role in meeting the drinking water requirements of a section of people in the area. CWRDM (1988) has identified many perennial springs with good discharge characteristics in the highland belt of Kerala. Water from these springs is generally good for drinking purposes when it is collected at the spring mouth. In highlands, there is very good scope for spring - based small scale rural water supply schemes. The springs in the coastal lands are generally associated with the cliffed coasts or scraps in the Neogene formations of the study area. They generally fall in the category of contact springs. Based on the point of emergence of water on the land surface, springs of the study area can be classified into two categories: (i) Free falling type wherein the water discharge occurs through an orifice located above ground surface and (ii) Boiling type or pool spring types wherein water emerges below water column or close to the ground surface. The boiling type springs usually form spring pools or small ponds around its orifice.

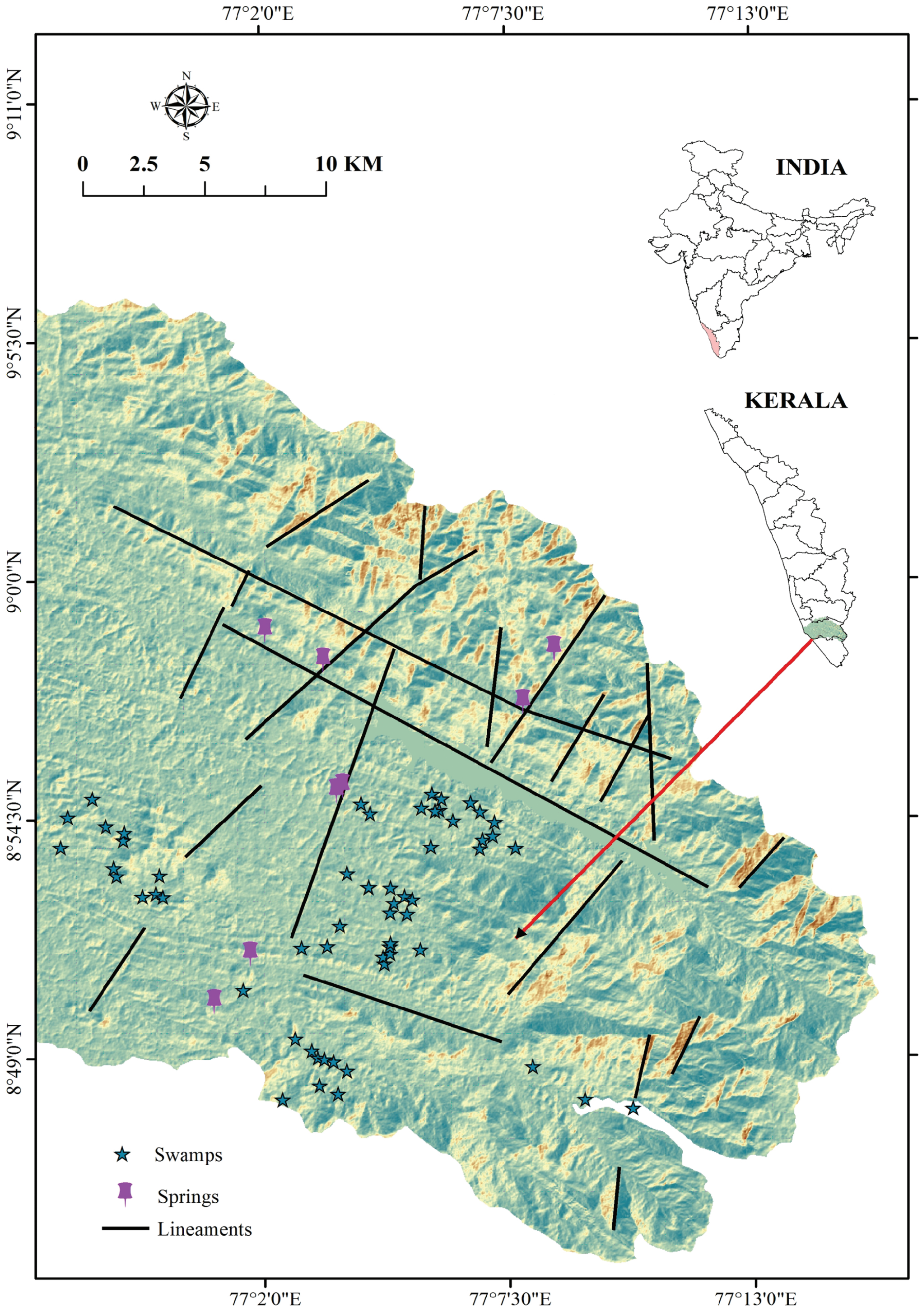


Fig. 1.3 Springs in the upper catchments of Kallada river aligned parallel to lineaments.

1.4.7 Wells

A well is a hole or shaft, excavated in the earth for bringing groundwater to the surface. Wells are constructed and designed depending on its purpose. Dating from Biblical times, dug wells are in use throughout the world. Depth of wells may range depending on the level of the water table. Diameter of the well varies generally from 1 to 10 m. In areas containing unconsolidated glacial and alluvial deposits dug wells can yield large quantity of water from shallow sources. Dug wells should be deep enough to extend a few meters below the water table.

Traditionally, collection of groundwater is done primarily through dug wells. People use wells for extraction of water for both drinking and irrigation purposes. It is cost-effective as compared to other methods of water extraction. The quality of water obtained from a well depends on intake source area, condition of terrain, annual rainfall flow, storage capacity of the ground, type of the well, hydrogeology of the area, distance of the well from pollution sources, elevation and slope, flora and fauna of the region, etc. Wells are classified generally into two types: (i) shallow well (dug well) and (ii) deep well (bore well or tube well). In the present study dug wells are chosen for detailed investigations.

A typical dug well in under-developed regions is often no more than an irregular hole in the ground that intersects the water table. A pick and shovel are the basic implements used for digging. Loose material is hauled to the surface in a container by means of suitable pulleys and lines. Large dug wells can be constructed rapidly with portable excavating equipments such as clamshell and orange-peel buckets. For safety and to prevent caving, lining (or cribbing) of wood or sheet piling should be placed in the hole to brace the walls. A domestic dug well is permanently lined with a casing (often referred to as a curb) of wood staves, brick, rock, concrete, or metal. Curbs should be perforated or contain openings for entry of water and must be firmly seated at the bottom. Dug wells should be deep enough to extend a few meters below the water table. Gravel should be backfilled around the curb and at the bottom of the well to control sand entry and possible caving.

Dug wells or open wells are the conventional groundwater extraction structures in Kerala. In the State, almost every house hold has their own well for meeting their domestic water requirements. The concept of community well is quite strange among the people of Kerala. Kerala state is reported to have the maximum well density (298 wells/sq.km) all over the world (Monahan, 2015). The State has a total of about 6.95 million wells within its administration boundary. In crystalline and lateritic terrains, groundwater is extracted through dug wells and bore wells. Along coastal alluvium, groundwater is exploited through a variety of structures – dug wells, filter point wells and tube wells. The culture of groundwater development through bore wells is gaining momentum in the area in recent years. Deep seated fractures in the crystalline rocks of the Ithikkara and Kallada rivers basin form potential aquifers. The lithology and groundwater level varies with respect to the physiographic divisions of the state. The number of open wells and well density also varies considerably with respect to the physiographic divisions of Kerala (Table 1.3).

Table 1.3 Details of dug wells in the different physiographic regions of Kerala.

Sl. No	Physiographic Region	Estimated no. of wells in lakhs (2003-2006)	Well density wells/sq.km (1980 – 1991)	Well density wells/sq.km (2003-2006)
1	Lowland	17.5	215	500
2	Midland	41	150	277
3	Highland	10.45	70	117
	Total	6.895 million	145	298

Source: (CWRDM, 2006)

In lowland region, 44 – 97% of the open wells are being used for drinking purpose and 1 – 27% of wells for irrigation purpose. A total of 6.5% of wells are seen abandoned. In the midland, 87% of wells are used for domestic use and 4% for irrigation purposes. The number of abandoned wells and ponds are more in the midland belt of Kasargod district. Kollam district drained by Ithikkara and Kallada rivers have the maximum well density in midland. In Thrissur district, most of the dug wells are used for irrigation purposes. In highland region, 77% of wells are used for domestic purpose and the rest for irrigation purpose. In 33 – 83% wells in the highland regions, water are found to be contaminated (Megha *et al.,* 2015). The well use pattern for the state of Kerala is given in Figure 1.4.

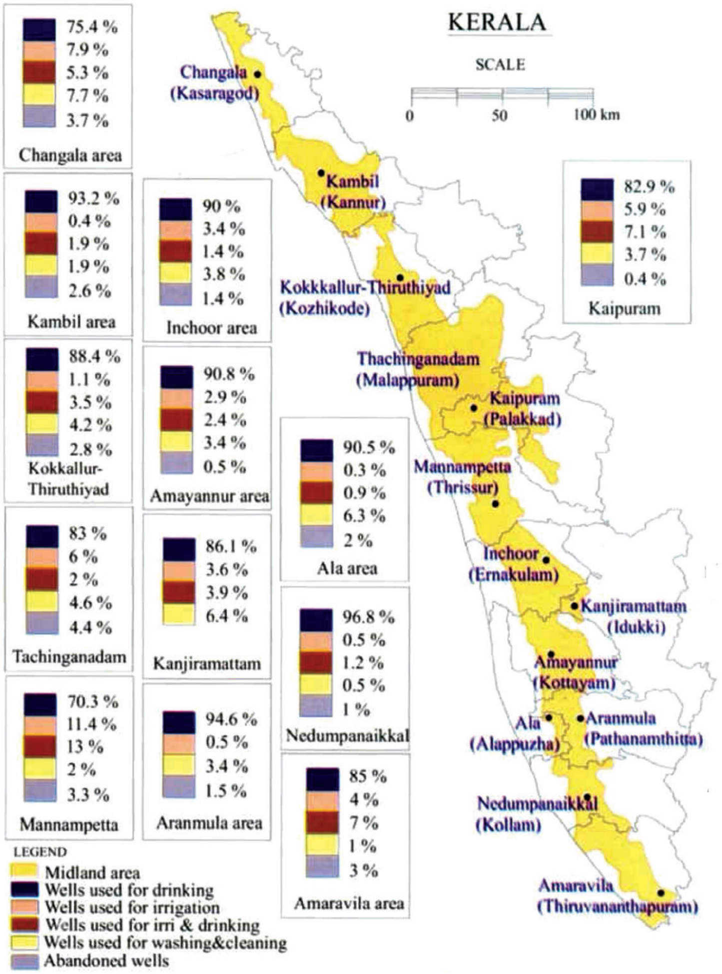


Fig. 1.4 Well use pattern (Source: CWRDM, 2006).

1.5 Aim and Objectives

The aim of the present study is to assess the water quality and drinking water potential of the groundwater resources of two important river basins of Southern Western Ghats - the Ithikkara and Kallada river basins.

The key objectives of the study are:

- To locate and map the natural springs in the study area and to assess their geo-environmental settings.
- To estimate the water quality and drinking water potential of the spring and well water sources of the study area.
- To evaluate the hydrogeochemical processes of spring and well waters of the study area with special reference to silicate weathering.
- To study the causes for water quality changes in the study area.
- To delineate the groundwater potential zones of the study area.
- To suggest necessary remedial measures for improving the quality and quantity of spring and well water sources of the study area.

1.6 Scope of the study

The present study deals with the hydrochemical characterization and water quality assessment of the spring and well water sources of the Ithikkara and Kallada river basins of Southern Kerala, SW India. The fresh water sources of these rivers and its basin area play a key role in sustaining the life, greenery and economic base of many of the developmental centers including the Kollam Corporation. Although many studies are available on the surface water sources, not much attention has hither to been made on the spring and well water sources of these river basins. As sustainable water management is fast becoming a necessity, with looming crisis over water resources threatening water security and livelihood of the population and the environment, systematic monitoring and assessment of water is imminent for designing effective, efficient and environment – inclusive development of the pristine freshwater resources. In this context, the study carried out in the spring and well water sources of Ithikkara and Kallada river basins receives considerable importance. The conclusions and recommendations drawn from the study will be useful not only for chalking out sustainable management strategies for the fresh water sources of the two rivers selected for the present study, but also will be useful to the other river basins in the country having similar geo-environmental settings.

Chapter - 2

GEOENVIRONMENTAL SETTING OF THE STUDY AREA

2.1 Introduction

This chapter deals with the geoenvironmental setting of the study area comprising the Ithikkara and the Kallada river basins of Southern Western Ghats. The Ithikkara and Kallada rivers are two perennial rivers of Kollam district in Southern Kerala. The salient features of the rivers are given in Table 2.1.

Table 2.1 Important features of Ithikkara and Kallada rivers selected for the present study.

Sl. No.	River characteristics	River	
		Ithikkara	Kallada
1	River length (km)	56	121
2	Basin area (km^2)	660	1699
3	Order of the river	6	7
5	Head water channel (m)	240	1524
6	Water discharge (Mm^3)	489	3375

(Source: CESS, 1984; CWRDM, 1995)

2.2 Location, Extent and Accessibility

Ithikkara and Kallada rivers are the life lines of Kollam district (Fig. 1.1). The entire area drained by these rivers lies between North latitudes 8°45’ - 9°15’ and East longitudes 76°30’ - 77°15’. The study area is bounded by Tirunelveli district of Tamil Nadu in the east, Lakshadweep Sea in the west, Alappuzha and Pathanamthitta districts in the north and Thiruvananthapuarm district in the south. The maximum distances between north and south, and east and west are 38.7 km and 77.3 km respectively. The area has a coastline of about 37 km. About 20% of the total area chosen for the present study belongs to the lowland – coastal plains, 63% belongs to midland and rest belongs to highland mountainous areas. In addition to the surface water sources, a considerable section of the people in the area also depends on well and spring water sources for their fresh water requirements.

2.3 Population

As per reports of Census of India, population of the study area in 2011 was 3,48,657; of which 1,68,006 were male and 1,80,651 were female. The population density was 1038 persons per sq km. The population density is more in the coastal areas and urban centers, and is low in highland areas (Jayadev, 2012). The sex ratio of the study area shows an increasing trend over the census years. According to the 1991 census, there were 1043 females for every 1000 males, while it was 1022 as per the 1981 census. According to 2001 census, the sex ratio of the study area was 1070 per 1000 males. The gender status of study area is at par with other districts of Kerala (Devi, 2004). The density of population of the study area has increased from 871 persons per sq. km. in 1981 to 963 in 1991. The total population of Kollam district according to 2001 census, was 2,585,208 and population density was 1037. As per 1991 census, the district had a literacy rate of 90.47% against 72.95% in 1981.

2.4. Topography

Physiographically, the study area comprises of three natural divisions viz., i) lowland bordering the sea coast, ii) midland consisting of undulating terrain with low hills and valleys and iii) highland covering mainly forests. The elevation of the terrain gradually increases towards the highlands. The height of the Western Ghats decreases generally from North to South. There are several peaks above 500m height in the study area, the highest of which is at Muthiramala (Mudramala) having a spot height of 1042 m. The Achankovil gap locally known as Aryankavu pass, gives an easy access by rail and road to the adjoining Tirunelveli district. The study area falls under the physiographic sub-divisions such as coastal zone, rolling plain, midland, foothill zone, valley zone and highland (Chattopadhyay, 1995).

2.5 Slope

The slope of a topographic landform refers to the amount of inclination of that surface to the horizontal. The slope of the study area ranges from nearly level surface to 67.430. Figure 2.1 depicts the slope map of the study area. The varying degree of slope is reflected in the positioning of different type of wetlands in the study area. The slope profile of the study area can broadly be divided into nearly level, gently sloping, moderately sloping and moderately steeply sloping to very steeply sloping. Of this, the land area with very steeply sloping category is confined to the south east part of study area. Moderately sloping terrain consists of about 30% of the total land area (Jayadev, 2012).

2.6 Geomorphology

The detailed geomorphic units of the study area is given in Figure 2.2. The geomorphology of the area includes coastalplain, floodplain, pediplain, denudational hills, denudational structural hills, piedmont zone, plateau, residual hill and valleys (Table 2.2). The area under the altitudinal range of 80-300m contours show rugged topography.

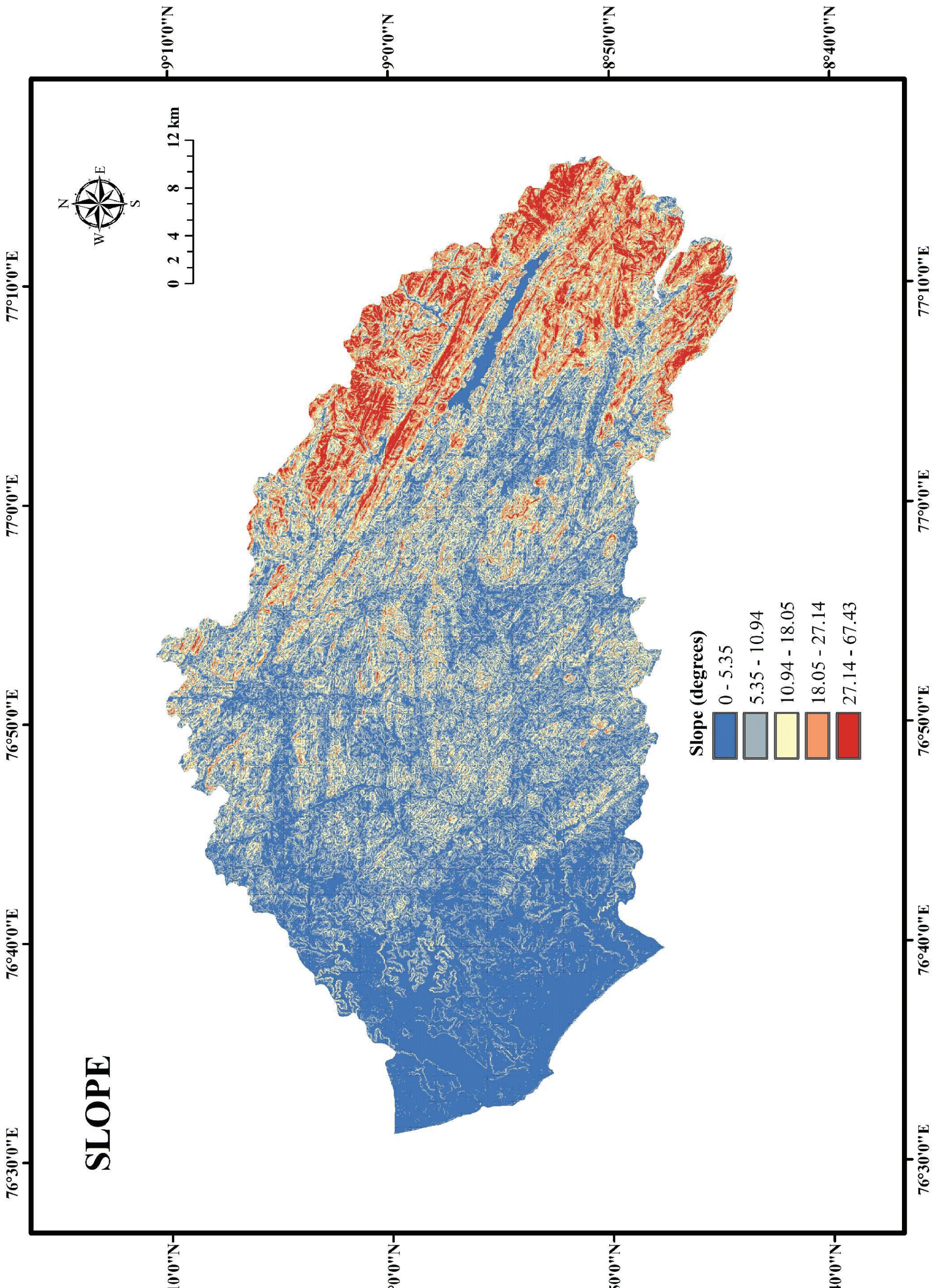


Fig. 2.1 Map showing the various slope categories of the study area.

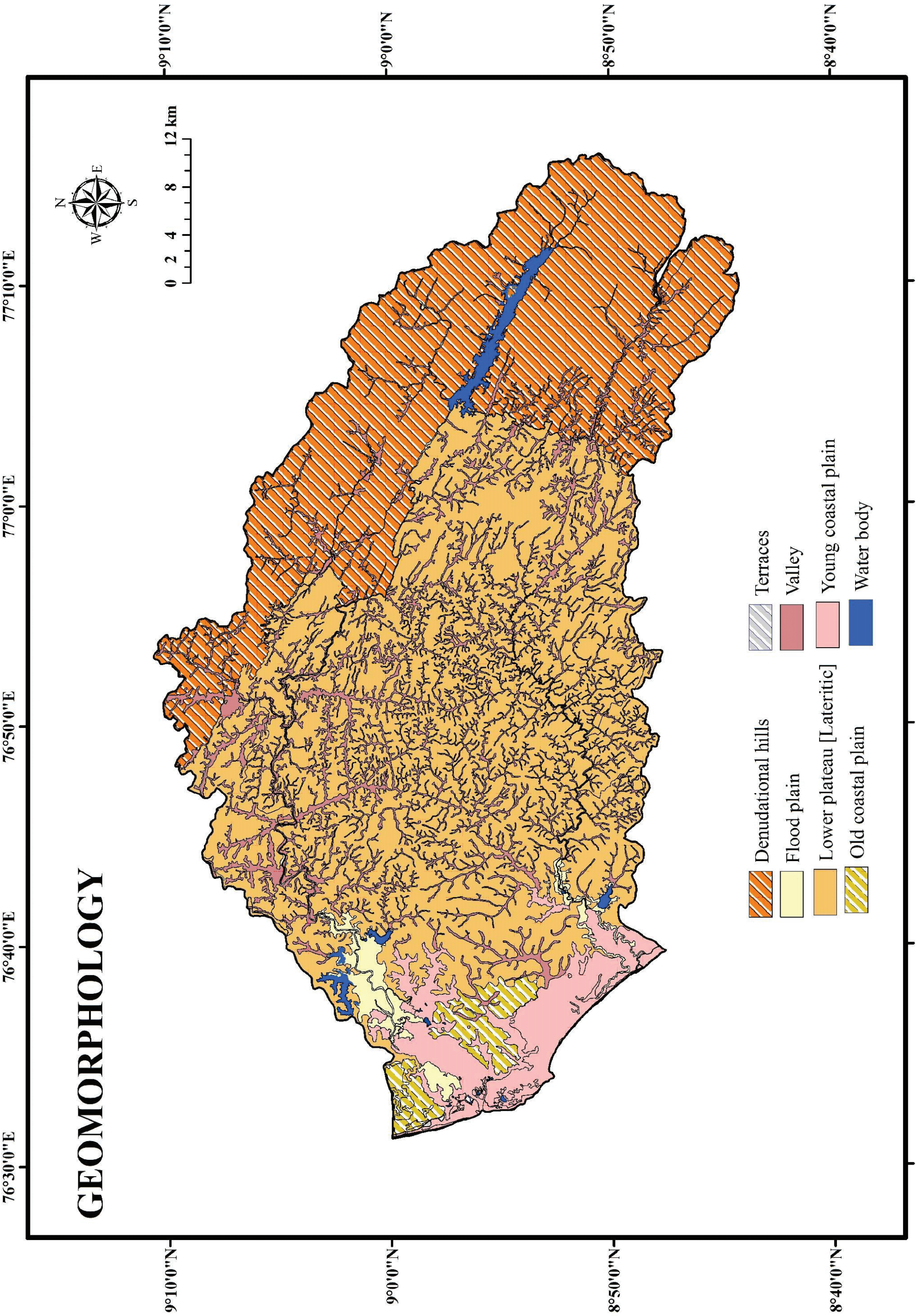


Fig. 2.2 The various geomorphic units identified in the study area.

The rivers Ithikkara and Kallada and their tributaries drain this zone, which has a land slope of more than 35%. This unit occupies the maximum area of Kollam district and consists of NW- SE trending ridges, circular ridges and narrow valleys with steep slopes.

Table 2.2 Geomorphologic units in the study area.

Sl. No.	Unit/Type	Area in sq.kms
1	Denudational hills	685.96
2	Flood plain	52.920
3	Islands	0.600
4	Lower plateau lateritic	1042.720
5	Old coastal plains	46.920
6	Terraces	0.530
7	Valleys	281.130
8	Canal	0.7420
9	Water body	44.980

2.7 Geology and Hydrogeology

Geologically, study area comprises crystalline rocks of Archaean age in the highlands and midlands and sedimentary formations of Miocene to Recent ages in the lowlands. The unconsolidated Tertiary (Neogene) deposits are exposed on the coastal cliffs facing the Arabian Sea. The area is represented by a variety of rock types which include crystalline rocks, charnockite, khondalite, biotite gneiss, etc. Groundwater occurs in all the geological formations from Archaean crystallines to recent alluvium. The river channels are covered by alluvial deposits. Figure 2.3 represents the geology map of the study area.

The important aquifer systems in the study area are: weathered, fissured and fractured crystalline formations, semi-consolidated tertiary formations occurring along the coastalplain, laterites covering midland region and recent alluvium occurring along the coast, major rivers and valleys.

The crystalline formations of the study area are composed of rocks such as khondalites, charnockites, granite gneisses and intrusives. These crystalline aquifers are highly heterogeneous in nature due to variation in lithology, texture and structural features even within short distances. Groundwater generally occurs under phreatic conditions in the weathered mantle and under semi-confined conditions in the fissured and fractured zones at deeper levels. Among the crystallines, khondalites are highly weathered and well joined and form good water bearing zones. In the case of charnockites, weathering is generally low and the joints in the rock massif are less interconnected. Moreover, most of them are tight and surfacial and neither provide place for storage nor allow free movement of groundwater. Hence wells piercing charnockites are generally dry during summer months. Deep seated fractures in the crystalline rocks form potential aquifers in the study area.

The Tertiary deposits occurring along the coastal plain consist of Vaikom, Quilon and Warkali formations and are overlain by 10-15 m thick recent alluvium. These sediments offer good aquifers in the lowlands of the study area. Laterites occurring as a cap over the crystalline and tertiary sediments cover a major portion of the Ithikkara and Kallada river basins. The thickness of laterite increases from east to west. Groundwater occurs under phreatic condition in this formation. Laterite forms a potential aquifer along the valleys and topographic lows. Due to the highly porous nature of this formation, the groundwater drains off from the aquifer in summer and thus water scarcity is prevalent in the flat topped lateralised hills and their slopes.

Groundwater occurs under phreatic condition in the recent alluvium occurring

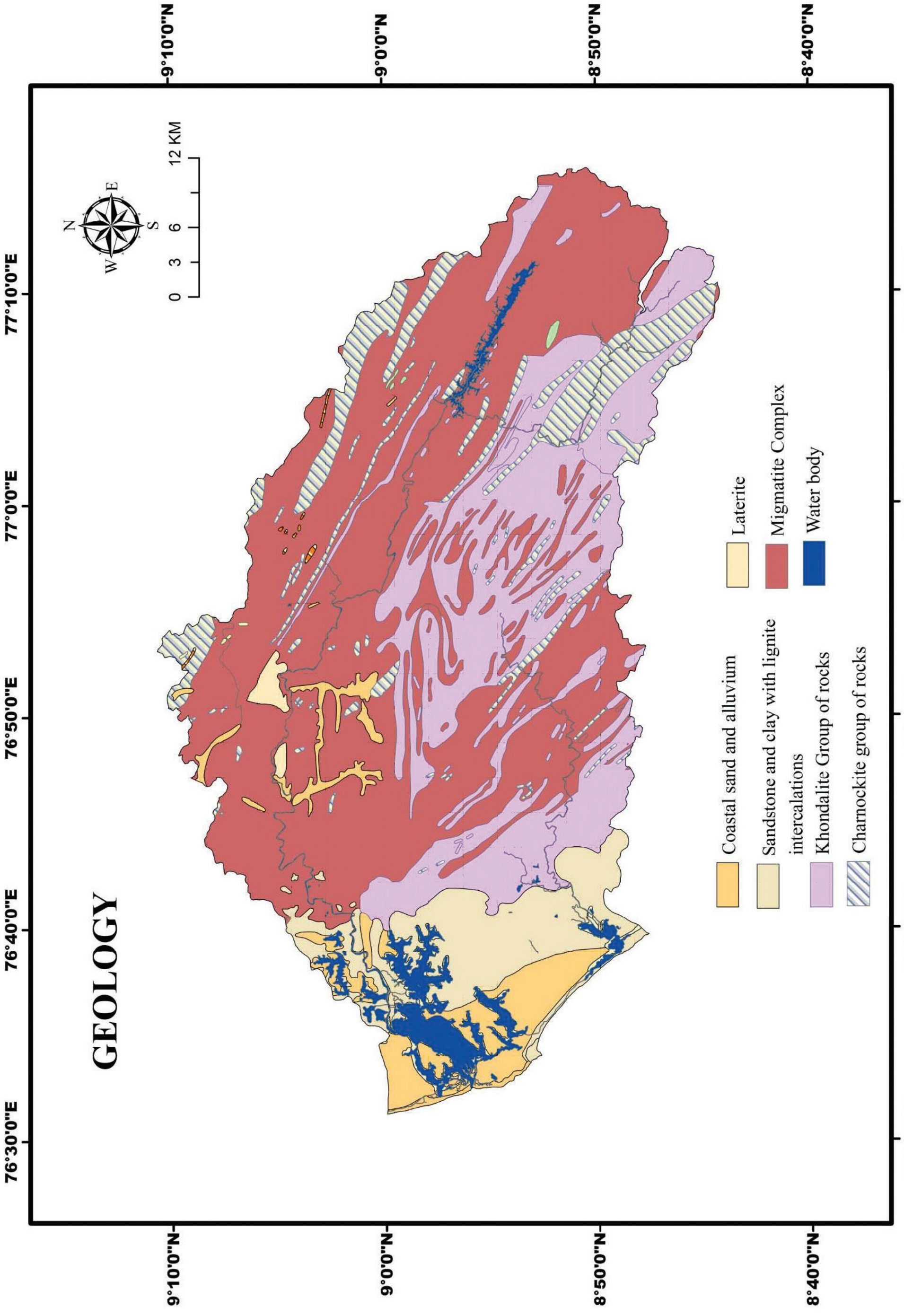


Fig. 2.3 Geological map of the study area (Source: GSI, 2005).

along the coastalplain and the valleys in the midland and highland regions. The alluvial deposits occurring along the coastal plain of the study area forms the most potential aquifer and is extensively extracted through a large number of dug wells. These alluvial deposits are composed principally of sand-clay interlayers. The alluvium occurring along the valley fills are composed of sand, gravel, pebbles and boulders which is in a highly assorted condition. And, as a result, they do not yield enough water despite having the required porosity.

2.8 Soil

Soils are categorized mainly based on the water draining capability. The major categories include imperfectly drained, moderately drained, moderately well drained to imperfectly drained, somewhat extensively drained to moderately drained, extremely drained to well drain rocky outcrops. About 80% of soil is included in the well drained category. The moderately well drained is another major group that occupies about 7% of total land area of the Ithikkara and Kallada river basins. On the basis of textural properties (i,e., sand, silt and clay contents), the soils of the study area are categorized into clayey, clayey-loamy and loamy soils (Fig. 2.4). On the basis of the erosion of the soil, the soils of the study area are categorized into 7 groups. They are: moderate, moderate to none, moderate rock outcrops, moderate-severe, none to slight and severe to moderate erosion. Moderate erosion category occupies about 65% of the total geographical area of the region. Except the lowland region, the moderate erosion category occupies premier position in the other two physiographic divisions. While in the coastal area, soils with moderate to none and none to slight erosion occupy prominent position as the area shows very less slope. The soils with moderate to severe erosion is more prominent in the highland as well as the foothill zones of the lowland, especially in Thenmala, Kulathupuzha, Anchal, and Chithara regions. Based on the place of occurrence, wetland soils in Kerala can be broadly classified into four groups.

They are wetland soils of coastal area, wetland soils of depressional land in and around river mouths (including those occurring at or below mean sea level and near lakes), wetland soils of broad valleys and plains of the lowland and midlands (Premachandran and Roshni, 2007). Varkala, Mannar, Ummanoor, Mylom and Karavaloor series are the major soil series in the study area. The soil characteristics along with sample locations are depicted in Table 2.3 (SSO, 2007).

2.9 Climate

The study area experiences heavy rainfall during the southwest and northeast monsoon seasons. During January to May, rainfall is considerably less. March and April months are the hottest months. December to February is the coldest months. The average mean monthly maximum temperature ranges from 29.9 to 36.40C and minimum from 19.4 to 23.80 C.

Rainfall increases from the coast to the eastern hilly regions. Southwest monsoon contributes nearly 55% of the total annual rainfall. Followed by this is the northeast monsoon season from October to December which contributes about 24% of rainfall. The balance 21% is received from January to May as pre-monsoon showers.

2.10 Stream Network

The study area is the part of Southern Western Ghats and is drained by Ithikkara and Kallada rivers. The Ithikkara basin has its highest elevation north of Madathara (271 m amsl) on the eastern side and slopes down to sea level west of Mayyanad. The river is a sixth order stream with a slope of 8.2 m/km. The length of the river is 56 km and the total drainage area comes to about 660 km^2. Two major tributaries of Ithikkara river are Ithikkara Ar and Pallimon Ar which joins near Chathanoor and before debouching into the Arabian Sea through the Paravur estuary. The river passes through the villages of Vayala, Pampira, Ayur, Chadayamangalam, Thruvambhagom,

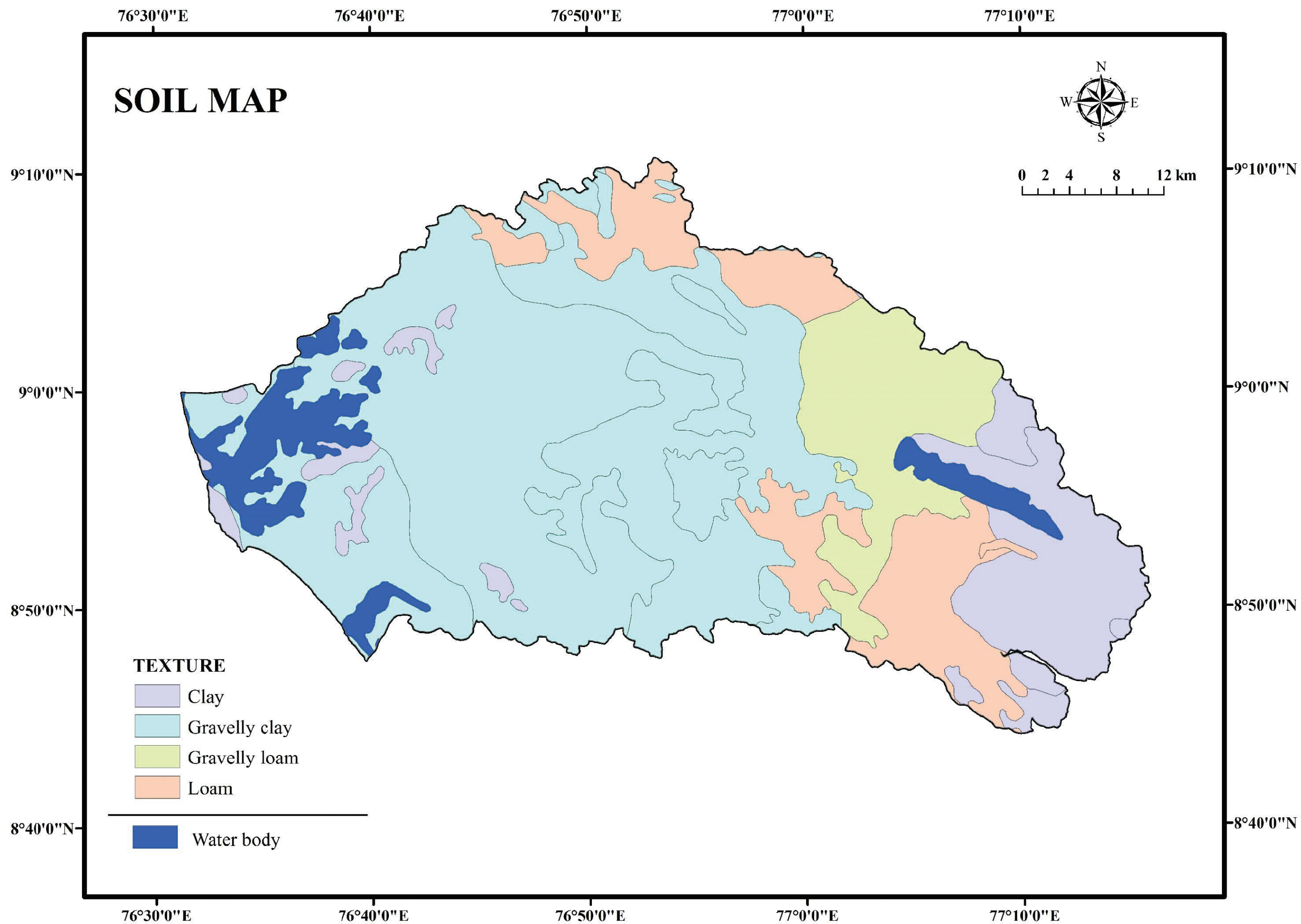


Fig. 2.4 Map of the study area showing different soil categories spread in the region (Source: NBSS and LUP, 2005).

Table 2.3 Soil characteristics of the study area (Source: SSO, 2007).

Soil Series	Varkala	Mannar	Ummanoor	Mylom	Karavaloor
Order	Ultisols	Entisols	Ultisols	Entisols	Ultisols
Sub-order	Ustults	Psamments	Ustults	Fluvents	Humults
Great group	Plinthustults	Quartzipsamments	Plinthustults	Ustifluvents	Plinthuohumults
Sub-group	Typic Plinthustults	Oxyaquic Quartzipsamments	Typic Plinthustults	Oxyaquic Ustifluvents	Typic Plinthuohumults
Family	Clayey-skeletal, mixed, isohyperthemic	Coated, mixed, isohyperthermic	Clayey-skeletal, mixed, isohyperthemic	Fine loamy, mixed, isohyperthermic	Clayey-skeletal, mixed, isohyperthemic
Pedogenesis	Warkallai formation; moderately sloping to moderately steep low hills; Elevation of 20 – 100 m amsl	Mixed alluvium; gentle slope; elevation < 10 m amsl.	Weathered gneissic rocks; moderately slope to steeply slope; elevation of 20 – 100 m amsl.	Alluvio-colluvial; very gently to gentle slope; elevation of 20 – 100 m	Weathered gneissic rocks; strongly sloping to very steep land; elevation of 200 – 600 m amsl
Texture	Gravelly sandy clay to gravelly clay (A Horizon) Gravelly clay (B Horizon)	Sand to loamy sand (A Horizon) Loamy sand to sandy loam (B horizon)	Gravelly sandy clay loam to gravely sandy clay sand (A Horizon) Gravelly sandy clay loam to gravely clay (B horizon)	Loamy sand to sandy clay loam (A Horizon) Gravelly sandy loam to clay (B horizon)	Gravelly sandy clay loam to gravely clay (A horizon) Gravelly clay (B Horizon)
Thickness (cm)	90 – 135	> 150	15 - 20	15 - 20	8-15
Drainage	Well drained	Moderately well drained	Well drained	Poorly drained	Well drained
Permeability	Slow	Rapid	Moderately slow	Slow	Slow
Productivity	Low to medium	Low	Medium	Medium	Low to medium
Erodibility	Severe	Poor	Severe	Low to medium	Severe
Vegetation	Coconut, tapioca, banana, fruit trees and pepper	Coconut, tapioca and banana	Coconut, Rubber, Tapioca	Paddy, banana, tapioca	Coconut, rubber, tapioca and fruit trees

Atturkonam, Adichanalloor, Kottiyam and Chathannor. The Kallada river basin has its highest elevation at Karimalaikodkal (1763 m amsl) on the eastern side and reaches almost the sea level west of Karunagapally town. The length of the river is 121 km and drainage area comes to about 1699 km^2. The general drainage patterns of both the basins are dendrictic. But certain parts of the Kallada river in its upland shows rectangular drainage pattern due to its structural control. Rainfall is the major source of recharge to groundwater in the study area. These rivers are in their youthful stage and are quick flowing and active in denudation processes. During summer season the flow in these rivers become lean and the base flow component is contributed by seepages from the groundwater regime. Figure 2.5 shows the drainage network in the study area.

2.11 Drainage Density and Lineament Density

Drainage density is an inverse function of permeability, and therefore it is an important parameter in evaluating the groundwater zone. Drainage density is the total length of all the streams. It is a measure of how well or how poorly a watershed is drained by stream channels. Drainage density of the study area varies from 3.44 km/km^2 to 14.39 km/km^2 (Fig. 2.6). Lineament density map is prepared by dividing the study area into 1 km/1km grids and the lineament density values then obtained were interpolated by inverse distance weighted (IDW) interpolation method (Rashid *et al.,* 2012) . The observed lineament density of the study area varies from 0.26 to 4.10 (Fig. 2.7).

2.12 Irrigation

The study area hosts one of the major irrigation projects of Kerala – the Kallada Irrigation Project (KIP). Minor irrigation projects in the area includes surface flow irrigation schemes and surface lift irrigation schemes. In surface flow irrigation schemes, water is diverted by means of weirs and used mainly for irrigating paddy,

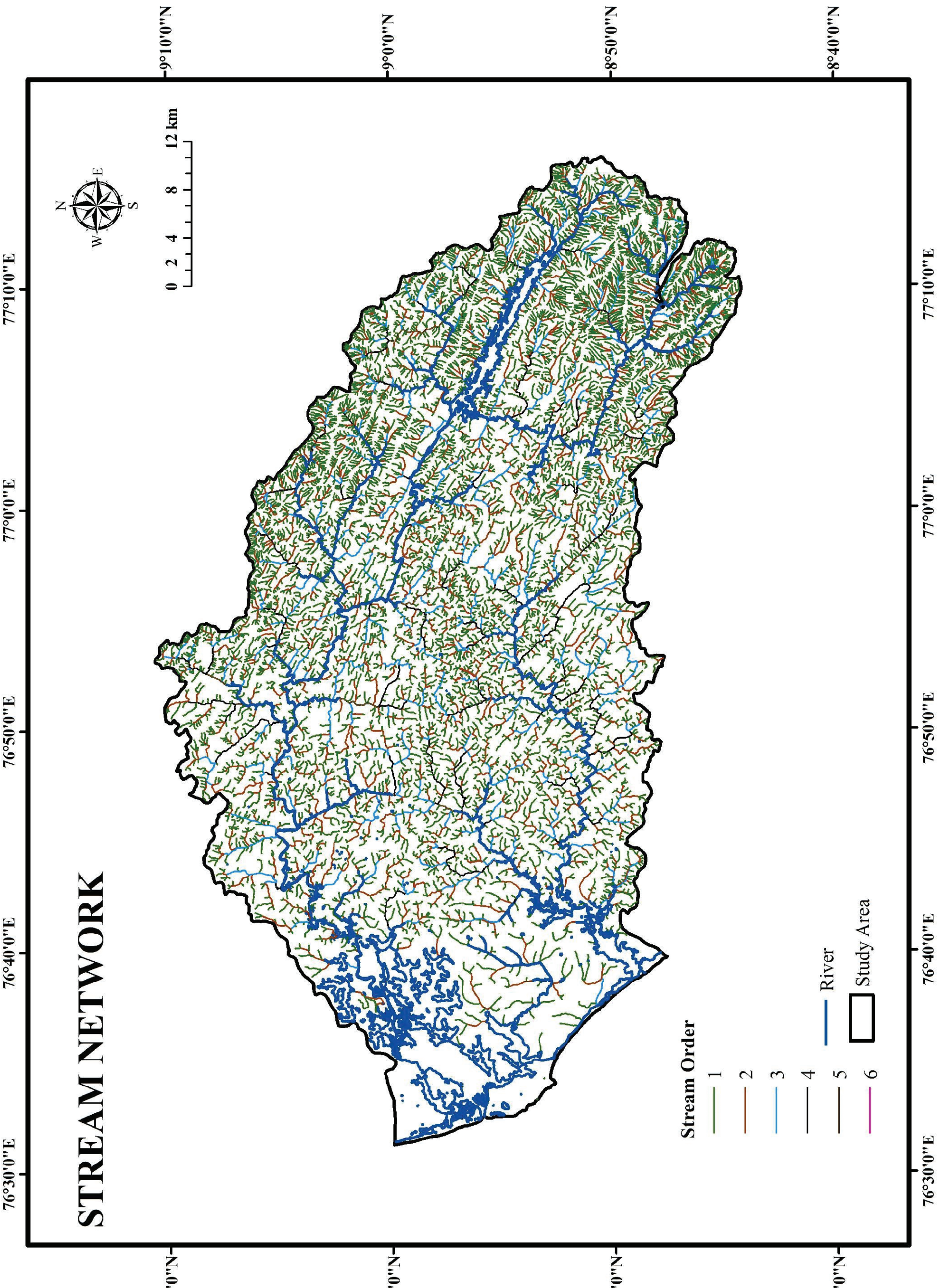


Fig. 2.5 Stream network of the study area. Note the structurally controlled drainage characteristics of the uplands of Kallada river basin

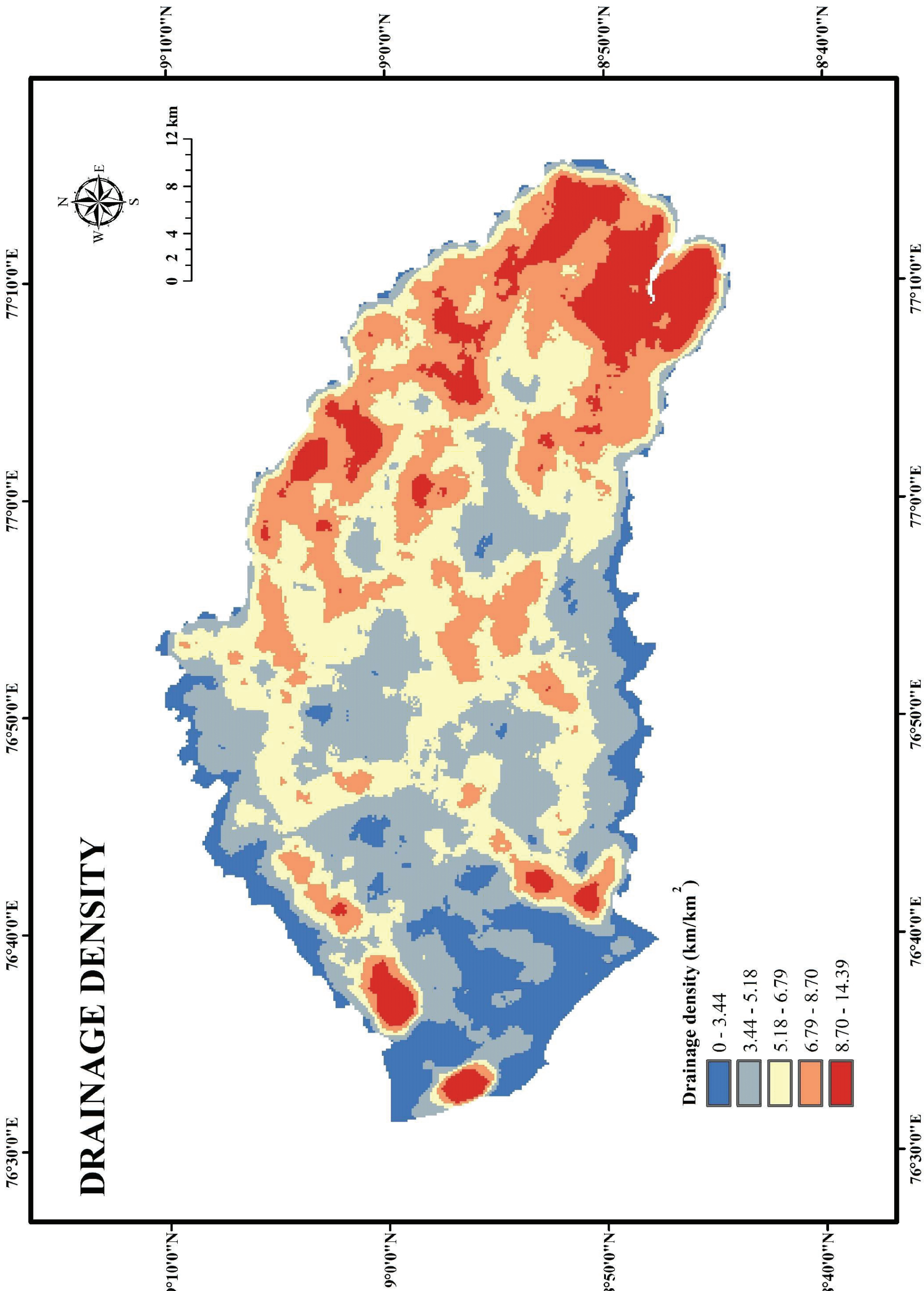


Fig 2.6 Map showing drainage density of the study area.

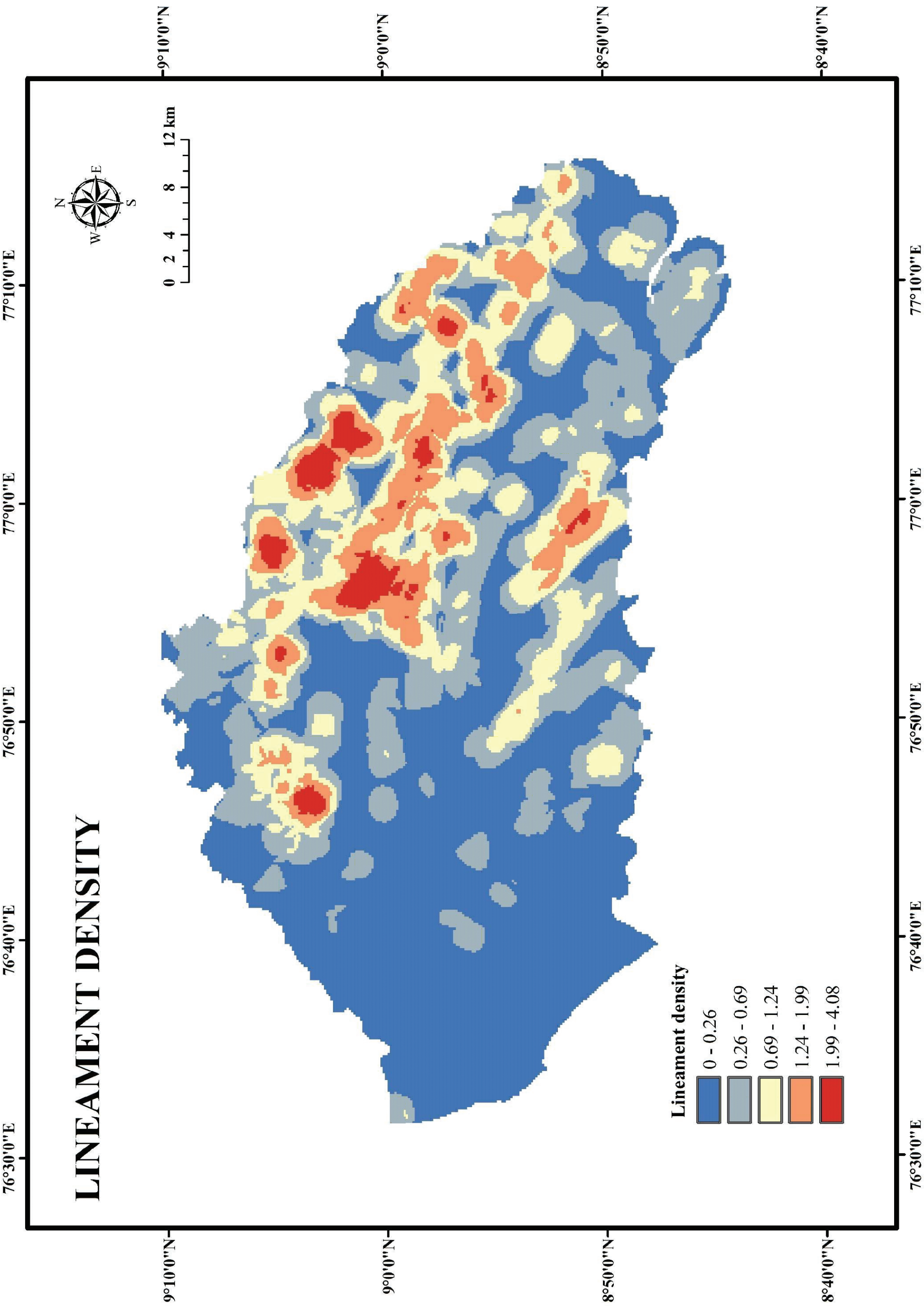


Fig 2.7 Lineament density map of the study area.

coconut, banana and arecanut. In surface lift irrigation schemes, water is lifted from rivers and streams by means of pumps and then used for irrigation of various crops. Groundwater is also used in the area for irrigating agricultural lands. It is done through dug wells, dug-cum-bore wells and bore wells. The dug wells located along the valleys of midland and hilly areas provide sufficient water to irrigate crops like paddy, coconut, banana and vegetables. About 368 *ha* of the land is being irrigated by groundwater.

2.13 Agriculture

The study area has a prominent place in the agriculture map of Kerala. The principal crops in the area are tapioca followed by paddy and rubber. In the case of land utilization of the study area, 25% area is under tapioca, 3% land under paddy, 5.7 % land under cashew, 7.4 % area under coconut, and 4% area under tea. Tapioca has replaced paddy in most of the traditional paddy growing areas. Coconut occupies more than 48% of the net sown area, followed by rubber 26.6%. In the case of paddy cultivation, majority of the paddy fields are rain fed. The study area is divided into three distinct agro-climatic zones namely malayoram, onattukara, and southern midland by department of agriculture. Malayoram and onatukara agro-climatic zones contribute more than 75% of the total geographical area of the Ithikkara and Kallada river basins.

2.14 Land use

The land use map of the study area shows a spectrum of land use categories which include built-up, barren land, forest, plantation, agricultural field, mixed vegetation and water body (Fig 2.8). Out of these different land use categories, forests, agricultural land and mixed tree crops together constitute a greater part of the study area.

2.15. Flora and Fauna

The study area is blessed with a wide variety of natural vegetation. However due to human interventions they are confined to some pockets in the eastern part

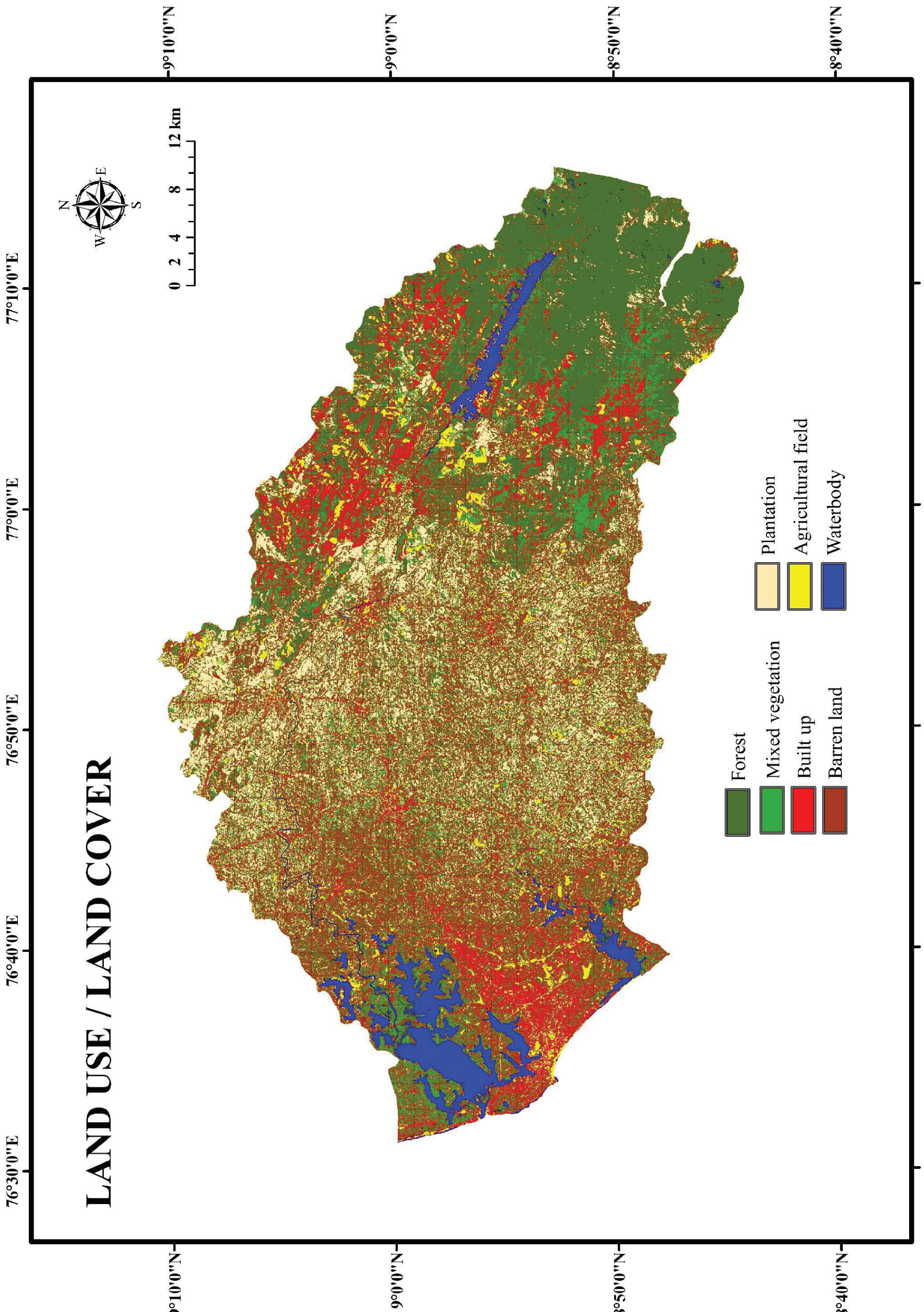


Fig 2.8 Map showing land use / land cover details of the study area

(Chattopadhyay, 1985). So is the case of rain forests which are now limited to Thenmala range and occur as tiny pockets. The grassland distribution is very minimal. The marshy and water logged areas, paddy fields associated with the backwaters and lakes and myristica swamps in the highlands are unique wetland ecosystems in the study area. About 53 patches of Myristica swamps have been located in Anchal and Kulathupuzha regions (Biju and Ajith, 2013). Table 2.4 gives a glimpse of flora of these wetlands. The area under forest is about 81438 *ha*. The forested area falls in Thenmala, Punalur and a portion of Achenkvoil forest divisions. Thenmala Range, Aryankavu Range and Shendurni Sanctuary together constitute the Thenmala division (211 sq.km).

Table 2.4 Details of flora of the study area (Source: Sabu and Ambat, 2007).

Sl. No	Type	Total Species	Trees	Shrubs	Climbers	Herbs	Mangroves
1	Asthamudi Lake and its catchments	256	31	19	25	180	11
2	Sasthamkotta lake and its catchments	131	21	10	10	100	-
3	Myristica swamps and adjoining regions	160	63	26	27	44	-

Achenkovil Range, Kallar Range and Kanayar Range fall in the Achenkovil division, and Pathanapuram and Anchal Ranges fall under the Punalur division. Teak and softwood form the major forest plantations in the study area. An artificial lake (reservoir area) of about 26 km^2 has been formed due to the construction of Parappar dam across the Kulathupuzha River. Sheeba (2009) studied that macro invertebrate fauna of the Ithikkara river. A total of 28 species belonging to three phyla and six classes were recorded. The most abundant group is arthropoda followed by mollusca. Crustaceans are predominant among the arthropods. Insects are abundant in the upstream region and crustaceans and molluscans are abundant in the downstream region.

2.16. Economic minerals

The study area is endowed with mineral deposits like beach sands containing ilmenite and monazite, clays, bauxite, graphite and laterite. Ilmenite and monazite bearing sands extend over a stretch of over 160 km from Kayamkulam to Manavalakurichi in Tamil Nadu. Rich concentrations are found at Chavara, Neendakara and Koilthottam beaches of the study area. The mineral deposits of Kollam coast containing monazite are one of the richest in the world and are reported to have the highest content of Thorium. These deposits were discovered in 1909 and since then mining had been going on more or less continuously in the region. These mineral resources are being mined and processed by Indian Rare Earths Ltd., and the Kerala Minerals and Metals Ltd., Kollam (Sekhar and Jayadev, 2003). In addition to the beach sand deposit, the study area is known for attractive deposit of china clay, tile/brick clay, construction grade sand, etc. The occurrences of flogipite mica and graphite are also reported from the study area.

2.17 Environmental Issues

Mining of sand and other minerals (major as well as minor) has caused many local adverse effects in the river basin environment of the area. Sand mining above the replenishment level has caused erosion of river banks and loss of precious agricultural lands. Increasing sand and mineral mining either by manual or mechanical processes has led to massive soil erosion, especially in the Kallada river basin (Elizabeth, 2009; Vishnu Mohan *et al.,* 2013). Sheeba (2009) reported that the biological environments of the Ithikkara river is under severe stress due to indiscriminate sand mining from the active channels as well as floodplain areas.

Deep mining for china clay (kaolin) has also become environmental threat in the study area. The clay is widely used in industries such as ceramics, cement, insecticides and fertilizers, textiles, and cosmetics. Declining water level, worsening water quality etc., are some of the major environmental impacts associated with clay mining.

Dumping municipal solid waste on land without any precautionary measures has also caused several environmental problems in the study area; some of the most striking environmental issues are (a) Groundwater contamination through leachates (b) Surface water contamination through runoff and (c) Air contamination due to gases, dust and bad odour. The degradation of the Sasthamkotta lake in the study area has resulted from leaching of excess quantity of nutrients into the lake system. This has lead to major changes in the chemical composition of the lake. Unauthorized sand mining in the proximate areas of the lake has damaged the sources of the water and resulted in fall of groundwater table (Vishnu Mohan *et al., 2016*).

Chapter - 3

MATERIALS AND METHODS

3.1 Introduction

The well being of the people is closely related to the health of the environment; but both can be damaged by pollution environmental degradation. The pollutants released into air, water and soil reaches the human body through breathing, drinking and eating. Water in its chemically pure form rarely occurs in nature and is found to carry a variety of organic and inorganic constituents. Man's influence on the quality of water is quite apparent and is presently a major concern. There are a number of water quality parameters that can be used to characterise natural waters. The water quality measurement objectives and previous history of the water body will have an important role in the selection of parameters for water quality assessment. Some parameters are of special importance and deserve periodic attention. The commonly monitoried parameters are dissolved oxygen, total dissolved solids (major cations and anions), nutrients, toxic metals, pathogenic or disease causing micro organisms, etc. The water quality parameters can be broadly classified into the following categories:

- Physical parameters: appearance, temperature, turbidity, colour, taste and odour.
- Chemical parameters: all inorganic and organic substances, i.e. pH, acidity, alkalinity, hardness, conductivity, chlorides, sulphates, nitrates, nitrites,

ammonia, fluoride, boron, heavy metals, pesticides, detergents, phenols, cyanide, radioactivity, oil and grease, organics, biochemical oxygen demand (BOD), chemical oxygen demand (COD), dissolved oxygen (DO), etc.

- Biological parameters: Total Coliform (TC), Fecal Coliform (FC), Escherichia coli (*E.coli*) and other disease causing micro organisms.

In the present study, the water samples collected from springs and dug wells of the study area were subjected to chemical analysis for some of the important water quality parameters (Eaton and Franson, 2005) and are compared with standard specifications of drinking water set by national and international agencies. All the chemicals used for the analysis were of analytical grade. Doubly distilled deionised water was used for the analytical work. All the glass wares and other containers used for analysis were thoroughly cleaned and rinsed using doubly distilled deionised water. The glass wares and reagents used for the bacteriological analysis were cleaned and sterilised before use.

3.2 Sampling of springs and well waters

Water samples from 19 springs and 20 wells spread across the Ithikkara and Kallada river basins were collected in pre-washed, high density polyethylene bottles, during pre-monsoon, monsoon and post-monsoon seasons of 2011-12 for physico-chemical analysis. The pre-monsoon sampling was done during third and fourth week of March 2011 and monsoon sampling during the first and second week of July 2011 and post-monsoon sampling during the first week of January 2012. A total of 57 samples were collected from the springs and 60 samples from wells. Water for the measurement of dissolved oxygen content was carefully collected in 300 ml capacity BOD bottles. The temperature measurement was made with good quality thermometer having 0.1^0C graduation. Electrical conductivity (EC) and pH of the samples were determined in the field using a portable conductivity and pH meter (Eutech PCSTEST-35). Standard methods (Eaton and Franson, 2005) were followed for analysis of various physico-chemical and bacteriological parameters in the samples.

3.3 Water quality analysis and analytical methods

Winkler's method was used to assess the dissolved oxygen content (DO) of the water samples of the study area. Sodium (Na^+) and Potassium (K^+) estimations were made using flame photometer (ESICO 1382). Total hardness and Calcium (Ca^{2+}) were determined by EDTA titrimetric method and Magnesium (Mg^{2+}) by deducting calcium hardness from Total hardness. Acid titration and argentometric titrations were followed for the estimation of Total alkalinity, Carbonate ($CO_3^{\ -}$), Bicarbonate (HCO_3) and Chloride (Cl^-). Silica (SiO_2), Iron (Fe) and anions such as Sulphate (SO_4^-), Nitrate-nitrogen (NO_3-N), Phosphate (PO_4^-) and Fluoride (F^-) were estimated using a UV-Visible Spectrophotometer (Spectro 2060 plus version 5). All the analysis were carried out after plotting calibration curve of a blank and standards in the suitable range which was verified with independently prepared known standards. Molybdo silicate method was applied for finding out the concentration of silica in water samples. The absorbance was measured at 410 nm. Phosphate was estimated using ascorbic acid method (absorbance measurements at 880 nm) using Spectrophotometer. Iron was estimated by phenanthroline method. Sulphate was measured by precipitating sulphate ions using $BaCl_2$ after adding conditional reagent. The absorbance was measured at 420 nm in UV-VIS Spectrophotometer. Nitrate – nitrogen in the samples was detected by ultra violet spectroscopic screening method. SPADANS colorimetric method was applied to determine the F^- content in the water samples (Eaton and Franson, 2005). A calibration curve was plotted for standard concentrations 0 - 1.5 mg/L. Reference solution was used as blank and absorbance was measured at 570 nm. The bacteriological parameters were counted applying multiple tube fermentation technique to determine the number of total coliform and feacal coliform. Presence of Escherichia coli (*E.coli*) was assessed by tryptone water and Kovac's reagent (Indole production) test. Appearance of a deep red colour in the upper layer in the inoculated tubes is considered as the positive response for *E.coli*. The presence of these organisms in water indicates feacal contamination.

Metals were estimated using ICP AES (Inductively Coupled Plasma and Atomic Emission Spectroscope Model: Thermo Electron IRIS Intrepid II XSP Duo). The trace metals such as Arsenic (As), Cadmium (Cd), Copper (Cu), Mercury (Hg), Lead (Pb), Nickel (Ni) and Zinc (Zn) were analysed in spring water samples. Non–breakable high density polyethylene plastic containers were used for the sample collection for metal analysis. The containers were soaked in 10% HNO_3 for 48 hours and then pre-rinsed with deionised water several times. The samples were subjected to analysis after filtering the water samples using 0.45µm cellulose nitrate filter paper and preserved by adding ultra pure HNO_3 to a $pH < 2$.

3.4 Data validation

Water quality data validation consists of a sequence of checks to see if errors have been made in water sampling, sample analysis or data entry (Eaton and Franson, 2005).

a) *Cation-Anion balance:* The anion-cation sums, when expressed in milliequivalents per litre, must balance since all potable waters are electrically neutral. The test is based on percentage difference and defined as follows:

$$\text{\% of balance error} = \left(\frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}}\right) \text{x} 100$$

$$\text{Cations} = Na^{+} + Ca^{2+} + Mg^{2+} + K^{+}$$

$$\text{Anions} = Cl^{-} + HCO_3^{-} + SO_4^{2-} + NO_3^{-}$$

If the error is too large (>10%), there has been an error occurred in at least one of the major ion analysis.

b) *Measured EC and Ion Sums:* Both the anion and cation sums should be 1/100 of the measured EC value. If either of the two sums does not meet this criterion, suspected parameter is to be reanalyzed. The acceptable criteria are as follows:

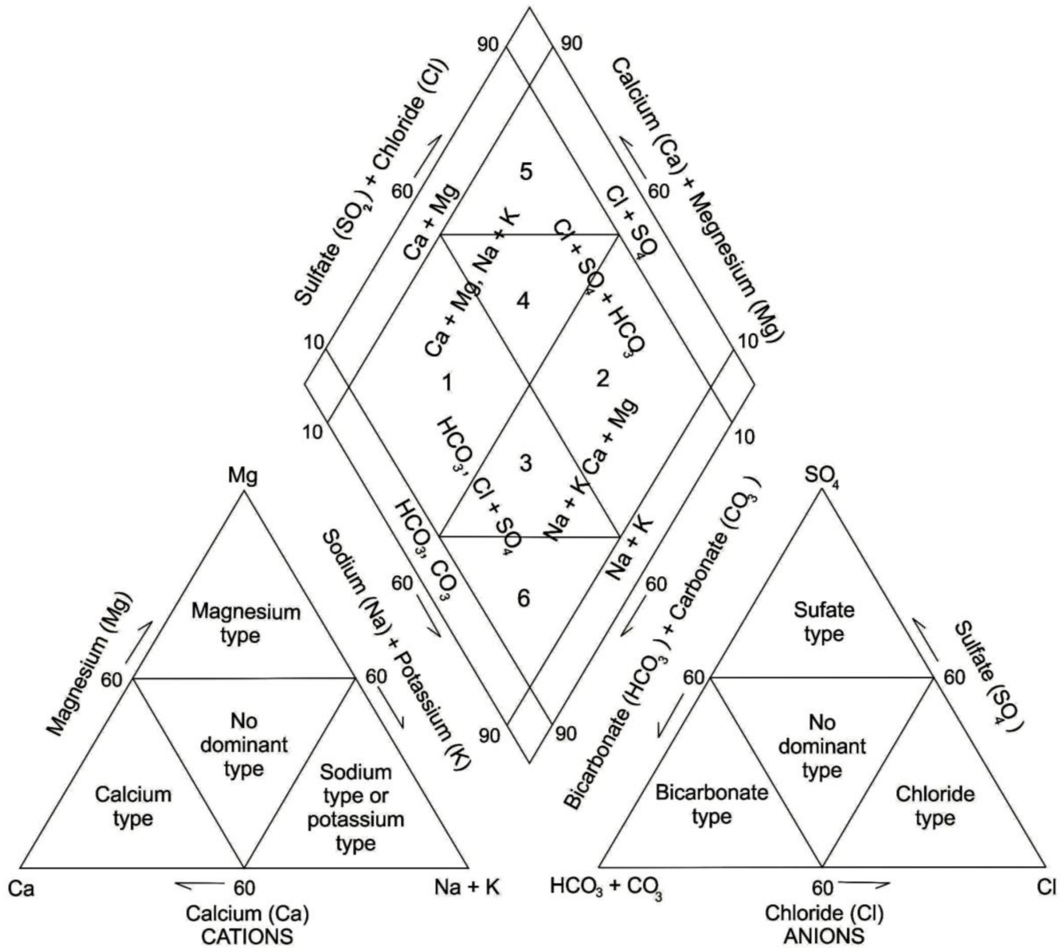
100 x anion (or cation) sum, meq/L = (0.9- 1.1) EC

The major ions in all the analysed samples were subjected to data validation and checked for percentage error and was found to be less than 10% in each case.

3.5 Graphical and statistical methods.

- **Piper trilinear diagram:** The hydrochemical process is explained with the help of piper trilinear diagram. Piper diagram is a graphical representation of the chemistry of major ions in water samples. The cations and anions are shown by separate ternary plots. The apexes of the cation plot are represented as Ca + Mg and Na + K. The apexes of the anion plot are SO_4 + Cl and CO_3 + HCO_3. The two ternary plots are then projected onto a diamond. The diamond is a matrix transformation of a graph of the anions (SO_4 + Cl/total anions) and cations (Na + K/total cations). The water samples are classified into hydrochemical facies representing water types based on the subdivisions of the Piper trilinear diagram in the manner suggested by Back (1961) and Hanshaw (1965) as shown in Fig. 3.1.

- **Indices of Base Exchange**: The variation in chemical composition of groundwater along its flow path is understood by studying the Chloro-Alkaline Indices (CAI). Schoeller (1965, 1977) has recommended two Chloro-Alkaline Indices CAI –I and CAI –II for the interpretation of ion exchange between groundwater and host environment. The Chloro-Alkaline Indices is expressed as:



1. $CaHCO_3$ type
2. NaCl type
3. Mixed $CaNaHCO_3$ type
4. Mixed CaMgCl type
5. CaCl type
6. $NaHCO_3$ type

Fig. 3.1 Water type classification using the Piper trilinear diagram.
Water types are designated according to the domain in which they occur on the diagram segments (after Back, 1961; Hanshaw, 1965).

$$CAI\text{-}I = Cl^- - (Na^+ + K^+) / Cl^-$$

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

- **Mixing diagrams:** For finding out the influence of weathering in solute acquisition processes the geochemical data plotted on bivariate plot of HCO_3^-/Na^+ versus Ca^{2+}/Na^+ and Ca^{2+}/Na^+ versus Mg^{2+}/Na^+ relating carbonate and silicate end members. The chemical composition assigned for the silicate end member is $Ca^{2+}/Na^+ = 0.35 \pm 0.15$, $Mg^{2+}/Na^+ = 0.24 \pm 0.12$, $HCO_3^-/Na^+ = 2 \pm 1$ (Gaillardet *et al.,* 1999).

- **Pearson correlation coefficient:** The close inspection of correlation matrix is useful since it can point out associations between variables that can show the overall coherence of the data set and indicate the participation of the individual chemical parameters in several influence factors, a fact which commonly occurred in hydrochemistry (Helena *et al.,* 2000). Correlation analysis measures the mutual relationship between independent and dependent variables. Correlation coefficient helps in judging the quality of water by identitifying the interrelationship between two variables. Direct correlation exists when increase or decrease in the value of one parameter is associated with a corresponding increase or decrease in the value of the other. The correlation is said to be positive when increase in one parameter causes the increase in the other parameter and it is negative then increase in one parameter causes the decrease in the other parameter. The correlation coefficient (r) has a value between +1 and -1. The correlation coefficient was computed using XLSTAT software with significant at $\alpha = 0.05$.

- **Assessment of drinking water suitability:** The water quality parameters for spring and well water samples are compared with the quality standards set by

WHO (2011) and BIS (2012) for drinking water. Another method used to assess drinking water quality is the determination of water quality index (WQI). WQI is calculated following the methodologies adopted by various researchers in the field (Tiwari and Mishra, 1985; Rao *et al.,* 1997; Mishra and Patel, 2001; Gebrehiwot *et al.,* 2011). The relative weight was computed from the following equation:

$$Wi = wi / \sum_{i=1}^{n} wi$$

where *Wi* is the relative weight, *wi* is the weight of each parameter and n is the number of parameters. The quality rating scale for each parameter is calculated by dividing its concentration in each water sample by its respective standards and multiplying the results by 100.

$$qi = (Ci / Si) \times 100$$

where *qi* is the quality rating, *Ci* is the concentration of each chemical parameter in each sample in milligrams per litre and *Si* is the World Health Organization standard for each chemical parameter in milligrams per litre (WHO, 2011).

$$SIi = Wi \times qi$$
$$WQI = \sum SIi$$

where *SIi* is the sub-index of *ith* parameter. An index value < 50 denotes excellent water, 50 - 100 stands for good water , 100 - 200 for poor water, 200 - 300 very poor water and a value >300 unfit for drinking purpose.

- **Assessment of irrigation water suitability**: Table 3.1 summarizes the various methods adopted and the equations used for the determination of the irrigation suitability of the groundwater samples of the study area.

(a) *US Salinity diagram*: The US salinity lab's diagram (Richards, 1954) is used for rating irrigation waters, where SAR is plotted against EC.

(b) *Wilcox Plot*: In Wilcox diagram (Wilcox, 1955) the EC is taken as salinity hazard and SAR as alkalinity hazard. This graphical method is used for checking the quality of water for irrigation purpose.

Table 3.1 Methods adopted for finding irrigation water suitability. The values used are expressed in meq/L.

Method	Formula	Reference
EC and Sodium Adsorption Ratio (SAR)	$SAR = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}}$	Hem, 1991
Percentage Sodium (% Na)	$\% Na = \{(Na^+ + K^+) / (Ca^{2+} + Mg^{2+} + K^+ + Na^+)\} \times 100$	Wilcox, 1955
Residual Sodium Carbonate (RSC)	$RSC = (CO_3^{2-} + HCO_3^-) + (Ca^{2+} + Mg^{2+})$	Ragunath,1987
Kelly Index (KI)	$KI = \frac{Na^+}{(Ca^{2+} + Mg^{2+})}$	Kelly, 1946
Permeability Index (PI)	$PI = \frac{[Na^+ + (HCO_3^-)^{0.5}]}{(Na^+ + Ca^{2+} + Mg^{2+})} x100$	Doneen, 1964
Magnesium Hazard (MH)	$MH = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} \times 100$	Szabolcs and Darab, 1964

- **<u>Determination of Saturation Indices (SI)</u>**: The equilibration of groundwater with a mineral is the primary criterion to decide whether or not a mineral is reactive in the aquifer environment. To predict the presence of reactive minerals in the groundwater system and to estimate mineral reactivity, saturation indicies can be used without analyzing the solid phase mineralogy (Deutsch, 1997). Saturation Indices (SI) are useful for the evaluation of equilibrium between water and mineral phase (Ruiz *et al.,* 2015). The SI of a given mineral is determined by the equation (Garrels and Mackenzie, 1967):

$$SI = \log_{10} (IAP/K_{sp})$$

where IAP is the ionic activity product and K_{sp} is the solubility product of the mineral at a given temperature. The saturation indices are calculated by using PHREEQC software (Parkhust and Appolelo, 1999).

- **Depth to water level analysis**: Water level data of 29 wells for 6 years during the period 2010 – 2015 were subjected to spatio - temporal analysis for water level fluctuation (Data Source: CGWB, Kerala region). Inverse distance weighted (IDW) interpolation technique was used for spatial modeling of water level data during pre-monsoon and post-monsoon seasons. In IDW interpolation method it is assumed that things that are close to one another are more alike than those are farther apart. To predict a value for any unmeasured location, IDW uses the measured values surrounding the prediction location. The measured values closest to the prediction location have more influence on the predicted value than those farther away. Hence greater weights are given to points closest to the prediction location, and the weights diminish as a function of distance. IDW technique is ideal for the analysis of water level data from various sampling points closely spread out.

- **Materials used for preparation of thematic layers**: The details of the materials and data sources for thematic layer preparation are Survey of India Toposheets for delineation of streams; Shuttle Radar Topographic Mission (SRTM) 30 m resolution data source (for digital elevation model, slope, topographic position index, topographic wetness index, roughness, curvature and dissection index); LISS III image (for geomorphology, land use/land cover and lineament); Geological Survey of India map (for geology); NBSS and LUP Soil map (for soil); and Central Ground Water Board (for water level).

3.6 Delineation of groundwater potential zones.

The Groundwater potential zones were obtained by integrating all the thematic maps in a linear combination model using the spatial analyst tool in ArcGIS 10.2.2 software. A Weighted Index Overlay Analysis (WIOA) method was adopted and the ranking values are assigned for each class of individual thematic maps according to the influence of the different parameters on groundwater potentiality. WIOA method takes into consideration the relative importance of the parameters and the classes belonging to each parameter. Figure 3.2 depicts the flow chart of the methodology used for delineation of groundwater potential zone in this study. There is no standard scale for a simple weighted overlay method. For this purpose, criteria for the analysis were defined and each parameter was assigned importance. Determination of weightage of each class is most crucial in integrated analysis, as the output is largely depended on the assignment of appropriate weightage to each thematic layer.

The spatial resolution of each thematic layer determines the quantity of information in that layer i.e., the higher the resolution, the more classes are resolved to assign appropriate weights to each class. Finer classes in each theme will increase the accuracy of results, which is useful for targeting interventions in the zones. Coarse resolution thematic layers generalize classes and less information over certain diverse landscapes may cause undue weightage to a particular class resulting in inappropriate priority rating. For validating the groundwater potential zones, the samples (springs and well water) are overlaid to the potential zones in GIS environment.

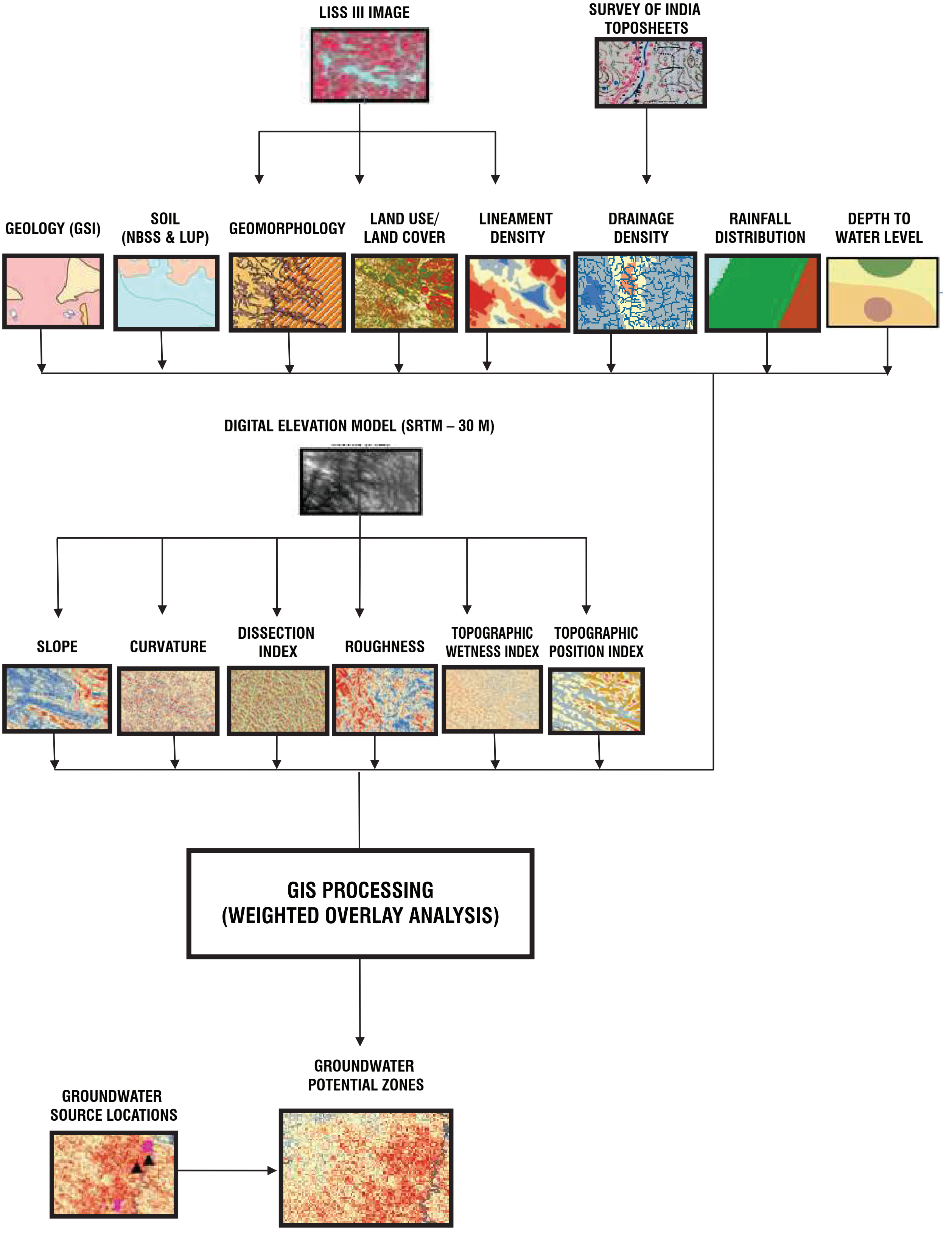


Fig. 3.2 Methodology flowchart used in determination of groundwater potential zones.

Chapter - 4

HYDROCHEMISTRY OF SPRING WATERS

4.1 Introduction

The increased and unscientific uses of conventional fresh water sources like rivers, reservoirs, lakes and wells have made severe adversities in its quality and availability. This has increased the search for alternate sources for meeting the requirement of potable water. Springs, harvested rain water, desalinated sea water etc., are some of the alternate sources of fresh water used in many parts of the world. Among these, springs are one of the very important sources of potable water in legally protected areas (Jang *et al.,* 2012). Springs react to changes that occur in ecosystems due to natural or man- made processes (Migaszewski and Galuskaa, 2003). A decrease in the number of springs or the drop in their discharge as well as changes in chemistry and discharge volume often indicate changes in the geo environmental settings of the area (Song *et al.,* 2005; Michalik, 2008; Singh *et al.,* 2013; Tiwari *et al.,* 2016).

In India, most of the studies have been centered on hot water springs (Evans *et al.,* 2001; Jeelani, 2005; Chandra and Ramaiah, 2007; Sooryanarayana and Kezo, 2008). The cliffed coast of south western coast of India, especially, the Kerala coast and its hinterlands, host many cold water springs of varying discharge characteristics (CWRDM, 1988). These springs are often used as sources of household water supply to rural population in the state. Lack of adequate base line data on the quality and quantity of these spring water sources is a major setback challenging their wise use, management and/or conservation. Therefore, in this chapter an attempt has been made to document hydrochemistry of the springs in two important river basins of Southern Western Ghats- the Ithikkara and Kallada river basins of Kollam District in Kerala State, as an example.

4.2 Previous studies

Springs attracted humans since the recorded history or long before. The forcing of spring water to the surface can be the result of an aquifer in which the recharge area of spring water table rests at a higher elevation than that of the outlet. Although many studies have been carried out on various aspects of springs, focussed studies pertaining to use springs as an alternative to drinking water source have been carried out in the beginning of this century.

Champion and Starks (2001) studied hydrology and water quality of springs in Southwest Florida. The study revealed that nitrate concentrations in spring waters showed an increasing trend towards northern Florida. Spring waters throughout the area reflect the dissolution of limestone in the Floridan aquifer. The quality of groundwater is controlled by combined interactive natural (including lithologic, tectonic, topographic, climatic, edaphic) and anthropogenic factors. This is the main reason why springs are assigned as the best environmental geo-indicators (Michalik, 2008). Spring water geochemistry is considered in a regional context of aquifer components including soil water, cave drip water, and phreatic groundwater. Isotopic and trace element variability allows us to identify both vadose and phreatic groundwater contributions to surface water (Musgrove *et al.,* 2010). Spring water is a system comprising both the main course and the tributaries, carrying the one-way flow of a significant load of matter in dissolved and particulate phases from both natural and anthropogenic sources (Geyikci *et al.,* 2012). Pehlivan *et al.* (2012) studied the effect of talus deposit excavations on hydrogeochemical characteristics of Kuvars Spring Water, Maltepe, Istanbul, Turkey. The degree of silica saturation varies according to the extent of atomic structuring of the silica minerals in springs of Cyprus. The most crystalline form is quartz, intermediate crystallinity is for chalcedony and chrystobalite and the highest solubility is for amorphous silica (Neal and Shand, 2002). Hydrogeochemical characteristics of spring water in the Harz Mountains, Germany was studied by Bozau *et al.* (2013). They reported that meteoric water is indicated as the main source of the springs sampled and high precipitation rates lead to a dilution of the measured elemental concentrations. Assessment of the chemical characteristics of a spring water source at Ife-Owutu, Ezinihite-Mbaise, Southeastern Nigeria suggests that the water is good for agricultural use (Ibeneme *et al.,* 2013). Springs in Ramallah, a Palestinian city have water type of (Ca-Mg- HCO_3) and lies in the areas of earth alkaline water (Jebreen, 2014). The study on environmental effect of the spring water in Matwi catchment of Palestine reveals higher incidence of faecal coliform and total coliform which is an indication of wastewater contamination (Ghanem and Ahmed, 2014). The study done by Ako *et al.* (2012) on spring water quality and usability in Mount Cameroon area revealed that CO_2 driven silicate weathering and reverse cation exchange are the most important natural determinants of hydrochemistry of the spring waters in the area. Hydrochemical characterization of springs in the northwest region of Cameroon Volcanic Line points that springs in the area are not suitable for drinking and should be treated properly before human consumption (Pierre *et al.,* 2015). Sappa *et al.* (2014) studied the hydrochemical processes that control the groundwater chemistry of springs in Central Italy. The results of the study suggested that groundwater has been evolved from Ca to HCO_3 recharge water, followed by mixing and reverse ion exchange processes, due to the respective dominance of Na–Cl and Ca– Cl water types and that chemical weathering of rock forming minerals is the major driving force controlling water chemistry in this area. Spring waters of south-western Nigeria has total hardness less than 70mg/L signifying soft, low mineralized water with no pronounced effects of rock-water interaction arising from transient residence time (Talabi *et al.,* 2014). Dinka *et al.* (2015) reported that due to the changing hydrological conditions and anthropogenic activities in rift Valley region of Oromiya, Ethiopia, the hydrochemistry of hot springs is changing over the years. Chen *et al.* (2015) revealed that spring water studies can be used as an indicator for earthquakes. The physico-chemical characteristics of the water flow from springs in the Hit–Kubaiysa region of Iraq has been studied in detail by Dulaymie *et al.* (2013). Jalali and Jalali (2016) studied about geochemistry and background concentration of major ions in spring waters in a high-mountain area of the Hamedan (Iran) and reported that the major water types in spring waters were $Ca–HCO_3$, $CaHCO_3–Cl$, $CaMg–HCO_3Cl$, and $CaMg–Cl–HCO_3$ which were derived mainly due to the dissolution of carbonate minerals and silicate weathering in addition to contribution of a part of the ions through exchange processes.

Many studies have been carried out in the spring water sources in India as well. Studies carried out by Jain *et al.* (2010) revealed that spring water samples of Nainital, Uttarakhand are contaminated by coliform bacteria. The hydrochemical facies indicate that majority of them fall in $Ca\text{-}Mg\text{-}HCO_3$ facies. Combined geological, geophysical, hydrological and geochemical studies on Bakreswar thermal springs show that the spring waters are a mixture of hot ascending water and shallow non-thermal groundwater (Majumdar *et al.,* 2010). Due to anthropogenic activities, the springs of Udhampur District, Jammu and Kashmir, India are under constant threat, resulting in ecologically adverse alterations (Khanna, 2012). Physico-chemical properties and bacteriological examination of hot springs from Vashisht region in Kullu district of Himachal Pradesh was studied by Naresh *et al.* (2013), and found that spring water in the area is potable for drinking purpose. The trace element characteristics of the spring waters in Tural and Rajvadi, Maharashtra are close to those measured on waters of granitic terrains, indicating the circulation of meteoric water through granitic basement, before its discharge in the form of thermal springs (Reddy *et al.,* 2013). The studies of Unkeshwar hot spring of Maharashtra, reveals that the spring possess therapeutic properties as it contains the presence of sulphur (Yannawar *et al.,* 2013). Mongra (2014) reported that water of spring in Tattapani, Himachal Pradesh is a good medium containing all essential inorganic ions which support considerable growth of both nitrogen and non nitrogen fixing cyanobacteria. Spring water quality in Anantnag and Kulgam districts of Jammu and Kashmir, shows that the quality of spring waters has deteriorated over the years because of human interferences (Rather *et al.,* 2013). Bhandary and Joshy (2013) studied the quality of spring water used for irrigation in the Almora district of Uttarakhand, and found that all springs have excellent to good quality with respect to irrigation parameters. Jeelani (2015) has done water quality studies of major springs in and around Anantnag, Jammu and Kashmir, and reported that calcium is the most abundant cation in most of the spring water samples. The chemical facies include Mg-rich bicarbonate waters and Ca-rich bicarbonate waters. Bhat and Jeelani (2016), in their study on hydrogeochemical assessment of water resources of Bringi watershed, Kashmir Himalayas points out that the spring samples are suitable for irrigation purposes. Hydrogeochemical assessment of the spring waters revealed that carbonate weathering is the dominant source of the major ions in water samples.

A cursory glance of literature reveals that, a few studies have been done on spring waters of Kerala as well. Several springs exist in the highlands as well as coastal lands of Kerala. Many of them are seasonal. The perennial springs in the area have been used by the settlers as their source of water for drinking, bathing and other domestic needs. CWRDM (1988) has done an inventory on springs of Kerala and they identified 236 springs in the State. About 80% of springs are located in the eastern side of Western Ghats belt. Majority of springs of Kerala have a discharge potential of 10 to 99 litres/minute. Basak *et al.* (2005) conducted a study on water harvesting with special reference to springs in Kerala. As per the studies of Babu *et al.* (2010) almost all the springs in coastal and midland regions of Thiruvananthapuram and Kollam districts are under constant threat from natural and human activities. Encroachments and changes in land use pattern have led to destruction of many of the springs while others are hit severely by water quality changes. Padmalal *et al.* (2012) studied hydrochemical characterization and water quality assessment of coastal springs of southern Kerala which reports that precipitation and weathering of minerals in the aquifer are the major causative factors responsible for water quality changes. Joji (2013) points out that there are numerous springs along the slope of the eastern hill ranges, which are the perennial sources for drinking water in Thrissur district. He suggests that attention may be given for the proper development of springs as they supply water to the downstream areas of the region. Development of a spring based water supply scheme at Kakkur panchayat of Kozhikode district was implemented by CRWDM (1988). Rani (2013) reports that in Trivandrum district, there are about 31 springs which are the perennial source for drinking water. These springs originate from sedimentaries and crystallines and have good discharge potential. These springs can effectively be used for drinking water supply to the rural areas, thereby reducing the stress on groundwater sources to a significant level.

4.3 Geoenvironmental setting of springs in the study area

Springs in the Ithikkara and Kallada river basins fall within the confined and unconfined categories (Fig. 4.1). The highland springs are generally of unconfined type whereas those in the lowland are of confined type. Figure 4.2 shows the generalised lithologic section noticed in the coastal lowland as well as highland of the study area where from the springs emerge to the ground surface. In both the regions, two broad varieties of springs occur – a) boiling type and b) free falling type. In boiling type, water emerges through an orifice located below the water column of the spring pool (Plate 4.1a & b); whereas in free falling type, water expels through an orifice located above the general ground level (Plate 4.1c & d). Rainfall is the major source of water for the surface and subsurface horizons in the study area. The average rainfall of the area is 2555 mm (CGWB, 2009). A major portion of the rainfall contribution is from south west monsoon (June to September) which have a stake of about 55% of the total annual rainfall contribution. The north east monsoon (October to December) contributes only 24% while the rest (21%) is received from summer (January to May) showers.

Although a considerable section of the people in the depend on open (dug) wells for their fresh water requirements, a few people in the area also depend on springs for meeting their potable water needs, particularly during summer season. Geologically, the study area is composed of crystalline rocks of Archaean age which covers a greater part (>90%) of the study area. Sedimentary deposits of Neogene to Recent ages occur in the lowland. The springs are seen emerging from the base of scarps/ valley heads in the highland as well as the coastal lowland. A major portion of the study area where springs occur is blanketed by lateritic soil. Brown hydromorphic soil, grayish onattukara soil, coastal/riverine alluvium and forest loam are also noticed in the area. The land use around the springs include settlements, dense scrub, dense forest, mixed plantation, open forest, plantations and open scrub. Major crops in the area comprise coconut, tea, pepper, rubber, tapioca and ginger. Table 4.1 gives the important environmental observations of the area surrounding the sampling locations in the lowland and highland regions of the Ithikkara and Kallada river basins.

4.4 Results

The major investigations carried out in the spring water samples include physico-chemical analysis, trace element estimations and bacteriological analysis. The following sections give a brief assessment of the hydrochemical and bacteriological studies carried out on the spring water samples of the Ithikkara and Kallada river basins.

4.4.1 Physico-chemical parameters

The results of the physico-chemical parameters of the spring water samples of Ithikkara and Kallada river basins during pre-monsoon, monsoon and post-monsoon seasons is given in Table 4.2. The averages and ranges of spring water quality parameters are illustrated in Table 4.3. Temperature plays an important role in chemical and biological activities of water samples. The temperature of the spring water of lowland region varies from 25.5^oC to 28.5^oC in pre-monsoon, 25^oC to 26.1^oC in monsoon and 28.1^oC to 30^oC in post-monsoon seasons. In highland the temperature ranges between 24.5^oC to 28.6^oC, 24^oC to 26^oC and 27.9^oC to 29.9^oC respectively in pre-monsoon, monsoon and post-monsoon seasons. At a given temperature the intensity of acidic or basic character of a solution is indicated by pH or hydrogen ion activity. Natural waters usually have pH values in the range of 4 – 9 and most are slightly basic because of the presence of bicarbonates and carbonates of the alkali and alkaline earth metals (Eaton and Franson, 2005).

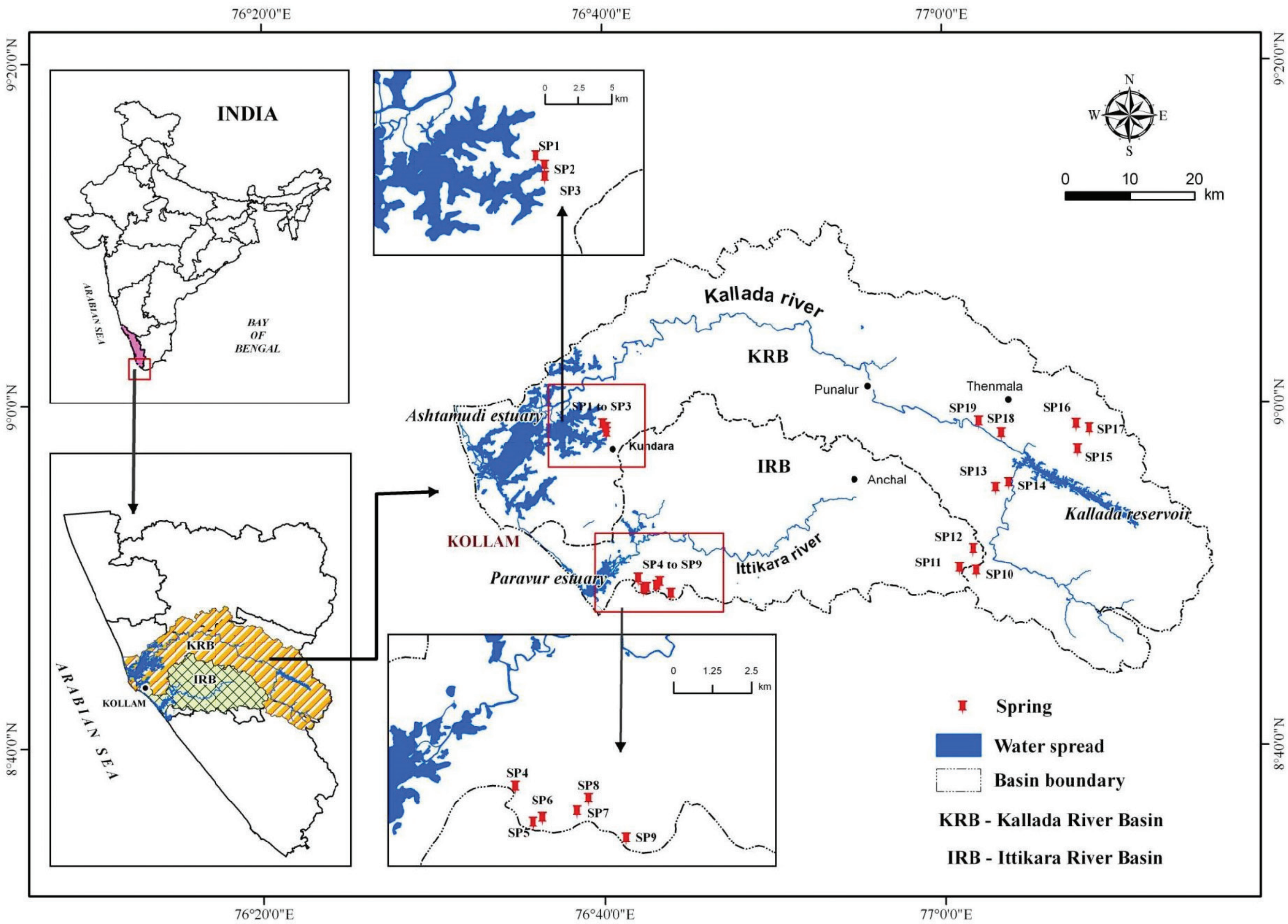


Fig. 4.1 Spring water sampling locations in the Ithikkara River Basin (IRB) and Kallada River Basin (KRB). Springs, SP1- SP3 and SP4- SP9 are from the lowlands and the others are from the highlands.

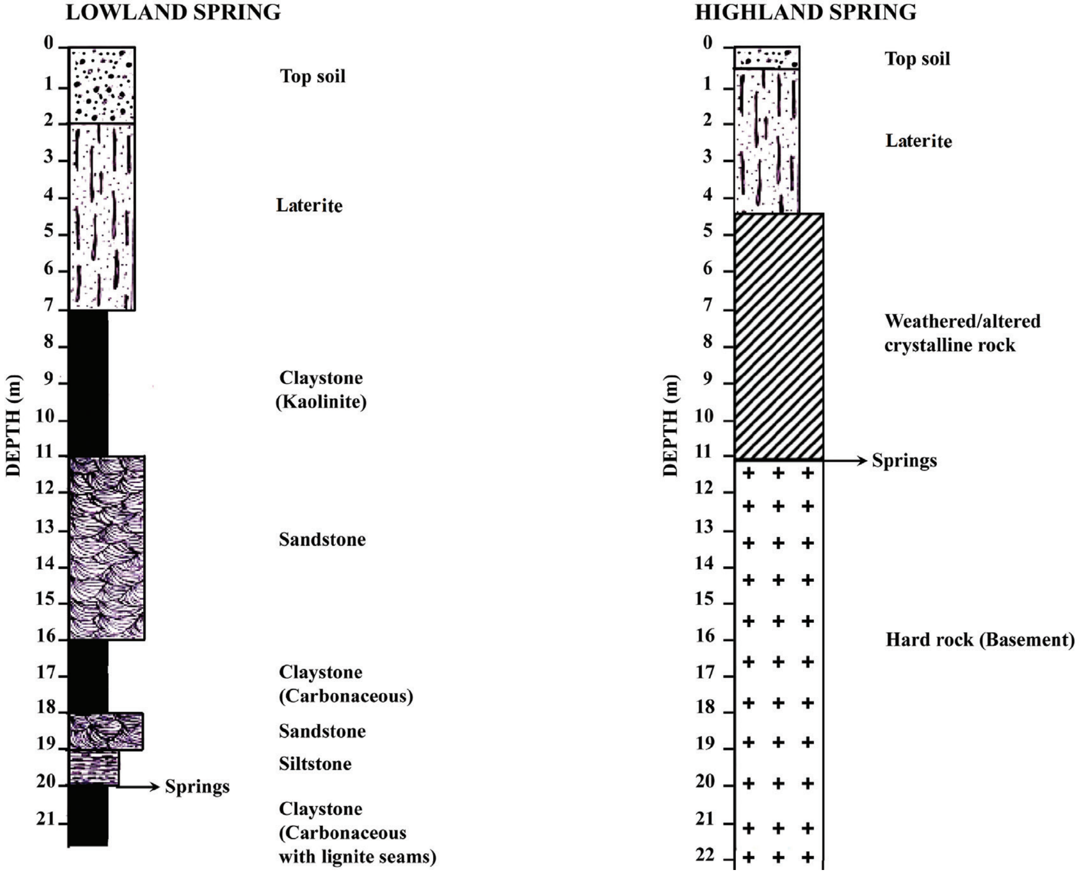


Fig. 4.2 Lithologic sequence (generalised) of the study area showing the point of emergence (orifice) of springs in the study area.

Plate 4.1 Springs in the study area.

(a) Spring pool in crystalline terrain,
(b) Spring pool in sedimentary terrain reflecting the image of a coconut tree top indicating the clearness of the water in the spring pool, (c) & (d) Free falling type springs.

Table 4.1 Geoenvironmental settings of the lowland and highland springs in the study area.

Spring code	Remarks	Type of spring	River basin/ watershed area of spring (km^2)
LOWLAND			
SP1	Mixed plantation; gravelly clayey soil; well drained; rock type is sandstone and claystone with lignite; semi-consolidated; area belongs to lower lateritic plateau; spring is protected.	Emerges above ground surface	Kallada / 78.43 km^2
SP2	Physiographic features are same as that of SP1; the area faces acute water scarcity in summer season and people depend springs for fresh water requirements.	Emerges above ground surface	Kallada / 78.43 km^2
SP3	Physiographic features are as same as SP1; it is a cluster of 4 small springs; hundreds of people in the area depend the spring for their fresh water requirements; spring is protected.	Emerges above ground surface	Kallada / 78.43 km^2
SP4	Dense scrub; gravelly clayey soil, well drained; rock type is sandstone and claystone with lignite; spring water is used for domestic purposes.	Emerges above ground surface	Ithikkara / 4.88 km^2
SP5	Physiographic features as same as SP4; the spring has storage and protection structures; spring water is used for drinking and irrigation purpose.	Emerges above ground surface	Ithikkara / 12.3 km^2
SP6	Physiographic features as same as SP4; spring water is used for drinking and irrigation purposes through gravity based water supply system; surrounding area is dominated by coconut plantation; more than 500 people depend on the spring for their domestic water requirements.	Emerges above ground surface	Ithikkara / 12.3 km^2

Contd...

Spring code	Remarks	Type of spring	River basin/ watershed area of spring (km^2)
SP7	Physiographic features as same as SP4; many people use water from this spring for domestic purposes.	Emerges above ground surface	Ithikkara / 12.3 km^2
SP8	Coconut and arecanut plantation around the springs; spring is protected; water flowing is used for washing, bathing etc.	Boiling type spring	Ithikkara / 12.3 km^2
SP9	Dense scrub; rock type is sandstone and claystone with lignite, sedimentary terrain. Water is used for domestic purposes.	Emerges above ground surface	Ithikkara / 12.3 km^2
HIGHLAND			
SP10	Forest plantations around the spring; soil type is loam and well drained; khondalite is the major rock type; the area belongs to denudational hills; clear water; people use the spring water for domestic purposes.	Boiling type spring	Ithikkara / 18.53 km^2
SP11	Physiographic features as same as that of SP10; water is used for washing, bathing etc.	Boiling type spring	Ithikkara / 18.53 km^2
SP12	Physiographic features as same as SP10; water is used for drinking and other domestic purposes.	Emerges above ground surface	Ithikkara / 11.59 km^2
SP13	Forest plantations around the spring; soil type is loam and well drained; water from the springs are collected in huge open wells; spring is perennial.	Boiling type spring	Kallada / 8.05 km^2
SP14	Physiographic features as same as SP13. water is used for washing, bathing etc.	Boiling type spring	Kallada / 8.05 km^2

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Spring code	Remarks	Type of spring	River basin/ watershed area of spring (km^2)
SP15	Forest plantations around the spring; soil type is gravelly loam and well drained; the terrain is metamorphic, the area belongs to denudational hills; the spring is well protected; people of the surroundings area use the spring water for domestic purposes.	Emerges above ground surface	Kallada / 6.92 km^2
SP16	Forest plantations around the springs; teak, sandal wood, rosewood plantation; soil type is well drained; the major rock type is charnockite; spring is protected; water is used for domestic purposes.	Emerges above ground surface	Kallada / 29.94 km^2
SP18	Dense forest around the springs; mixed vegetation around the area; soil type is gravelly clayey soil and well drained; the terrain is metamorphic; spring is protected; water is used for drinking and other domestic purposes.	Emerges above ground surface	Kallada / 32.71 km^2
SP19	Mixed vegetation around the springs; soil type is gravelly clay and well drained; metamorphic terrain; the area belongs to denudational hills; people use the water for drinking and other domestic uses.	Emerges above ground surface	Kallada / 32.71 km^2

Table 4.2 Water quality parameters estimated in the spring samples of the study area collected during pre-monsoon, monsoon and post-monsoon seasons.

Physiography/ Season	Spring code	pH	EC (µS/cm)	TDS (mg/L)	DO (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	TH (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	TA (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^--N (mg/L)	SiO_2 (mg/L)	Fe^{2+} (mg/L)	F^- (mg/L)	Temp.
I) LOWLAND																			
Pre-monsoon	SP1	4.5	72.0	43.0	5.1	10.3	0.76	10.0	2.0	1.22	2.1	2.50	16.20	BDL	2.13	5.64	0.06	0.45	28.5
	SP2	4.2	77.0	46.0	3.2	10.1	0.40	10.0	2.0	1.22	4.1	5.00	17.10	BDL	1.18	4.67	0.09	0.45	28.0
	SP3	3.8	104.0	62.0	3.4	13.4	1.70	20.0	4.0	2.44	0.0	0.00	21.90	BDL	3.60	4.78	0.02	0.50	28.0
	SP4	4.3	104.0	62.0	7.6	15.4	1.80	10.0	4.0	BDL	4.0	4.90	26.60	BDL	2.32	4.50	BDL	0.53	26.0
	SP5	4.5	88.0	53.0	3.2	14.2	0.24	15.0	2.0	2.44	6.2	7.50	20.00	2.70	2.44	4.97	BDL	0.50	28.3
	SP6	4.2	73.0	44.0	6.7	10.4	0.50	10.0	2.0	1.22	2.1	2.50	17.10	1.60	1.95	5.53	0.18	0.50	28.3
	SP7	6.0	68.0	41.0	8.0	9.9	0.70	10.0	4.0	BDL	8.0	9.80	16.20	2.50	0.36	5.40	1.90	0.50	27.7
	SP8	4.1	80.0	48.0	4.6	11.0	0.40	15.0	2.0	2.44	4.1	5.00	20.00	1.40	2.07	4.94	BDL	0.50	28.3
	SP9	4.8	44.0	26.0	6.5	4.7	0.20	6.60	0.8	1.10	2.2	2.70	8.80	0.51	0.83	3.65	0.15	0.04	25.5
Monsoon	SP1	4.4	66.0	40.0	4.9	10.4	0.80	10.0	2.0	1.22	2.0	2.44	17.46	BDL	1.91	5.41	BDL	BDL	26.0
	SP2	4.4	45.0	27.0	1.8	7.0	0.58	10.0	4.0	BDL	2.0	2.44	16.50	BDL	0.26	3.97	0.11	BDL	25.3
	SP3	4.4	103.0	62.0	4.4	14.3	1.91	15.0	2.0	2.44	2.0	2.44	25.20	BDL	3.32	4.63	0.03	BDL	26.0
	SP4	4.7	101.0	61.0	7.3	14.6	2.00	15.0	2.0	2.44	4.0	4.90	27.10	BDL	2.12	3.83	0.01	BDL	25.0
	SP5	4.8	85.0	51.0	3.8	14.5	0.47	12.5	2.0	1.83	6.0	7.32	22.30	1.96	1.33	4.84	0.07	BDL	26.0
	SP6	4.2	71.0	43.0	3.9	10.9	0.46	10.0	2.0	1.22	2.0	2.44	18.40	BDL	1.81	7.77	0.05	BDL	26.1
	SP7	6.5	64.0	38.0	5.9	8.8	0.65	15.0	2.0	2.44	6.0	7.32	16.50	3.40	0.93	4.91	0.96	BDL	25.3
	SP8	4.8	68.0	41.0	3.2	10.5	0.56	10.0	2.0	1.22	4.0	4.90	18.40	BDL	1.85	4.44	0.03	BDL	26.0
	SP9	4.8	45.0	27.0	7.6	6.3	0.52	10.0	4.0	BDL	4.0	4.90	13.60	BDL	0.97	6.78	0.09	1.00	25.0

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Physiography/ Season	Spring code	pH	EC (µS/cm)	TDS (mg/L)	DO (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	TH (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	TA (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^--N (mg/L)	SiO_2 (mg/L)	Fe^{2+} (mg/L)	F^- (mg/L)	Temp.
Post-monsoon	SP1	4.7	71.0	43.0	3.1	11.7	0.72	10.0	1.0	1.83	4.0	4.90	18.90	0.83	2.02	15.29	0.03	BDL	29.5
	SP2	4.7	70.0	42.0	3.0	11.0	0.58	10.0	2.0	1.22	2.0	2.44	17.80	1.07	1.41	4.55	0.09	BDL	29.2
	SP3	4.6	121.0	73.0	2.8	18.4	2.40	15.0	4.0	1.22	2.0	2.44	28.80	0.95	4.02	3.25	0.10	BDL	28.7
	SP4	5.0	111.0	67.0	4.9	17.2	2.40	15.0	2.0	2.44	4.0	4.90	27.80	1.07	2.85	2.91	0.05	0.35	30.0
	SP5	4.6	102.0	61.0	4.1	16.6	0.36	10.0	2.0	1.22	6.0	7.32	22.80	1.31	2.75	4.18	0.09	BDL	29.7
	SP6	4.8	85.0	51.0	3.3	13.7	0.63	10.0	2.0	1.22	10.0	12.2	20.90	1.54	BDL	4.77	0.12	0.10	29.4
	SP7	6.4	73.0	44.0	6.6	11.0	0.55	15.0	2.0	2.44	6.0	7.30	18.90	2.40	1.01	4.12	0.91	BDL	29.3
	SP8	4.7	85.0	51.0	3.0	13.8	0.51	10.0	2.0	1.22	4.0	4.90	21.80	0.71	1.94	3.75	0.09	BDL	28.0
	SP9	5.3	49.0	29.0	5.8	10.1	0.39	10.0	2.0	1.22	4.0	4.90	15.90	1.54	1.19	5.26	0.05	BDL	28.1
II) HIGHLAND																			
Pre-monsoon	SP10	6.1	54.0	32.0	3.9	4.7	2.2	15.0	2.0	2.44	16.0	19.5	7.60	2.40	0.05	23.78	0.21	0.01	27.7
	SP11	6.2	54.0	32.0	3.2	4.7	2.3	15.0	2.0	2.44	16.0	19.5	7.60	2.40	BDL	24.30	0.28	0.01	27.7
	SP12	5.0	39.0	23.0	5.5	3.8	2.4	10.0	2.0	1.22	12.0	14.6	4.80	2.50	0.03	19.80	0.14	0.01	28.6
	SP13	5.8	79.0	47.0	4.1	6.0	3.3	25.0	4.0	3.66	24.0	29.3	10.50	2.40	0.05	16.60	0.14	0.04	28.0
	SP14	5.5	66.0	40.0	3.5	5.6	4.1	15.0	4.0	1.22	16.0	19.5	10.50	1.70	BDL	20.36	0.09	0.08	26.3
	SP15	5.9	71.0	43.0	2.3	6.3	1.7	20.0	4.0	2.44	11.6	14.2	11.90	1.33	0.21	24.40	0.47	0.50	24.5
	SP16	5.6	72.0	43.0	3.8	7.5	1.8	22.5	3.0	3.70	24.0	29.3	13.30	1.46	BDL	27.10	0.20	0.50	27.0
	SP17	5.6	80.0	48.0	5.5	7.7	1.5	22.5	3.0	3.70	30.0	36.6	11.40	1.33	BDL	37.56	0.12	0.50	25.0
	SP18	6.2	39.0	23.0	6.5	4.3	1.4	12.5	2.0	1.83	9.0	11.0	9.50	0.70	BDL	10.50	0.05	0.50	25.0
	SP19	5.8	44.0	26.0	4.4	4.2	2.2	15.0	2.0	2.44	16.0	19.5	10.50	0.80	0.14	27.10	0.09	0.51	25.1

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Physiography/ Season	Spring code	pH	EC (µS/cm)	TDS (mg/L)	DO (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	TH (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	TA (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3-N (mg/L)	SiO_2 (mg/L)	Fe^{2+} (mg/L)	F^- (mg/L)	Temp.
Monsoon	SP10	6.2	46.0	28.0	8.1	4.8	2.7	15.0	2.0	2.40	20.0	24.4	8.70	1.70	BDL	25.38	0.08	BDL	25.5
	SP11	6.2	46.0	28.0	6.2	4.7	2.6	10.0	2.0	1.22	18.0	22.0	6.80	4.20	BDL	23.90	0.31	BDL	25.5
	SP12	5.3	38.0	23.0	6.7	4.3	2.3	5.0	1.0	0.61	12.0	14.6	6.80	0.52	0.20	20.20	0.25	BDL	26.0
	SP13	6.0	63.0	38.0	4.3	4.1	2.2	20.0	6.0	1.20	20.0	24.0	7.80	2.20	BDL	16.00	0.30	BDL	25.5
	SP14	5.7	62.0	37.0	7.1	5.3	3.7	15.0	3.0	1.83	12.0	14.6	12.60	1.18	1.13	15.91	0.01	0.05	25.5
	SP15	6.2	51.0	31.0	9.5	4.4	1.2	17.5	4.0	1.83	18.0	22.0	6.80	BDL	BDL	17.70	0.54	0.15	24.0
	SP16	5.7	71.0	43.0	3.3	6.8	1.7	20.0	4.0	2.44	26.0	31.7	10.70	0.92	0.10	24.20	0.15	BDL	26.0
	SP17	5.7	17.0	42.0	7.6	8.8	1.3	15.0	4.0	1.22	26.0	31.7	9.70	1.57	BDL	29.90	0.02	BDL	25.0
	SP18	6.1	41.0	25.0	8.1	4.1	2	10.0	2.0	1.22	10.0	12.2	7.80	2.61	0.29	8.02	0.32	BDL	24.5
	SP19	5.9	48.0	29.0	5.7	3.6	2.4	20.0	2.0	3.66	18.0	22.2	8.70	2.97	BDL	18.60	0.01	0.10	25.0
Post-monsoon	SP10	6.6	45.0	27.0	7.1	5.2	2.3	10.0	2.0	1.22	10.0	12.2	7.00	3.60	BDL	20.40	0.17	0.70	28.3
	SP11	6.8	52.0	31.0	6.6	4.7	2.2	15.0	4.0	1.22	14.0	17.1	7.00	4.04	BDL	18.80	0.28	BDL	28.2
	SP12	5.7	32.0	19.0	8.0	4.7	2	5.0	2.0	BDL	6.0	7.32	7.00	2.40	BDL	17.20	0.53	BDL	29.0
	SP13	6.0	101.0	61.0	6.6	11	3.7	20.0	4.0	2.40	17.0	20.7	17.00	1.50	1.2	11.00	0.10	0.50	29.2
	SP14	5.9	93.0	56.0	5.6	10.7	3.8	20.0	4.0	2.40	18.0	22.0	16.90	1.07	1.2	10.24	0.05	BDL	29.1
	SP15	6.4	41.0	25.0	6.0	6.4	1.2	10.0	2.0	1.22	10.0	12.2	9.90	1.78	BDL	21.90	0.16	BDL	29.0
	SP16	6.5	76.0	46.0	6.0	8.74	2.0	25.0	2.0	4.90	28.0	34.2	12.90	2.85	BDL	24.60	0.11	BDL	29.6
	SP17	6.6	60.0	36.0	6.4	7.0	1.2	15.0	4.0	1.22	16.0	19.5	11.90	1.20	0.02	7.68	0.10	BDL	29.5
	SP18	6.5	47.0	28.0	5.9	3.6	2.7	10.0	4.0	BDL	4.0	4.90	12.90	1.42	0.14	10.30	0.43	BDL	27.9
	SP19	7.2	52.0	31.0	7.2	6.9	1.6	10.0	2.0	1.22	8.0	9.80	10.90	1.90	0.39	16.40	0.09	BDL	29.9

Detection Limit and Accuracy: SO_4:0.5mg/L ±0.97; NO_3-N: 0.01 mg/L, Fe: 0.01 mg/L, ±0.024, F: 0.02 mg/L, ±0.04, Si: 1.1 mg/L, ±2.1, BDL: Below Detection Level, Temp: Temperature.

Table 4.3 Ranges and mean with standard deviation (given in parenthesis) of spring water quality parameters of the present study with that of WHO (2011) and BIS (2012).

Parameters	Pre-monsoon		Monsoon		Post-monsoon		WHO (2011)	BIS (2012)	
	Lowland	Highland	Lowland	Highland	Lowland	Highland		AL	PL
pH	3.8 – 6.0 (4.5, ± 0.63)	5- 6.2 (5.8, ± 0.37)	4.2 – 6.5 (4.8, ± 0.68)	5.3 – 6.2 (5.9, ± 0. 3)	4.6– 6.4 (4.98, ± 0.58)	5.7 – 7.2 (6.4, ± 0.45)	6.5-8.5	6.5-8.5	NR
EC(μS/cm)	44 - 104 (79, ± 18.58)	39 – 80 (60, ± 15.9)	45 – 103 (72, ± 21.05)	17 – 71 (48.3, ± 15.2)	49 – 121 (85.2, ± 22.7)	32 – 101 (60, ± 22.9)	1500	-	-
TDS (mg/L)	26 - 62 (47.3, ± 11)	23 – 48 (35.7, ± 9.71)	27 – 62 (43.3, ± 12.7)	23 – 43 (32.4, ± 7.1)	29 – 73 (51.29, ± 13.71)	19 – 61 (36, ± 13.9)	500	500	2000
DO (mg/L)	3.2 – 8 (5.4, ± 1.9)	2.3 – 6.5 (4.3, ± 1.25)	1.8 – 7.6 (4.8, ± 1.9)	3.3 – 9.5 (6.7, ± 1.9)	2.8 – 6.6 (4.07, ± 1.39)	5.6 – 8 (6.5, ± 0.73)			
Na (mg/L)	4.7 – 15.4 (11, ± 3.12)	3.8 – 7.7 (5.5, ± 1.38)	6.3 – 14.6 (10.8, ± 3.2)	3.6 – 8.8 (5.1, ± 1.6)	10.1 – 18.4 (13.72, ± 3.05)	3.6 – 11 (6.9, ± 2.6)	200	-	-
K (mg/L)	0.2 – 1.8 (0.74, ± 0.6)	1.4 – 4.1 (2.3, ± 0.84)	0.46 – 2 (0.88, ± 0.62)	1.2 – 3.7 (2.2, ± 0.73)	0.36 – 2.4 (0.95, ± 0.83)	1.2 – 3.8 (2.3, ± 0.9)	12	-	-
TH (mg/L)	6.6 – 20 (11.8, ± 4.05)	10 – 25 (17.3, ± 4.92)	10 - 15 (12, ± 2.4)	5 – 20 (14.8, ± 5.1)	10 – 15 (11.67, ± 2.5)	5 – 25 (14, ± 6.2)	-	200	600
Ca (mg/L)	0.8- 4 (2.5, ± 1.17)	2 - 4 (2.8, ± 0.92)	2 – 4 (2.4, ± 0.88)	1 – 6 (3, ± 1.5)	1 – 4 (2.11, ± 0.78)	2 – 4 (3, ± 1.1)	75	75	200
Mg (mg/L)	BDL - 2.44 (1.73, ± 0.67)	1.2 – 3.7 (2.5, ± 0.94)	BDL – 2.44 (1.4, ± 0.96)	0.61 – 3.7 (1.8, ± 0.9)	1.22 – 2.44 (1.56, ± 0.54)	BDL – 4.9 (1.6, ± 1.4)	50	30	100

Contd...

Parameters	Pre-monsoon		Monsoon		Post-monsoon		WHO (2011)	BIS (2012)	
	Lowland	Highland	Lowland	Highland	Lowland	Highland		AL	PL
TA (mg/L)	0 - 8 (3.6, ± 2.4)	9 - 30 (17.5, ± 6.56)	2 – 6 (3.6, ± 1.7)	10 – 26 (18, ± 5.5)	2 – 10 (4.67, ± 2.45)	4 – 28 (13.1, ± 7.06)	-	200	600
HCO_3 (mg/L)	0 - 9.8 (4.4, ± 2.94)	11 – 36.6 (21.3, ± 0.8)	2.44 – 7.32 (4.3, ± 2.04)	12.2 – 31.7 (21.9, ± 6.7)	2.44 – 12.2 (5.7, ± 2.98)	4.9– 34.2 (16, ± 8.6)	500	-	-
Cl(mg/L)	8.8- 26.6 (18.2, ± 4.87)	4.8 – 13.3 (9.8, ± 2.5)	13.6 – 27.1 (19.5, ± 4.44)	6.8 – 12.6 (8.6, ± 1.9)	15.9 – 28.8 (21.51, ± 4.38)	7 – 17 (11.3, ± 3.8)	250	250	1000
SO_4 (mg/L)	BDL - 2.7 (1.74, ± 0.89)	0. 7 – 2.5 (1.7, ± 0.69)	BDL – 3.4 (0.6, ± 1.23)	BDL – 4.2 (1.8, ± 1.3)	0.71 – 2.4 (1.27, ± 0.51)	1.1 – 4.0 (2.2, ± 1.02)	250	200	400
NO_3-N (mg/L)	0.36 - 3.6 1.88, ± 0.97)	BDL – 0.21 (0.05, ± 0.07)	0.26 – 3.32 (1.61, ± 0.88)	BDL – 1.1 (0.17, ± 0.4)	BDL – 4.02 (2.15, ± 1.01)	BDL – 1.2 (0.3, ± 0.5)	45	45	NR
SiO_2 (mg/L)	3.65 - 5.6 (4.9, ± 0.61)	10.5 – 37.6 (23.2, ± 7.18)	3.8 – 7.8 (5.2, ± 1.31)	8 – 30 (20, ± 6.2)	2.9 – 15.3 (5.34, ± 3.8)	7.7 – 24.6 (15.9, ± 5.75)	-	-	-
Fe (mg/L)	BDL - 1.9 (0.4, ± 0.74)	0.05 – 0.47 (0.18, ± 0.12)	0.01 – 0.96 (0.17, ± 0.32)	0.01 – 0.54 (0.2, ± 0.2)	0.03 – 0.91 (0.17, ± 0.28)	0.05 – 0.53 (0.2, ± 0.16)	0.3	0.3	NR
F (mg/L)	0.04 - 0.53 (0.44, ± 0.15)	0.01 – 0.51 (0.27, ± 0.25)	BDL – 1	BDL – 0.15 (0.03, ± 0.05)	BDL – 0.35 (0.23, ± 0.18)	BDL – 0.7 (0.12, ± 0.26)	-	1	1.5
Temp.	25.5 – 28.5 (27.6, ± 1.09)	24.5 – 28.6 (26.4, ± 1.5)	25 – 26.1 (25.6, ± 0.47)	24 – 26 (25.3 ± 0.63)	28 – 30 (29.1, ± 0.69)	27.9 – 29.9 (28.9, ± 0.65)			

TH, TA estimated as $CaCO_3$; AL: Acceptable Limit, PL: Permissible Limit in the absence of alternate source, BDL: Below Detection Limit., NR: No Relaxation.

The pH of the samples in the study area varies from 3.8 to 7.2. In lowland, the pre-monsoon spring water samples had the lowest pH (mean. 4.5; range 3.8 - 6.0) compared to monsoon (mean 4.8; 4.2-6.5) and post-monsoon (4.9; 4.6 - 6.4) samples. In highland the ranges of pH values are 5 – 6.2, 5.3 – 6.2 and 5.7 – 7.2 with mean values of 5.8, 5.9 and 6.4 in pre-monsoon, monsoon and post-monsoon seasons, respectively. pH value increases marginally during monsoon and post-monsoon seasons.

Electrical Conductivity (EC) is a measure of salt content of water in the form of ions and is expressed in microsiemens/cm (µS/cm); (Karanth, 1987). A sudden rise in conductivity in the water will indicate addition of some pollutants to it. It is an important criterion in determining the suitability of water and waste water for irrigation. EC measurements are often employed to monitor salinity intrusions to the groundwater in coastal regions and to determine the total dissolved solids. In drinking water the individual concentrations of different substances are more important than total dissolved solids. The conductivity increases with increase in concentration of dissolved salts in the spring water samples which in turn is governed by soil depth, rainfall, catchment characteristics etc., of the region. On an average, the highland samples are accounted for the lowest EC (pre-monsoon 60 µS/cm; monsoon 48.3 µS/cm and post-monsoon 60 µS/cm) than the lowland counter parts (79 µS/cm; 72 µS/cm; 85 µS/cm). The average values for TDS in lowland samples are 47.3 mg/L, 43.3 mg/L and 51.3 mg/L in pre-monsoon, monsoon and post-monsoon seasons respectively whereas highland samples the values are 35.7 mg/L, 32.4 mg/L, and 36 mg/L.

The amount of oxygen in water is called dissolved oxygen. Dissolved oxygen (DO) is one of the most important parameters in water quality assessment and reflects the physical and biological processes prevailing in water. DO is important in precipitation and dissolution of inorganic substances. Low oxygen concentrations are generally associated with heavy contamination by organic matter. The DO values varies from 3.2 mg/L to 8 mg/L, 1.8 mg/L to 7.6 mg/L and 2.8 mg/L to 6.6 mg/L in lowland samples during pre-monsoon, monsoon and post-monsoon seasons whereas that in highland the values ranges from 2.3 mg/L to 6.5 mg/L, 3.3 mg/L to 9.5 mg/L and 5.6 mg/L to 8 mg/L. Most of the samples collected from the highland have DO values greater than 6 mg/L during monsoon and post-monsoon seasons.

Sodium (Na) is derived geologically from decomposition (hydrolysis) of various minerals like plagioclase feldspars. Human activities contribute through de-icing and washing products. The observed ranges of sodium are 4.7 – 15.4 mg/L in pre-monsoon, 6.3 – 14.6 mg/L in monsoon and 10.1 – 18.4 mg/L in post-monsoon seasons respectively in lowland region and that in highland counterpart are 3.3 – 7.7 mg/L, 3.6 to 8.8 mg/L and 3.6 – 11 mg/L during the three seasons.

Potassium (K) is also a naturally occurring element, the concentration of which remains quite lower compared to other cations. It has similar chemistry like Na and remains mostly in solution without undergoing any precipitation. In the present study the spatial variation of potassium observed are from 0.2 mg/L to 2.4 mg/L in lowland, and 1.2 mg/L to 4.1 mg/L in highland samples.

Total hardness (TH) results from the metallic ions dissolved in the water reported as concentration of calcium carbonate. Principle cations imparting hardness are calcium and magnesium. The anions responsible for hardness are mainly bicarbonate, carbonate, sulphate, chloride, nitrate, silicates etc. The TH concentration ranges between 6.6 mg/L to 15 mg/L in lowland region and in highland region it ranges between 5 mg/L to 25 mg/L.

Calcium (Ca) in natural water generally varies from 10 mg/L to 100 mg/L depending upon the types of the rock. It has got high affinity to adsorb on the soil particles, therefore the cation exchange equilibria and presence of other cations greatly influence its concentration in water. Natural softening of water takes place when water percolates to aquifers by the ion exchange process with sodium. At higher pH, calcium is reduced due to its precipitation as calcium carbonate ($CaCO_3$). In the present study the ranges of Ca in spring waters of lowland region are from 0.8 mg/L to 4 mg/L, 2 mg/L to 4 mg/L and 1 mg/L to 4 mg/L whereas in highland it recorded from 2 mg/L to 4 mg/L, 1 mg/L to 6 mg/L and 2 mg/L to 4 mg/L respectively during pre-monsoon, monsoon and post-monsoon seasons.

Magnesium (Mg) occurs in natural water with calcium but in lower concentration. Like Ca, Mg also undergoes ion exchange equillibria during the percolation of water through soil. The Mg concentration ranges from BDL to 2.4 mg/L in lowland region and in highland region it ranges from BDL to 4.9 mg/L.

Alkalinity of the water is its capacity to neutralise a strong acid. The total alkalinity (TA) is the number of milliequivalents of acid used in the titration to combine all the hydroxyl ions. Acidity of water is its quantitative capacity to react with a strong base to a designated pH. TA values of all the spring samples are significantly low. In lowland samples the average values of TA during pre-monsoon, monsoon and post-monsoon seasons are 3.6 mg/L, 3.6 mg/L and 4.6 mg/L respectively and in highland the values are 17.5 mg/L, 18 mg/L and 13.1 mg/L. The pH determines the distribution of carbonate species. The spring SP3, has a zero TA value in pre-monsoon as the sample is acidic with a pH value 3.8. Strong mineral acids, weak acids such as carbonic and acetic and hydrolyzing salts such as iron or aluminium, sulphates may contribute to measured acidity (Eaton and Franson*,* 2005). However during monsoon and post-monsoon seasons the TA value for sample SP3 is 2 mg/L, and pH values are slightly increased to 4.4 and 4.6. Bicarbonate values are the measure of total alkalinity (TA x 1.22) as the carbonate ions are not detected in spring samples.

Sulphate (SO_4^{2-}) is an important constituent of hardness with calcium and magnesium. In arid and semi arid regions it occurs in higher concentrations due to the accumulation of soluble source in soils and shallow aquifers. Discharge of industrial waste and domestic sewage in water may increase its concentration. In the spring samples the SO_4^{2-} concentration ranges between BDL and 3.4 mg/L in lowlands and in highlands it ranges between BDL and 4.2 mg/L.

Chloride (Cl^-) is associated with the presence of sodium in drinking water when present in high concentrations. Chloride comes into water often from salt water intrusion, mineral dissolution, industrial and domestic waste etc. Chloride concentration is an indicator of pollution by sewage. The lowland region recorded higher values of Cl^- concentration compared to highland counterparts with an average of 18.2 mg/L, 19.5 mg/L and 21.5 mg/L during pre-monsoon, monsoon and post-monsoon seasons. In highland the values are 9.8 mg/L, 8.6 mg/L and 11.3 mg/L respectively.

Nitrate as nitrogen (NO_3-N) occurs naturally in mineral deposits, soils, sea water, fresh water systems, the atmosphere and biota. It is formed when nitrogen from ammonia or other sources combines with oxygenated water. NO_3-N enters the environment from fertilizer, feedlots and sewage. All the spring water samples show the presence of NO_3-N but with varying concentrations. Majority of the samples in the highland exhibit low NO_3-N values compared to lowland springs. The average NO_3-N in the spring water samples collected from the highland are 0.05 mg/L (range: BDL – 0.21 mg/L), 0.17 mg/L (BDL – 1.1 mg/L) and 0.30 mg/L (BDL – 1.2 mg/L) during pre-monsoon, monsoon and post-monsoon season, respectively. The corresponding NO_3-N values for the lowland spring water samples are 1.88 mg/L (range: 0.36 – 3.6 mg/L) for pre-monsoon, 1.61 mg/L (0.26 – 3.32 mg/L) for monsoon and 1.91 mg/L (0 – 4 mg/L) for post-monsoon.

Silicon (Si) in water is in the form of its oxide silica (SiO_2). About 60% of earth's crust is composed of silicate minerals. The SiO_2 values for pre- monsoon, monsoon and post-monsoon seasons in lowland spring water samples of the Ithikkara and Kallada river basins vary between 3.6 mg/L and 5.6 mg/L, 3.8 mg/L and 7.8 mg/L, 2.9 mg/L and 15.3 mg/L, respectively. In the highland region, the ranges of the values are 10.50 mg/L – 37.6 mg/L, 8 mg/L – 30 mg/L and 7.7 mg/L – 24.6 mg/L respectively during pre-monsoon, monsoon and post-monsoon seasons. Silicon dioxide is enriched in the highland samples manifold higher than the lowland samples. As the pH of the water increases above 9, the solubility of hydrated form increases because of the formation of silicate ions. All the spring samples possess pH values less than 8 and hence silica will occur in the unionized state even though present in small quantities (Raju, 2007).

Iron (Fe^{2+}) is one of the most abundant elements of rocks and soil. All kinds of water including groundwater have appreciable quantities of Fe^{2+}. It is most soluble at acidic pH. The iron content in the spring water samples of lowland varies from BDL to 1.9 mg/L and in highland from 0.01 mg/L to 0.54 mg/L. Springs (SP7) emerging from extensively lateritised areas like Chathannor (GSI, 2005) registered comparatively higher values for Fe^{2+} content during all the three seasons and is found to be above the limit of BIS (2012).

Fluoride (F^-) is a common constituent of groundwater. Natural sources are connected to various types of rocks and to volcanic activity. Agricultural (use of phosphatic fertilizers) and industrial activities (clays used in ceramic industries or burning of coals) also contribute to high fluoride concentrations in groundwater. Fluoride is absent in most of the stations in lowland and highland during monsoon and post-monsoon seasons. However, stations SP14, SP15 and SP19 in the highland and SP9 in lowland have fluoride levels in the range of 0.05 - 0.15 mg/L in monsoon season. During post-monsoon, F^- occurrence is confined only to stations SP10 and SP13 in the highland, and SP4 and SP6 in the lowland. Among these samples the content of F^- ranges from 0.1 mg/L to 0.7 mg/L during post-monsoon.

4.4.2 Trace elements in spring waters

The contamination of water resources by heavy metals is of major concern to mankind. Heavy metals particularly those metals which are in the toxic category even in trace quantities in water may create unnatural physical responses in human beings and animals. A total of 19 samples (lowland – 9 and highland – 10) were subjected to heavy metal estimation. The samples were studied for Arsenic (As), Copper (Cu), Cadmium (Cd), Mercury (Hg), Lead (Pb), Nickel (Ni) and Zinc (Zn).

Arsenic is present in waste waters of many industries such as ceramics, tanneries, chemicals, metal preparation and pesticides. It affects liver, heart and is reported to be carcinogenic. Copper in the natural waters results in higher concentration due to pollution. It is used with sulphate as pesticide and separately as an algaecide. Cadmium is present in waste water from electroplating, chemical industries etc. It causes a painful bone disease called *'itai – itai'*. The seepage of waste is the main source of contamination of groundwater. Mercury is a highly poisonous substance and increases in natural waters by the industrial waste. It affects central nervous system. Mercury caused *'minamata'* incident in Japan. Lead is a toxic element and it enters environment from industry, mining, plumbing, coal etc. Nickel occurs naturally in soils, groundwater and surface water. Zinc is present in high concentration in waste from pharmaceuticals, galvanizing, paint pigments, several insecticides, cosmetics etc., and their discharge increases its concentration in natural water.

The results of the metal analysis for lowland and highland regions in three seasons are given in Tables 4.4 and 4.5. The concentration of cadmium and mercury were found to be below detection limit (0.01 mg/L and 0.05 mg/L) in all the samples of lowland and highland region. In the case of copper, two samples in highland (SP15 and SP16) registered its presence in monsoon season within the permissible limit of 1.5 mg/L (BIS, 2012), but none of the samples in lowland region detected its presence. Arsenic was detected only in one sample (SP1) in lowland and two pre-monsoon samples (SP15 and SP18) in highland and the value is 0.05 mg/L. Lead was detected in a few samples of the lowlands (SP2, SP3 and SP5) and the highlands (SP16, SP17, SP18, SP19) during pre-monsoon season and its concentration was above the permissible limit (0.01 mg/L). Unlike the case of other heavy metals, the presence of nickel and zinc were noticed in many of the spring water samples. In 33.3% of lowland and 43.3% of highland samples nickel was detected whereas 48% of lowland and 63% of highland samples registered the presence of zinc. The ranges of nickel and zinc were respectively BDL to 0.12 mg/L and BDL to 0.06 mg/L in lowland and BDL to 1.02 mg/L and BDL to 0.19 mg/L in highland. The highland sample SP14 (pre-monsoon and sample SP10 (post-monsoon) registered nickel values above the permissible limit. The metal zinc is below detection limit i.e., < 0.01mg/L in all the spring water samples of the lowlands during post-monsoon season. Metals tend to dissolve more in low pH water. Comparative evaluation of the dissolved heavy metal values reveals that with the exception of nickel and lead in a few samples, the concentration of other metals detected in spring samples are below the standards set by WHO (2011) and BIS (2012) which is given in Table 4.6.

Table 4.4 Trace metal concentration (mg/L) in the lowland springs of the study area.

Season	Spring code	As	Cd	Cu	Hg	Pb	Ni	Zn
Pre-monsoon	SP1	0.05	BDL	BDL	BDL	BDL	BDL	BDL
	SP2	BDL	BDL	BDL	BDL	0.03	BDL	BDL
	SP3	BDL	BDL	BDL	BDL	0.04	BDL	BDL
	SP4	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	SP5	BDL	BDL	BDL	BDL	0.05	BDL	0.01
	SP6	BDL	BDL	BDL	BDL	BDL	BDL	0.01
	SP7	BDL	BDL	BDL	BDL	BDL	BDL	0.06
	SP8	BDL	BDL	BDL	BDL	BDL	BDL	0.01
	SP9	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Monsoon	SP1	BDL	BDL	BDL	BDL	BDL	BDL	0.01
	SP2	BDL	BDL	BDL	BDL	BDL	BDL	0.01
	SP3	BDL	BDL	BDL	BDL	BDL	BDL	0.01
	SP4	BDL	BDL	BDL	BDL	BDL	BDL	0.01
	SP5	BDL	BDL	BDL	BDL	BDL	BDL	0.01
	SP6	BDL	BDL	BDL	BDL	BDL	BDL	0.01
	SP7	BDL	BDL	BDL	BDL	BDL	0.01	0.01
	SP8	BDL	BDL	BDL	BDL	BDL	BDL	0.01
	SP9	BDL	BDL	BDL	BDL	BDL	BDL	0.01
Post-monsoon	SP1	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	SP2	BDL	BDL	BDL	BDL	BDL	0.01	BDL
	SP3	BDL	BDL	BDL	BDL	BDL	0.12	BDL
	SP4	BDL	BDL	BDL	BDL	BDL	0.03	BDL
	SP5	BDL	BDL	BDL	BDL	BDL	0.012	BDL
	SP6	BDL	BDL	BDL	BDL	BDL	0.013	BDL
	SP7	BDL	BDL	BDL	BDL	BDL	0.013	BDL
	SP8	BDL	BDL	BDL	BDL	BDL	0.011	BDL
	SP9	BDL	BDL	BDL	BDL	BDL	0.01	BDL

BDL : Below Detection Limit.
Detection Limit: As:0.05mg/L; Cd: 0.01 mg/L, Cu: 0.01 mg/L, Hg: 0.05 mg/L, Pb: 0.03 mg/L, Ni: 0.01 mg/L, Zn: 0.01 mg/L.

Table 4.5 Trace metal concentration (mg/L) in the highland springs of the study area.

Season	Spring code	As	Cd	Cu	Hg	Pb	Ni	Zn
Pre-monsoon	SP10	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	SP11	BDL	BDL	BDL	BDL	BDL	BDL	0.01
	SP12	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	SP13	BDL	BDL	BDL	BDL	BDL	0.02	0.05
	SP14	BDL	BDL	BDL	BDL	BDL	1.02	0.02
	SP15	0.05	BDL	BDL	BDL	BDL	BDL	0.01
	SP16	BDL	BDL	BDL	BDL	0.03	BDL	BDL
	SP17	BDL	BDL	BDL	BDL	0.03	BDL	BDL
	SP18	0.05	BDL	BDL	BDL	0.03	BDL	0.01
	SP19	BDL	BDL	BDL	BDL	0.06	BDL	0.01
Monsoon	SP10	BDL	BDL	BDL	BDL	BDL	BDL	0.02
	SP11	BDL	BDL	BDL	BDL	BDL	BDL	0.02
	SP12	BDL	BDL	BDL	BDL	BDL	0.01	0.02
	SP13	BDL	BDL	BDL	BDL	BDL	0.01	0.03
	SP14	BDL	BDL	BDL	BDL	BDL	BDL	0.03
	SP15	BDL	BDL	1.004	BDL	BDL	0.01	0.01
	SP16	BDL	BDL	1.002	BDL	BDL	BDL	0.01
	SP17	BDL	BDL	BDL	BDL	BDL	0.01	0.02
	SP18	BDL	BDL	BDL	BDL	BDL	0.01	0.02
	SP19	BDL	BDL	BDL	BDL	BDL	BDL	0.01
Post-monsoon	SP10	BDL	BDL	BDL	BDL	BDL	0.34	BDL
	SP11	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	SP12	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	SP13	BDL	BDL	BDL	BDL	BDL	BDL	0.19
	SP14	BDL	BDL	BDL	BDL	BDL	0.014	0.16
	SP15	BDL	BDL	BDL	BDL	BDL	0.01	0.01
	SP16	BDL	BDL	BDL	BDL	BDL	0.01	BDL
	SP17	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	SP18	BDL	BDL	BDL	BDL	BDL	0.01	BDL
	SP19	BDL	BDL	BDL	BDL	BDL	0.01	BDL

BDL: Below Detection Limit
Detection Limit: As:0.05mg/L; Cd: 0.01 mg/L, Cu: 0.01 mg/L, Hg: 0.05 mg/L, Pb: 0.03 mg/L, Ni: 0.01 mg/L, Zn: 0.01 mg/L.

Table 4.6 Summary table showing trace element concentration (mg/L) in the spring water samples of the study area, with that of BIS (2012) and WHO (2011).

Parameters	Lowland	Highland	BIS (2012)		WHO 2011
			AL	MPL	
As	(BDL - 0.05)	(BDL - 0.05)	0.01	0.05	0.05
Cu	BDL	(BDL - 1.004)	0.05	1.5	2
Pb	(BDL - 0.04)	(BDL - 0.06)	0.01	NR	0.01
Ni	(BDL - 0.12)	(BDL - 1.02)	0.02	NR	0.07
Zn	(BDL - 0. 6)	(BDL - 0.19)	5	15	-
Cd	BDL	BDL	0.003	NR	-
Hg	BDL	BDL	0.001	NR	-

Ranges are given in parenthesis; BDL: Below Detection Level; AL: Acceptable Limit; MPL: Maximum Permissible Limit; NR: No relaxation.

4.4.3 Bacteriological analysis

Bacteriological analysis revealed that, 44% samples in the lowland recorded the presence of coliform and 50% of these samples were detected for faecal coliform during pre-monsoon season (Table 4.7). None of the samples were detected for *E.coli*. On the contrary 78% monsoon samples were contaminated with coliform of which 71% of samples had faecal coliform. Four springs out of the nine springs examined during the monsoon season showed the presence of *E.coli* confirming faecal contamination. About 89% of water samples collected from lowland during the post-monsoon had the incidence of coliform and 63% of these were contaminated by faecal coliform bacteria. The presence of *E.coli* was noticed in two springs out of the total of nine spring sources studied.

The samples collected from highland have higher total coliform counts than lowland. The entire pre-monsoon and monsoon samples and 70% of post-monsoon samples of highland region confirmed the presence of total coliform. Faecal coliform bacteria were detected in 80% of pre-monsoon, 90% of monsoon and 71% of post-monsoon samples. Among the ten springs examined 50% of pre-monsoon and 30% of monsoon samples were positive for the presence of *E.coli*. During post-monsoon period *E.coli* was detected in 30% of the samples.

Table 4.7 Bacteriological parameters of the spring water samples of the study area collected during pre-monsoon, monsoon and post-monsoon seasons.

Physiography	Spring code	Pre-monsoon			Monsoon			Post-monsoon		
		TC*	FC#	*E.coli*	TC*	FC#	*E.coli*	TC*	FC#	*E.coli*
Lowland	SP1	9	4	-ve	1600	1600	+ve	50	Nil	-ve
	SP2	Nil	Nil	-ve	33	22	-ve	240	27	-ve
	SP3	Nil	Nil	-ve	Nil	Nil	-ve	Nil	Nil	-ve
	SP4	Nil	Nil	-ve	1600	500	+ve	300	Nil	-ve
	SP5	Nil	Nil	-ve	500	110	+ve	30	17	-ve
	SP6	Nil	Nil	-ve	300	300	+ve	900	900	+ve
	SP7	39	23	-ve	1600	Nil	-ve	1600	900	+ve
	SP8	4	Nil	-ve	Nil	Nil	-ve	50	Nil	-ve
	SP9	810	Nil	-ve	190	Nil	-ve	50	7	-ve
Highland	SP10	150	23	-ve	1600	7	-ve	140	140	-ve
	SP11	1600	1600	+ve	1600	1600	+ve	1600	Nil	-ve
	SP12	500	110	+ve	1600	1600	+ve	34	Nil	-ve
	SP13	150	Nil	-ve	900	7	-ve	Nil	Nil	-ve
	SP14	9	Nil	-ve	50	7	-ve	Nil	Nil	-ve
	SP15	2400	1100	+ve	1600	280	+ve	17	8	-ve
	SP16	150	150	-ve	17	30	-ve	1600	500	+ve
	SP17	1100	11	-ve	300	Nil	-ve	Nil	Nil	-ve
	SP18	2400	1100	+ve	1600	70	-ve	1600	500	+ve
	SP19	460	150	+ve	1600	9	-ve	1600	500	+ve

** TC –Total Coliform, # FC – Fecal Coliform; All values in MPN/100ml;*
+ve : Positive, -ve: Negative.

4.5 Discussion

4.5.1 Hydrochemical processes

There are different factors responsible for the quality and quantity of dissolved salts in spring waters. The subsurface geochemical milieu, exchange of ions between water and host rocks, duration of contact of water with the host rock, sources of groundwater, specific surface area of the aquifer material etc., are some of the natural determinants regulating solute concentration in spring waters (Sarin *et al.,* 1989; Berner and Berner, 1995; Singh *et al.,* 2011). In addition to these, the depth of occurrence of groundwater and the extent of anthropogenic activities in the spring catchments may also influence the hydrochemical properties of spring waters (Todd, 1980; Appelo and Postma, 2005).

Inter-comparison of spring water pH between highland and lowland shows that the latter is more acidic than the former. Natural weak acid water occurs in the unconfined and confined aquifers of Quaternary and Neogene unconsolidated sediments. The H^+ ions in the springs of the study area may be derived from the dissociation of H_2CO_3, release of the absorbed H_3O^+ in clay layers and from the acidity of rainwater. Lack of alkaline substances in the spring water may also cause accumulation of acidity (Zhou *et al.,* 2015).

The DO values of the samples exhibited marked spatial variation. The samples collected from the source point of spring discharge usually have chances of low miscibility with atmospheric oxygen. This may be one of the reasons for the observed low DO values in the spring water samples (e.g. SP2, SP3 & SP5). Many springs in the different parts of world reported low DO levels, generally less than 1 mg/L (Scott *et al.*, 2004). Under anaerobic conditions in the subsurface formations, the oxidized species like NO_3^-, Fe^{3+} and SO_4^{2-} may be reduced chemically and persist in groundwater for significant periods of time (Darling and Gooddy, 2006).

Among the major cations, Na^+ is the most dominant ion followed by Ca^{2+}, Mg^{2+} and K^+. With the exception of Na^+, all the other cations (K^+, Ca^{2+} and Mg^{2+}) are enriched in the highland samples than the lowland counterparts. In the lowland, in addition to weathering contributions, Na^+ could also reach the spring waters from sources like marine aerosols falling through rainfall contributions, sewages and agricultural lands.

A comparison of TA values of lowland samples with that of total hardness (TH) shows that all the spring samples have a higher TH values than TA which indicates that the spring water in this region is characterized by non-carbonated hardness (Chow, 1964). In highland samples the total alkalinity values are almost similar or even higher which shows the presence of HCO_3 alkalinity. All the spring samples have a zero phenolphthalein alkalinity and hence carbonate ions are found to be absent.

Among the anions, HCO_3^- and SO_4^{2-} are enriched in the highland samples than the lowland counterparts. On the contrary, Cl^- exhibits a reverse trend with about double the enrichment in the lowland springs. The variations of Cl^- are similar to that of Na^+ with a correlation coefficient of 0.93.

It is inferred from trace metal analysis that lead and nickel exceeds permissible limit in a few spring samples. Lead may be leached to the environment from solid waste materials like batteries and pipes dumped near the sample locations. Lead contamination in groundwater may occur from sources such as gasoline, pipes, pigments and batteries (Hem, 1985). This metal has serious cumulative effects and can accumulate in bones, causing nausea, nervous and reproductive disorders and kidney damage in humans (Friberg *et al*., 1986). Negative effects of nickel in humans are believed to be minimal but may be toxic to certain flora and fauna (Vetrimurugan *et al.,* 2016).

Bacteriological analysis revealed that contamination of spring water by coliforms and faecal coliforms is widespread. The presence of *E.coli* in certain springs has confirmed the occurrence of faecal contamination. Free falling types of springs are found to be more contaminated with respect to *E.coli* compared to boiling type springs. The catchment area of free falling type springs may be at a far location from which water may infiltrate into the soil and entering into confined aquifer. Hence these springs are often contaminated by faecal bacteria because of the interaction between rocks having high permeability and microbial pollutants introduced into the environment by grazing and/or manure spreading (Celico *et al.,* 2004). Among the boiling type springs, only SP11 is found to be contaminated. Except SP11 all other boiling type springs under study are well protected by the people of locality and is free from anthropogenic pollution. Water infiltration from agricultural areas that heavily use biomanure for raising agricultural productivity, climatic conditions, soil and geologic characteristics, land use patterns etc., may contribute to the presence and survival of coliform bacteria in spring discharge (Saldutti, 2009).

4.5.1.1 Hydrochemical facies

The data plots on trilinear diagram (Fig 4.3) belonging to the lowland region of the study area shows that the samples of the three seasons fall into the $Na^+ + K^+$ group in the triangular cationic field and Cl^- type in the anionic field. All the samples in the Zone 2 of diamond shaped field (Refer Fig 3.1, Chapter III) indicate the predominance of NaCl type water. The spring waters of the lowland region show dominance of Cl^- in the anionic group and Na^+ in the cationic group.

The triangular cationic field in pre-monsoon for highland samples indicates that 80% of the samples fall in no dominant type and 20% samples in Na type. From the anionic triangle 80% of sample fall into HCO_3 type and the remaining 20% in Cl^-

Lowland springs **Highland springs**

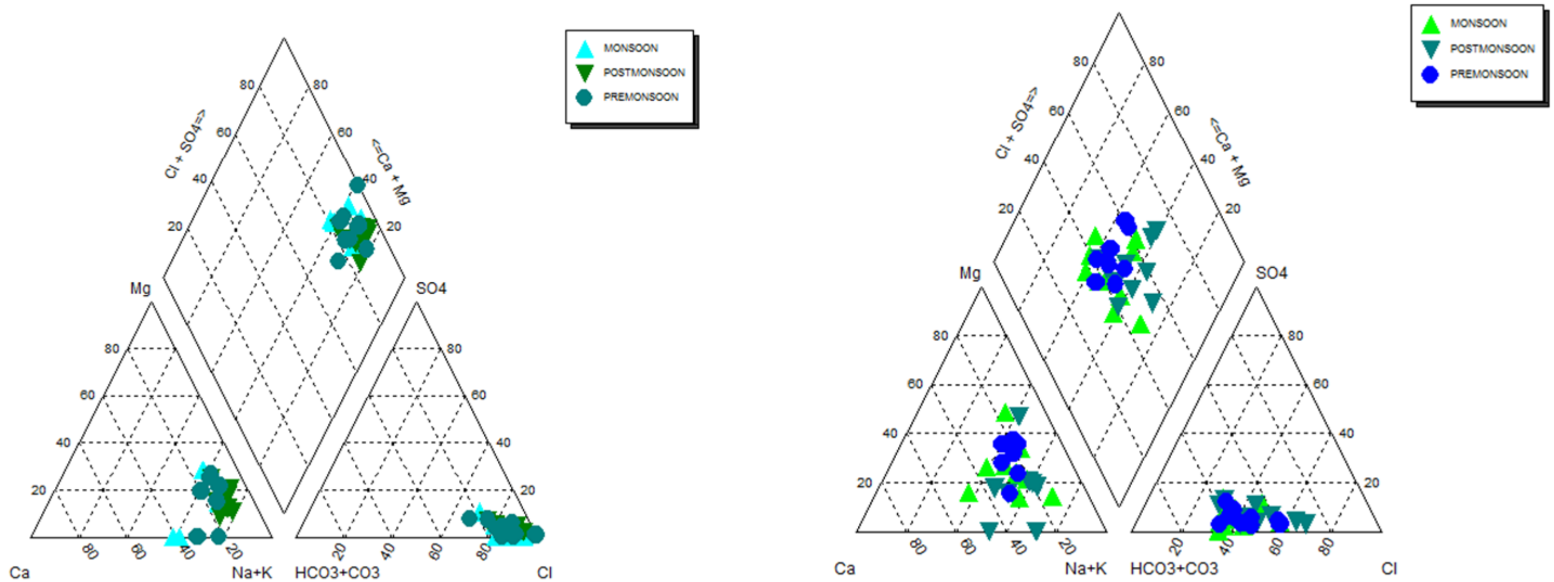

Fig. 4.3 Piper (1953) diagram showing the relationship between dissolved ions in the spring water samples in the lowland and highland regions of Ithikkara and Kallada river basins.

type. 40% of the samples are distributed in Zone 1 of diamond shaped field which indicate the predominance $CaHCO_3$ type. 30% of the sample fall into mixed CaMgCl and the rest 30% in mixed $CaNaHCO_3$ class. Samples present in Zone 4 indicate the dissolution of sedimentary rocks and Na feldspar minerals, secondary evaporation and ion exchange processes which eventually increase the concentration of milliequivalent percentage of Na and Cl and decrease in the percentage of HCO_3, SO_4 and Ca (Ahamed *et al.,* 2015). During monsoon season 60% of sample in the cationic field are present in no dominant class followed by 40% in Na type where as in anionic triangle 70% fall in bicarbonate, 20% in no dominant category and the rest 10% in chloride type. No sulphate types were identified. About 40% samples exhibit the dominance of $CaHCO_3$ type and 30% each in mixed $CaNaHCO_3$ and NaCl category. In the post-monsoon season 50% of the sample fall in no dominant class and the rest 50% in Na type in the cationic triangular field. About 40% samples in the anionic triangle account for HCO_3 type and further 30% each account for Cl type and no-dominant type. In the diamond field 30% samples fall in mixed $CaNaHCO_{3,}$ 50% NaCl type and 20% $CaHCO_3$ type.

4.5.1.2 Data analysis using correlation matrix

The Pearson correlation matrix describes interrelationship between variables and results for 17 hydrochemical parameters are generated. The Pearson correlation matrix (Table 4.8) along with p values (Table 4.9) for spring samples in lowland region showed that pH had a positive moderate correlation with TA (r = 0.55), HCO_3^- (r = 0.55) and SO_4^{2-} (r = 0.68) and strong correlation with Fe^{2+} (0.77). EC showed strong to moderate correlation with Na^+, Cl^-, K^+ and NO_3-N, (Table 4.8). This suggests that EC is controlled by these ions. The strong positive correlation between Na^+ and Cl^- (0.97) and K^+ and Cl^- (0.78) in spring water suggest their association and common source for these ions (Kura *et al.,* 2013). There exist a perfect correlation between TA and HCO_3^- showing that TA is imparted mainly by HCO_3 ions present in water.

Table 4.8 Correlation matrix (Pearson) for lowland spring water samples (also see table 4.2 for details).

Variables	pH	EC	TDS	DO	Na^+	K^+	TH	Ca^{2+}	Mg^{2+}	TA	HCO_3^-	Cl^-	SO_4^{2-}	NO_3-N	SiO_2	Fe^{2+}	F^-
pH	**1.00**																
EC	-0.26	**1.00**															
TDS	-0.26	**1.00**	**1.00**														
DO	**0.41**	-0.17	-0.17	**1.00**													
Na^+	-0.19	**0.94**	**0.94**	-0.24	**1.00**												
K^+	-0.14	**0.73**	**0.74**	0.08	**0.63**	**1.00**	**0.54**										
TH	0.03	**0.59**	**0.59**	-0.09	**0.47**	**0.54**	**1.00**										
Ca^{2+}	-0.08	0.16	0.15	0.12	0.09	0.37	0.22	**1.00**									
Mg^{2+}	0.08	**0.42**	**0.42**	-0.17	0.36	0.23	**0.73**	**-0.50**	**1.00**								
TA	**0.55**	0.01	0.01	0.17	0.14	-0.28	-0.09	-0.10	-0.01	**1.00**							
HCO_3^-	**0.55**	0.01	0.01	0.17	0.14	-0.28	-0.09	-0.10	-0.01	**1.00**	**1.00**						
Cl^-	-0.20	**0.92**	**0.93**	-0.17	**0.93**	**0.78**	**0.56**	0.22	0.34	0.03	0.03	**1.00**					
SO_4^{2-}	**0.68**	-0.04	-0.04	0.15	0.06	-0.29	0.21	-0.15	0.30	**0.64**	**0.64**	-0.08	**1.00**				
NO_3-N	**-0.46**	**0.76**	**0.77**	-0.21	**0.68**	**0.65**	**0.55**	0.10	**0.42**	**-0.50**	**-0.50**	**0.67**	-0.27	**1.00**			
SiO_2	-0.07	-0.25	-0.25	-0.08	-0.19	-0.23	-0.21	-0.23	-0.03	-0.01	-0.01	-0.23	-0.05	-0.06	**1.00**		
Fe_{2+}	**0.77**	-0.20	-0.20	**0.45**	-0.23	-0.14	0.02	0.23	-0.14	**0.47**	**0.47**	-0.25	**0.59**	**-0.43**	-0.04	**1.00**	
F^-	-0.22	-0.02	-0.03	**0.39**	-0.15	0.00	0.08	**0.45**	-0.24	0.01	0.01	-0.14	-0.06	0.03	0.02	0.06	**1.00**

Values in bold are with a significance level alpha=0.05

Table 4.9 P values for lowland spring water samples

Variables	pH	EC	TDS	DO	Na^+	K^+	TH	Ca^{2+}	Mg^{2+}	TA	HCO_3^-	Cl^-	SO_4^{2-}	NO_3-N	SiO_2	Fe^{2+}	F^-
pH	**0.00**																
EC	0.18	**0.00**															
TDS	0.19	**< 0.0001**	**0.00**														
DO	**0.03**	0.41	0.40	**0.00**													
Na^+	0.35	**< 0.0001**	**< 0.0001**	0.22	**0.00**												
K^+	0.49	**< 0.0001**	**< 0.0001**	0.70	**0.00**	**0.00**											
TH	0.88	**0.00**	**0.00**	0.65	**0.01**	**0.00**	**0.00**										
Ca^{2+}	0.71	0.44	0.45	0.55	0.65	0.06	0.26	**0.00**									
Mg^{2+}	0.69	**0.03**	**0.03**	0.41	0.07	0.26	**< 0.0001**	**0.01**	**0.00**								
TA	**0.00**	0.97	0.96	0.40	0.49	0.15	0.65	0.61	0.97	**0.00**							
HCO_3^-	**0.00**	0.97	0.97	0.40	0.49	0.16	0.65	0.62	0.96	**< 0.0001**	**0.00**						
Cl^-	0.32	**< 0.0001**	**< 0.0001**	0.40	**< 0.0001**	**< 0.0001**	**0.00**	0.28	0.08	0.89	0.88	**0.00**					
SO_4^{2-}	**< 0.0001**	0.86	0.85	0.44	0.75	0.14	0.29	0.44	0.13	**0.00**	**0.00**	0.69	**0.00**				
NO_3-N	**0.02**	**< 0.0001**	**< 0.0001**	0.30	**< 0.0001**	**0.00**	**0.00**	0.62	**0.03**	**0.01**	**0.01**	**0.00**	0.18	**0.00**			
SiO_2	0.75	0.20	0.21	0.71	0.35	0.25	0.29	0.25	0.90	0.95	0.95	0.25	0.80	0.75	**0.00**		
Fe_{2+}	**< 0.0001**	0.31	0.31	**0.02**	0.24	0.50	0.93	0.25	0.47	**0.01**	**0.01**	0.22	**0.00**	**0.03**	0.83	**0.00**	
F^-	0.27	0.90	0.88	**0.04**	0.44	0.98	0.68	**0.02**	0.22	0.96	0.97	0.49	0.75	0.90	0.90	0.76	**0.00**

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

Table 4.10 Correlation matrix (Pearson) for highland spring water samples (also see table 4.2 for details).

Variables	pH	EC	TDS	DO	Na^+	K^+	TH	Ca^{2+}	Mg^{2+}	TA	HCO_3^-	Cl^-	SO_4^{2-}	NO_3-N	SiO_2	Fe^{2+}	F^-
pH	**1.00**																
EC	-0.03	**1.00**															
TDS	-0.11	**0.86**	**1.00**														
DO	**0.28**	-0.42	-0.33	**1.00**													
Na^+	0.03	**0.63**	**0.84**	-0.05	**1.00**												
K^+	-0.26	**0.44**	**0.35**	-0.17	**0.13**	**1.00**											
TH	-0.09	**0.74**	**0.79**	-0.44	**0.49**	**0.12**	**1.00**										
Ca^{2+}	0.00	0.45	0.59	-0.23	0.29	0.15	0.51	**1.00**									
Mg^{2+}	-0.10	**0.58**	**0.55**	-0.36	0.38	0.04	**0.85**	**-0.03**	**1.00**								
TA	**-0.26**	0.43	0.62	-0.25	0.47	-0.05	0.78	0.28	0.73	**1.00**							
HCO_3^-	**-0.26**	0.43	0.62	-0.25	0.47	-0.05	0.78	0.28	0.73	**1.00**	**1.00**						
Cl^-	0.07	**0.72**	**0.77**	-0.20	**0.77**	**0.33**	**0.52**	0.37	0.37	0.22	0.22	**1.00**					
SO_4^{2-}	**0.30**	-0.14	-0.18	-0.01	-0.19	0.13	-0.11	-0.19	0.00	**-0.04**	**-0.04**	-0.38	**1.00**				
NO_3-N	**-0.06**	**0.51**	**0.50**	0.12	**0.52**	**0.58**	**0.11**	0.17	**0.02**	**-0.13**	**-0.13**	**0.66**	-0.26	**1.00**			
SiO_2	-0.29	-0.07	0.08	-0.30	0.07	-0.26	0.24	-0.19	0.41	0.57	0.57	-0.18	0.06	-0.42	**1.00**		
Fe_{2+}	**0.08**	-0.17	-0.30	**0.07**	-0.38	-0.25	-0.27	0.12	-0.38	**-0.35**	**-0.35**	-0.35	**0.06**	**-0.27**	-0.09	**1.00**	
F^-	-0.07	0.23	0.18	**-0.15**	0.16	-0.09	0.22	**-0.04**	0.28	0.03	0.03	0.24	-0.17	0.05	0.22	-0.07	**1.00**

Values in bold are with a significance level alpha=0.05

Table 4.11 P values for highland spring water samples

Variables	pH	EC	TDS	DO	Na^+	K^+	TH	Ca^{2+}	Mg^{2+}	TA	HCO_3^-	Cl^-	SO_4^{2-}	NO_3-N	SiO_2	Fe^{2+}	F^-
pH	**0.00**																
EC	0.86	**0.00**															
TDS	0.56	**< 0.0001**	**0.00**														
DO	**0.13**	0.02	0.07	**0.00**													
Na^+	0.87	**0.00**	**< 0.0001**	0.79	**0.00**												
K^+	0.16	**0.01**	**0.06**	0.38	**0.49**	**0.00**											
TH	0.65	**< 0.0001**	**< 0.0001**	0.02	**0.01**	**0.52**	**0.00**										
Ca^{2+}	0.99	0.01	0.00	0.21	0.12	0.41	0.00	**0.00**									
Mg^{2+}	0.60	**0.00**	**0.00**	0.05	0.04	0.84	**< 0.0001**	**0.88**	**0.00**								
TA	**0.16**	0.02	0.00	0.18	0.01	0.81	< 0.0001	0.13	< 0.0001	**0.00**							
HCO_3^-	**0.16**	0.02	0.00	0.18	0.01	0.81	< 0.0001	0.13	< 0.0001	**< 0.0001**	**0.00**						
Cl^-	0.72	**< 0.0001**	**< 0.0001**	0.29	**< 0.0001**	**0.07**	**0.00**	0.05	0.04	0.24	0.23	**0.00**					
SO_4^{2-}	**0.11**	0.47	0.34	0.97	0.31	0.49	0.58	0.31	0.98	**0.82**	**0.83**	0.04	**0.00**				
NO_3-N	**0.75**	**0.00**	**0.00**	0.53	**0.00**	**0.00**	**0.56**	0.38	**0.93**	**0.49**	**0.49**	**< 0.0001**	0.16	**0.00**			
SiO_2	0.12	0.71	0.67	0.11	0.71	0.16	0.19	0.31	0.03	0.00	0.00	0.35	0.75	0.02	**0.00**		
Fe_{2+}	**0.68**	0.36	0.10	**0.71**	0.04	0.19	0.15	0.52	0.04	**0.06**	**0.06**	0.06	**0.77**	**0.15**	0.64	**0.00**	
F^-	0.72	0.22	0.34	**0.41**	0.40	0.64	0.25	**0.84**	0.14	0.86	0.86	0.21	0.37	0.78	0.24	0.72	**0.00**

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

TH is strongly correlated to Mg^{2+} (0.73), moderately to Cl (r = 0.56), SO_4^{2-} (r=0.55) and NO_3-N (r = 0.55) which shows the role of these ions in contributing hardness to water. A moderate correlation between Na^+ and K^+ (r = 0.63) indicate that they are of the same rock source. The correlation existing between Na^+ - NO_3-N (r= 0.68), K^+ - NO_3-N (r = 0.65), Cl^- – NO_3-N (r = 0.67), Mg^{2+} – NO_3-N (r = 0.42) points towards a possibility of contamination from point and non-point sources (Selvakumar *et al.,* 2014). There exists a moderate correlation between Fe^{2+} and SO_4^{2-} (0.59) and a weak positive correlation is observed between Ca^{2+} and F^- (0.45) which indicated their partial association in the solute phase.

The Pearson correlation matrix (Table 4.10) along with p values (Table 4.11) for highland springs shows that pH does not show a significant correlation with any of the water quality parameters. A strong correlation exists for EC with TH (r = 0.74) and Cl^- (0.72) and a moderate correlation with Na^+, Mg^{2+} and NO_3-N and is weakly correlated to K^+, Ca^{2+}, HCO_3^-. TDS is strongly correlated to EC and strongly to Na^+ (r = 0.84), TH (r = 0.79) and Cl^- (r = 0.77); moderately correlated to Ca^{2+} (r = 0.59), Mg^{2+} (r = 0.55), HCO_3^- (r = 0.62) and NO_3-N (r = 0.5). This suggests that EC and TDS are controlled by these ions (Sundaray, 2010). The correlation matrix shows that Na^+ is strongly correlated with Cl^- and also that the variation of Na^+ and Cl^- is significantly correlated to NO_3-N reflecting that a major part of these ions reaches in spring samples through anthropogenic sources as well (Giridharan *et al*., 2009). Cl^- is strongly correlated to Na^+ (r = 0.77) and weakly to Ca^{2+} and Mg^{2+} (r = 0.37). Mg^{2+} and TH are strongly correlated (r = 0.85) where as Ca is moderately correlated to TH (r = 0.51). Mg^{2+} is strongly correlated to HCO_3^- (r = 0.73). Na^+, K^+ and Cl^- showed moderate correlation with NO_3-N (r = 0.52, 0.58 and 0.66). SiO_2 is moderately correlated to TA and HCO_3^- (0.57). Mg-SO_4^{2-} , Ca-SO_4^{2-} and Na- SO_4^{2-} shows no correlation, suggesting that the overall water chemistry is not predominant by a dissolution / precipitation reaction alone (Giridharan *et al*., 2009).

Although the spring water samples of the Ithikkara and Kallada river basins contain cations like Na^+, K^+, Ca^{2+} and Mg^{2+}, the former one (i.e., Na^+) is enriched markedly over the rest of the cations, both in the highland and lowland regions. The concentration of Na^+ shows about 2-fold enrichment in lowland than its highland counterparts. At the same time, the other cations (Ca^{2+}, Mg^{2+} and K^+) are enriched in highland spring samples. Among the anions, Cl^- exhibits a trend similar to that of Na^+. But the relation is very strong in the lowland (r = 0.93) than highland (r = 0.77). All these observations point the role of silicate weathering in contributing a significant proportion of dissolved solids to spring waters, especially in the highland. The observed higher concentration of Na^+ over K^+ in the spring waters of the highland may be attributed to comparatively high stability index of K^+ bearing minerals (to chemical weathering) over Na^+ bearing minerals (Goldich, 1938). Furthermore, a significant portion of the K^+ ions will usually be absorbed onto clay mineral particles in the weathering front, a feature also reported earlier by Rao (2008).

4.5.1.3 Scatter Plots

The plots of $Ca^{2+} + Mg^{2+}$ v*s* $HCO_3^- + SO_4^{2-}$, worked out for the highland springs spread around the equiline and show an increasing trend (Fig. 4.4). This indicates clearly the inequilibrium of the ions in highland and any difference in the ionic content will be compensated by other anions and cations of the weathering front. But in the lowland, except one, all the other samples are seen above the equiline indicating that a significant proportion of the Ca^{2+} and Mg^{2+} are compensated by other anions (Fig. 4.5). The plots of total cations against $Na^+ + K^+$ and Cl^- as well as $Na^+ + K^+$ against Cl^- give strong positive correlation both in highland and lowland regions (Refer: Fig. 4.4 and 4.5). This shows that the alkalis in spring waters of the study area occur mainly with chlorides than other types of anions. But if any excess Cl^- occurs in the lowland will be balanced by the other available cations in the spring water samples.

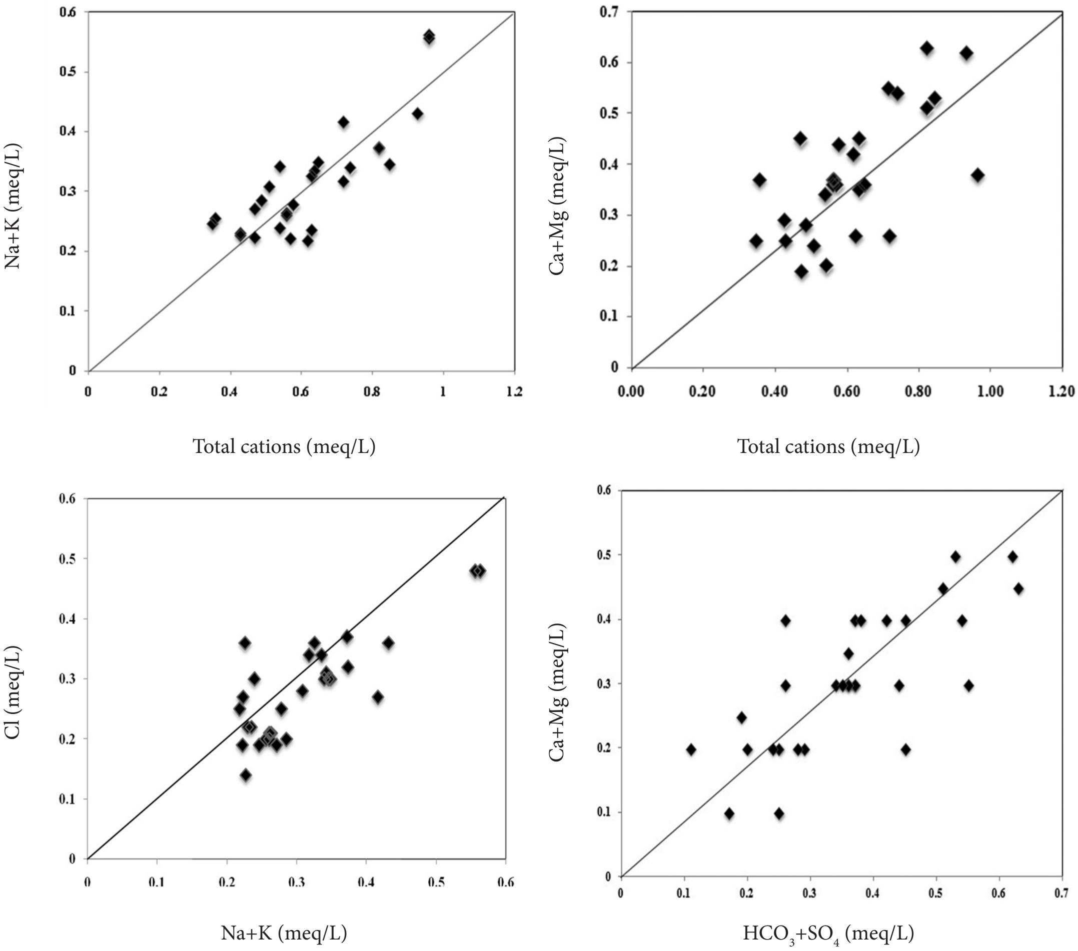

Fig.4.4 Variation diagram showing total cations *vs* alkali and alkaline earth metals, alkaline metals *vs* chloride and alkaline earth metals *vs* bicarbonate plus sulphate in the spring water samples in the highland region.

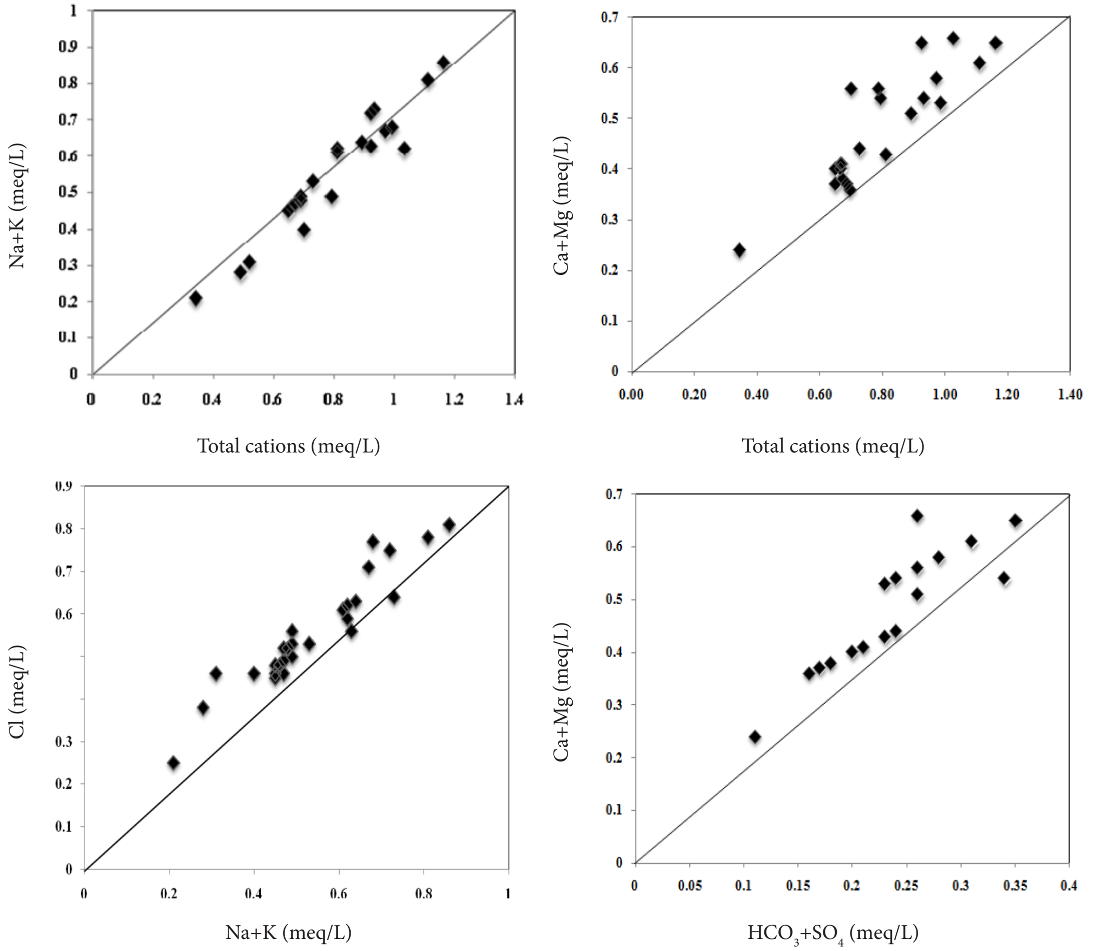

Fig.4.5 Variation diagram showing total cations *vs* alkali and alkaline earth metals, alkaline metals *vs* chloride and alkaline earth metals *vs* bicarbonate plus sulphate in the spring water samples in the lowland region.

4.5.1.4 Ion-exchange

Ion-exchange is an important factor that determines the geochemical processes responsible for changes in spring/groundwater quality. Ion- exchange process can be understood best by chloro- alkaline indices or Schoeller index (Schoeller 1965, 1977) and is expressed as:

$$CAI\text{-}I = Cl^- - (Na^+ + K^+)/\ Cl^-$$

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

In the case of spring water samples of the highlands of Ithikkara and Kallada river basins, 80% of the samples have CAI values negative indicating chloro- alkaline disequilibrium and prevalence of cation- anion exchange reaction. During this process, the host rock is the primary source of dissolved solids in water. In about 20% of the samples, the values are positive indicating the prevalence of base exchange reaction. At the same time, in the lowland spring water samples, 67% of the samples exhibit positive CAI values, indicating base exchange reaction in which alkaline earths (Ca^+ and Mg^+) have been exchanged for Na^+. The remaining 33% samples in the lowland undergo cation- anion exchange reaction (Tables 4.12 and 4.13).

4.5.1.5 Terrain and geologic factors

The total solute content of the spring waters of the Ithikkara and Kallada river basins is significantly lower than those reported for the other springs in India (Table 4.14). This may be attributed to the combined effect of terrain gradients and lithological characteristics of the study area. The high gradient nature of the spring catchments, especially in the highlands, offer low residence time to the groundwaters to interact with mineral phases in the host rock imparting only low amounts of solutes to the subsurface waters (Walling, 1980). Further from the Figure 2.3,Chapter II it is clear that the Ithikkara and Kallada river basins are occupied mainly by granulitic rock types which are more resistant to weathering compared to basaltic and other ferromagnesian rich host rocks in other parts of the country where spring occurrences are noticed. The low temperature of spring water will be another reason for the observed low solute content of the spring water samples in the study area. In the lowlands of the study area the aquifers are made up essentially of quartzose sandstones of the Neogene deposits which can yield only marginal amounts of ions to the surface waters. Therefore, a greater proportion of the cationic (Na^+) and anionic (Cl^-, NO_3^-) contribution in the spring waters in the lowlands might be of have derived from anthropogenic sources and/or aerosol contributions, a feature also observed earlier by Padmalal *et al.* (2012).

Table 4.12 Total ions concentration, CAI, SAR, % Na, RSC values for lowland spring water samples.

Season	Spring Code	TZ-	TZ+	CAI - I	CAI-II	SAR	% Na	RSC
Pre-monsoon	SP1	0.66	0.67	-0.02	-0.06	1.42	70	-0.16
	SP2	0.65	0.65	0.07	0.19	1.39	69.2	-0.12
	SP3	0.88	1.03	-0.02	-0.04	1.3	61	-0.4
	SP4	1	0.92	0.04	0.13	2.12	78.2	-0.12
	SP5	0.92	0.92	-0.11	-0.17	1.59	67.5	-0.18
	SP6	0.7	0.66	0.03	0.08	1.43	69.9	-0.16
	SP7	0.69	0.65	0.02	0.03	1.36	69.1	-0.04
	SP8	0.82	0.79	0.13	0.29	1.23	61.9	-0.22
	SP9	0.36	0.34	0.15	0.34	0.8	61.7	-0.09
Monsoon	SP1	0.67	0.67	0.04	0.11	1.43	70.3	-0.16
	SP2	0.53	0.52	0.31	2.17	0.96	61.5	-0.16
	SP3	0.99	0.97	0.06	0.14	1.61	69.1	-0.26
	SP4	1	0.99	0.1	0.34	1.64	69.6	-0.22
	SP5	0.88	0.89	-0.02	-0.05	1.78	71.9	-0.13
	SP6	0.69	0.69	0.06	0.2	1.5	70.9	-0.16
	SP7	0.72	0.7	0.14	0.25	0.99	57.1	-0.18
	SP8	0.73	0.67	0.09	0.23	1.44	70.2	-0.12
Post-monsoon	SP9	0.53	0.49	0.25	0.64	0.87	58.9	-0.12
	SP1	0.77	0.73	0.01	0.02	1.61	72.5	-0.12
	SP2	0.66	0.69	0.01	0.04	1.52	71.2	-0.16
	SP3	1.16	1.16	-0.06	-0.14	2.07	74.1	-0.26
	SP4	1.09	1.11	-0.03	-0.09	1.93	72.9	-0.22
	SP5	0.99	0.93	-0.14	-0.26	2.28	78.5	-0.08
	SP6	0.82	0.81	-0.04	-0.1	1.88	75.4	0
	SP7	0.77	0.79	0.08	0.17	1.23	62.1	-0.18
	SP8	0.85	0.81	0	0	1.9	75.4	-0.12
	SP9	0.64	0.65	0	-0.01	1.39	69.2	-0.12

TZ- - Total Anions, TZ+ - Total Cations, CAI– Chloro Alkali Index, SAR – Sodium Adsorption Ratio, % Na – Percent Sodium, RSC – Residual Sodium Carbonate (All concentrations expressed in meq/L)

Table 4.13 Total ions concentration, CAI, SAR, % Na, RSC values for highland spring water samples.

Season	Spring Code	TZ+	TZ-	CAI-I	CAI-II	SAR	% Na	RSC
Pre-monsoon	SP10	0.56	0.59	-0.22	-0.12	0.53	47.1	0.02
	SP11	0.56	0.58	-0.23	-0.13	0.53	47.1	0.02
	SP12	0.43	0.43	-0.68	-0.31	0.52	49.6	0.04
	SP13	0.85	0.83	-0.17	-0.09	0.52	41.5	-0.02
	SP14	0.65	0.65	-0.18	-0.15	0.63	47.8	0.02
	SP15	0.72	0.61	0.05	0.06	0.61	45.7	-0.17
	SP16	0.82	0.89	0.01	0	0.68	48.2	0.03
	SP17	0.82	0.95	-0.16	-0.08	0.7	48.7	0.15
	SP18	0.54	0.64	0.19	0.16	0.47	44.9	0.02
	SP19	0.47	0.46	0.17	0.23	0.53	48.3	-0.07
Monsoon	SP10	0.58	0.68	-0.13	-0.07	0.54	47.7	0.1
	SP11	0.47	0.64	-0.42	-0.18	0.65	54.1	0.16
	SP12	0.35	0.46	-0.28	-0.21	0.84	66.9	0.14
	SP13	0.63	0.67	-0.07	-0.04	0.4	34.4	0
	SP14	0.63	0.7	0.08	0.09	0.59	48	-0.06
	SP15	0.57	0.55	-0.16	-0.08	0.46	40.5	0.01
	SP16	0.74	0.85	-0.13	-0.07	0.66	47.2	0.12
	SP17	0.72	0.83	-0.52	-0.26	0.99	57.9	0.22
	SP18	0.62	0.67	0.11	0.07	0.35	38.5	-0.04
	SP19	0.43	0.49	-0.05	-0.04	0.56	51.2	0
Post-monsoon	SP10	0.49	0.47	-0.46	-0.32	0.71	56.3	0.2
	SP11	0.56	0.56	-0.33	-0.18	0.53	43.9	0.06
	SP12	0.36	0.37	-0.31	-0.35	0.91	67.1	0.1
	SP13	0.96	0.93	-0.17	-0.17	1.03	56.7	-0.16
	SP14	0.96	0.94	-0.18	-0.19	1.04	56.9	-0.2
	SP15	0.51	0.52	-0.1	-0.12	0.88	60.8	0.12
	SP16	0.93	0.98	-0.19	-0.11	0.76	50.2	0.06
	SP17	0.64	0.68	0	0	0.79	52.8	0.14
	SP18	0.43	0.48	0.38	1.15	0.49	43.9	-0.04
	SP19	0.54	0.53	-0.11	-0.15	0.95	62.4	0.12

TZ- - Total Anions, TZ+ - Total Cations, CAI– Chloro Alkali Index, SAR – Sodium Adsorption Ratio, % Na – Percent Sodium, RSC – Residual Sodium Carbonate (All concentrations expressed in meq/L)

Table 4.14 Hydrochemical parameters of the present study (average and ranges) with that of the other springs in India.

Parameters	Kallada & Ithikkara springs	Varkala springs[1]	Karnataka[2]	Ananthnag Kashmir[3]	Bhutan Himalaya[4]	Rajpur/ putur[5]	Kashmir Himalaya[3]	Palk Bay[6]
pH	4.1-7.2 (5.53)	4.2-6.07 (4.83)	6.71 - 8.39 (7.76)	6.2 – 7.6 (6.99)	7 - 8.5 (7.76)	8.36	-	7.3 -788 (7.53)
EC (µS/cm)	39-121 (66.5)	39-302 (110.41)	240- 3800 (1185)	172 - 570 (272)	108 - 9398 (4220)	-	-	1528- 3900 (2394)
HCO_3^- (mg/L)	2.52-36.6 (13.38)	1.1-21.5 (4.5)	-	-	-	-	-	-
Cl^- (mg/L)	6.7-27.8 (14.033)	5-38.5 (17.2)	134 – 578 (358)	38- 176 (90)	37 – 1918 (875)	219	110 - 160	244- 320 (295)
SO_4^{2-} (mg/L)	0.27 - 4.2 (1.57)	0.24-23.2 (4.66)	8 – 550 (84.2)	2.8- 17 (10.8)	6- 1830 (802)	40	11.4- 17.0	298- 1015 (560)
Ca^{2+} (mg/L)	1.22-6 (2.99)	0.8-16.6 (2.32)	0.09 - 7.5 (1.75)	0.02- 1.09 (0.34)	0.2 -4.0 (1.69)	-	-	-
Mg^{2+} (mg/L)	0.61-3.66 (5.22)	0.3-4.4 (2.04)	19- 173 (74)	8.0 - 39.6 (23.6)	12 – 88 (44.7)	8	28.8 - 35.3	30- 110 (68.2)
Na^+ (mg/L)	8.80	3.5-20.5 (10.59)	8 – 48 (25.5)	1.0 - 18.5 (10.9)	4- 25 (15.4)	2	5.8 -6.8	16-90 (46)
K^+ (mg/L)	1.53	0.2-3.8 (0.85)	4 -652 (137)	1.8 – 53.6 (8.29)	4-1800 (755)	109	25.3 - 53.6	217 -568 (365)

[1] Padmalal et al., 2012; [2]Chandra and Ramaiah, 2007; [3] Jeelani, 2005; [4] Singh et al., 2004; [5] Ramanathan and Chandrasekharam, 1997; [6]Vaz et al., 2006. Average is given in parenthesis

4.5.2 Silicate weathering and water - mineral equilibria

Chemical weathering is the breakdown of rock-forming minerals under the new geo-environmental and/or climatic conditions prevailing in the region. The tropical areas of the world are noted for high rate of rock weathering arising from the effect of abundant rainfall and round the year sunshine. The rate and nature of chemical weathering are often governed by many variables such as parent rock characteristics, topography, climate, leaching conditions, biological activity and so on and so forth (Green *et al.,* 2006). Chemical weathering determines the mobilization and redistribution of major and trace elements in the environments through the effect of various processes such as decomposition of primary rock forming minerals, formation of secondary phases, co- precipitation and ion exchange. However, nature strikes balance in the concentration of metals and metalloids released from weathered rocks resulting in distinct chemical characteristics of the soil and associated subsurface groundwater. In addition, human activities coupled with the usage of industrial and manufactured products have been regarded as an important source of heavy metals released into the environment. Therefore, for better understanding of dynamics of the metal released into the environmental media (soils and waters), are very essential for suggesting mitigation measures that are undertaken to protect these unique fresh water sources of nature.

Weathering of silicate is an incongruent process. This means that the primary silicate mineral do not completely dissolve but leaves a secondary silicate mineral in the weathering front.

$$\text{Cation} - \text{Al} - \text{Silicate} + CO_2 + H_2O \rightarrow \text{Hydrated Al} - \text{Silicate} + \text{Cation} + \text{Dissolved Silica} + HCO_3^-$$

The solid residue of silicate weathering forms soil profiles over rock massifs.

The basic mechanism for weathering and soil formation is relative solubility of SiO_2 and $Al(OH)_3$ in the weathering environment. The solubility of SiO_2 can be depicted by the reaction:

$$SiO_2 + 2H_2O = H_4SiO_4$$

When plagioclase feldspar weathers to kaolinite, the Ca/Na and HCO_3/SiO_2 mole ratios in water increase with increasing anorthite ($CaAlSi_3O_8$) content (Garrels, 1967) as shown by the following equations:

i) Albite + 2 CO_2 + 3 H_2O = Kaolinite + 2 Na^+ + 2 HCO_3^- + 4 SiO_2

ii) 3 An_{33} + 4 CO_2 + 4 H_2O = 2 Kaolinite + 2 Na^+ + Ca^{2+} + 4 HCO_3^- + 4 SiO_2

iii) 4 An_{50} + 6 CO_2 + 9 H_2O = 3 Kaolinite + 2 Na^+ + 2 Ca^{2+} + 6 HCO_3^- + 4 SiO_2

iv) 8 An_{75} + 14 CO_2 + 21 H_2O = 7 Kaolinite + 2 Na^+ + 6 Ca^{2+} + 14 HCO_3^- + 4 SiO_2

The groundwater will be closer to equilibrium because of its long and more intimate contact with mineral phases. Hence rock weathering would control the Na^+, Ca^{2+}, SiO_2 and HCO_3^- contents of groundwater. That is, the nature and amount of dissolved species in natural water is strongly influenced by mineralogy of the host rocks. In an unpolluted environment the river and/or groundwater quality will be controlled essentially by the minerals in host rocks or aquifer (Drever, 1988).

The molar ratio HCO_3^-/SiO_2 can be used to study the influence of silicate dissolution in spring water samples. If the ratio is greater than 10, (i.e., $HCO_3^- >> SiO_2$), carbonate weathering predominates. However, if the ratio is less than 5, silicate weathering predominates (Hounslow, 1995). In the present study the computed ratio lies in the range of 0.44 – 2.52 in lowland region and 0.42 – 2.50 in the highlands, which is less than 5 points towards the role of silicate weathering in determining the water chemistry.

Saturation indices of spring waters

A positive Saturation Index value (SI > 0) indicates supersaturation and therefore incapable of dissolving more of the mineral and a tendency for the mineral to precipitate from groundwater under suitable physico-chemical conditions. A negative SI i.e., (SI < 0) exhibits undersaturation condition and dissolution of mineral phases. Such a value could reflect either that the mineral is not present, if it is reactive, or if it is present then it is not reactive. It also depicts insufficient amount of mineral for solution or short residence time. When SI = O, the water is assumed to be in equilibrium with a particular mineral phase.

The calculated SI values with respect to various mineral phases such as aragonite ($CaCO_3$), calcite ($CaCO_3$), chalcedony (SiO_2) dolomite ($CaMg(CO_3)_2$), fluorite (CaF_2), gypsum ($CaSO_4 2H_2O$), halite (NaCl), quartz (SiO_2), talc ($Mg_3Si_4O_{10}(OH)_2$) using the PHREEQC Software (Parkhust and Appolelo, 1999) for the spring samples in lowland regions is given in Table 4.15. Majority of the lowland spring water samples have a negative SI values which indicates undersaturation with all the mineral phases, with the exception of SP9 (monsoon) and SP1 (post-monsoon). These samples are saturated with respect to quartz, as the springs rise from highly permeable sandstone formation rich in quartz grains. The undersaturation of gypsum suggests that soluble sulphate mineral phases are rare in the host aquifer and the application of fertilizer through irrigation return flow may be contributing bulk of the sulphates to the springs.

In the highland region the calculated SI values with respect to various mineral phases such as aragonite ($CaCO_3$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), fluorite (CaF_2), gypsum ($CaSO_4$ $2H_2O$), halite (NaCl), chalcedony (SiO_2), quartz (SiO_2),

Table 4.15 Saturation Indices (SI) values for mineral phases worked out for lowland springs.

Season	Spring Code	Water Type	SI aragonite	SI calcite	SI chalcedony	SI dolomite	SI gypsum	SI fluorite	SI halite	SI quartz	SI talc
Pre-monsoon	SP1	Na-Cl	-5.94	-5.80	-0.52	-11.43	-	-3.12	-8.31	-0.10	-23.17
	SP2	Na-Cl	-5.95	-5.81	-0.59	-11.46	-	-3.15	-8.29	-0.17	-25.36
	SP3	Na-Mg-Ca-Cl	-	-	-0.58	-	-	-2.88	-8.07	-0.16	-26.85
	SP4	Na-Ca-Cl	-5.64	-5.49	-0.59	-	-	-2.68	-7.91	-0.16	-
	SP5	Na-Mg-Cl	-5.63	-5.49	-0.57	-10.52	-4.41	-3.04	-8.08	-0.15	-22.55
	SP6	Na-Cl	-6.09	-5.95	-0.52	-11.73	-4.62	-3.07	-8.28	-0.10	-25.04
	SP7	Na-Ca-Cl-HCO_3	-3.82	-3.67	-0.53	-	-4.12	-2.68	-8.32	-0.11	-
	SP8	Na-Mg-Cl	-6.01	-5.87	-0.57	-11.27	-4.70	-3.10	-8.19	-0.15	-24.95
	SP9	Na-Mg-Cl	-6.16	-6.01	-0.67	-11.54	-5.48	-5.54	-8.90	-0.24	-22.56
Monsoon	SP1	Na-Cl	-6.05	-5.90	-0.51	-11.66	-	-	-8.26	-0.08	-24.13
	SP2	Na-Ca-Cl	-5.75	-5.61	-0.63	-	-	-	-8.46	-0.20	-
	SP3	Na-Mg-Cl	-6.06	-5.91	-0.57	-11.38	-	-	-7.97	-0.15	-23.52
	SP4	Na-Mg-Cl	-5.67	-5.53	-0.64	-10.63	-	-	-7.93	-0.21	-22.17
	SP5	Na-Cl	-5.43	-5.28	-0.55	-10.24	-4.55	-	-8.02	-0.13	-21.42
	SP6	Na-Cl	-6.14	-5.99	-0.35	-11.84	-	-	-8.22	0.08	-24.69
	SP7	Na-Mg-Cl	-3.79	-3.64	-0.54	-6.85	-4.30	-	-8.36	-0.11	-10.89
	SP8	Na-Cl	-5.56	-5.42	-0.59	-10.70	-	-	-8.24	-0.17	-22.07
	SP9	Na-Ca-Cl	-5.27	-5.12	-0.40	-	-	-2.05	-8.58	0.03	-
Post-monsoon	SP1	Na-Mg-Cl	-5.90	-5.76	-0.09	-10.86	-5.21	-	-8.19	0.32	-19.61
	SP2	Na-Cl	-5.81	-5.67	-0.62	-11.16	-4.79	-	-8.24	-0.20	-22.15
	SP3	Na-Cl	-5.61	-5.47	-0.76	-11.06	-4.57	-	-7.81	-0.34	-23.55
	SP4	Na-Cl	-5.35	-5.21	-0.82	-9.93	-4.82	-3.35	-7.86	-0.41	-20.30
	SP5	Na-Cl	-5.54	-5.40	-0.66	-10.62	-4.72	-	-7.96	-0.25	-22.99
	SP6	Na-Cl-HCO_3	-5.17	-5.03	-0.60	-9.88	-4.65	-4.43	-8.08	-0.18	-21.59
	SP7	Na-Mg-Cl	-3.83	-3.69	-0.66	-6.89	-4.45	-	-8.21	-0.25	-11.35
	SP8	Na-Cl	-5.66	-5.52	-0.69	-10.88	-4.98	-	-8.05	-0.27	-23.05
	SP9	Na-Cl	-5.07	-4.92	-0.54	-9.68	-4.63	-	-8.32	-0.12	-0.12

talc ($Mg_3Si_4O_{10}(OH)_2$), siderite ($FeCO_3$), goethite (FeOOH) and hematite (Fe_2O_3) are illustrated in Table 4.16. The spring samples of highland region are found to be supersaturated with respect to the minerals chalcedony, quartz, goethite and hematite with a positive SI value. The phase controlling silica concentrations may be chalcedony, because the samples are more saturated with respect to chalcedony, or the controlling phase may be an aluminosilicate. In highland region also all the samples are undersaturated with respect to fluorite. The saturation index values for the minerals goethite and hematite reflects that 97% of the samples in highland for which iron is detected is supersaturated with respected to these minerals, suggesting that these phases control the Fe concentration in solution (Sracek *et al.,* 2010). In almost all the samples in highland the SI for hematite are greater than 10 which indicate oversaturation. This is because ferrihydrite may convert to the more stable hematite form of iron, if given sufficient time, by a mechanism that does not limit dissolved iron concentration to the hematite saturation value (Deutsch, 1997).

There is remarkable difference in saturation index of chalcedony, quartz, goethite) and hematite in lowland and highland regions. In lowland, the water bearing formation is mostly friable sandstone. Recharge of aquifers occurs mainly from alluvium and/ or top soil. Alluvium can modify the water chemistry to a significant level so that the signature of silicate weathering and weathering of iron bearing minerals will be overshadowed. In highlands rock weathering would control the Na, Ca, SiO_2, and HCO_3 contents of spring water. The relative proportion of dissolved ions is controlled by the composition (Al: Si ratio) of primary and secondary minerals. From the study, it is clear that a significant proportion of major dissolved contents of spring waters are derived from weathering of minerals in the host rocks.

Table 4.16 Saturation Indices (SI) values for mineral phases worked out for the highland springs

Season	Spring Code	Water Type	SI aragonite	SI calcite	SI chalcedony	SI dolomite	SI gypsum	SI fluorite	SI halite	SI quartz	SI talc	SI siderite	SI Geothite	SI hematite
Pre-monsoon	SP10	Na-Mg-HCO_3-Cl	-3.72	-3.58	0.12	-6.69	-4.45	-6.38	-8.97	0.54	-10.27	-2.3	4.95	11.91
	SP11	Na-Mg-HCO_3-Cl	-3.62	-3.48	0.13	-6.49	-4.45	-6.38	-8.97	0.55	-9.63	-2.08	5.37	12.76
	SP 12	Na-Mg-Ca-HCO_3-Cl	-4.91	-4.76	0.03	-9.36	-4.41	-6.39	-9.26	0.45	-17.97	-3.66	1.53	5.09
	SP13	Mg-Na-Ca-HCO_3-Cl	-3.55	-3.41	-0.04	-6.48	-4.17	-4.9	-8.73	0.38	-12.16	-2.61	3.87	9.76
	SP14	Na-Ca-HCO_3-Ca	-4.04	-3.89	0.07	-7.94	-4.3	-4.26	-8.76	0.49	-15.21	-3.29	2.7	7.4
	SP15	Na-Mg-Ca-Cl-HCO_3	-3.81	-3.66	0.16	-7.2	-4.41	-2.65	-8.65	0.6	-11.79	-2.34	4.51	11.02
	SP16	Na-Mg-HCO_3-Cl	-3.89	-3.75	0.18	-7.03	-4.53	-2.82	-8.53	0.61	-12.61	-2.67	3.37	8.76
	SP17	Na-Mg-HCO_3-Cl	-3.82	-3.68	0.35	-6.92	-4.55	-2.79	-8.58	0.78	-12.27	-2.83	3.02	8.06
	SP18	Na-Mg-Ca-Cl-HCO_3	-3.9	-3.76	-0.21	-7.2	-4.97	-2.94	-8.91	0.22	-11.75	-3.1	4.47	10.95
	SP19	Mg-Na-HCO_3-Cl	-4.06	-3.91	0.2	-7.39	-4.92	-7.39	-8.88	0.63	-12.13	-3	3.53	9.06
Monsoon	SP10	Na-Mg-HCO_3-Cl	-3.56	-3.41	0.17	-6.39	-4.6	-	-8.9	0.59	-9.82	-2.56	4.69	11.39
	SP11	Na-HCO_3-Cl	-3.56	-3.46	0.15	-6.77	-4.19	-	-9.02	0.57	-10.81	-2.01	5.28	12.58
	SP12	Na-HCO_3-Cl	-4.95	-4.8	0.07	-9.46	-5.38	-	-9.05	0.49	-17.31	-3.15	2.54	7.09
	SP13	Ca-Na-HCO_3-Ca	-3.29	-3.15	-0.03	-6.64	-4.02	-	-9.02	0.4	-12.74	-2.19	4.67	11.34
	SP14	Na-Mg-Ca-Cl-HCO_3	-4.09	-3.96	-0.03	-7.77	-4.58	-4.78	-8.69	0.4	-13.98	-4.17	2.3	6.61
	SP15	Ca-Na-Mg-HCO_3-Cl	-3.32	-3.18	0.03	-6.36	-	-3.68	-9.04	0.46	-10.97	-1.79	5.44	12.88
	SP16	Na-Mg-Ca-HCO_3-Cl	-3.64	-3.5	0.15	-6.85	-4.58	-	-8.66	0.57	-12.85	-2.68	3.49	8.99
	SP17	Na-Ca-HCO_3-Cl	-3.65	-3.51	0.25	-7.19	-4.34	-	-8.59	0.68	-13.49	-3.56	2.55	7.12
	SP18	Na-Mg-Ca-Cl-HCO_3	-3.96	-3.82	-0.32	-7.51	-4.39	-	-9.01	0.11	-13.4	-2.36	4.95	11.91
	SP19	Mg-Na-HCO_3-Cl	-3.91	-3.77	0.04	-6.92	-4.36	-4.36	-9.03	0.47	-11.68	-3.82	2.86	7.73

Contd...

Season	Spring Code	Water Type	SI aragonite	SI calcite	SI chalcedony	SI dolomite	SI gypsum	SI fluorite	SI halite	SI quartz	SI talc	SI siderite	SI Geothite	SI hematite
Post-monsoon	SP10	Na-Mg-Ca-HCO_3-Cl	-3.41	-3.37	0.04	-6.37	-4.26	-2.69	-8.96	0.46	-8.36	-2.11	6.37	14.75
	SP11	Na-Ca-HCO_3-Cl	-2.77	-2.63	0.01	-5.39	-3.92	-	-9.01	0.43	-7.33	-1.62	7.11	16.25
	SP12	Na-Ca-Cl-HCO_3	-4.51	-4.36	-0.04	-	-4.41	-	-9.01	0.38		-2.68	4.24	10.51
	SP13	Na-Ca-Mg-Cl-HCO_3	-3.49	-3.34	-0.23	-6.52	-4.37	-2.72	-8.26	0.18	-12.09	-2.69	4.4	10.82
	SP14	Na-Ca-Mg-Cl-HCO_3	-3.56	-3.42	-0.26	-6.66	-4.52	-	-8.28	0.15	-12.82	-3.07	3.79	9.61
	SP15	Na-Cl-HCO_3	-3.58	-3.44	0.07	-6.7	-4.56	-	-8.73	0.48	-9.23	-2.29	5.86	13.74
	SP16	Mg-Na-HCO_3-Cl	-3.07	-2.93	0.11	-5.07	-4.41	-	-8.49	0.53	-6.73	-1.96	5.93	13.89
	SP17	Na-Ca-Cl-HCO_3	-2.89	-2.76	-0.39	-5.63	-4.45	-	-8.62	0.02	-9.94	-2.14	6.19	14.41
	SP18	Ca-Na-Cl	-3.61	-3.46	-0.25	-	-4.35	-	-8.86	0.17		-2.19	6.47	14.96
	SP19	Na-Cl-HCO_3	-2.89	-2.75	-0.07	-5.31	-4.53	-	-8.65	0.34	-4.96	-2.47	7.38	16.78

Thermodynamic stability diagram

In a variety of weathering reactions, the equilibrium constants are simple functions of cation / H^+ activity ratios. The exact value of equilibrium constant of many geochemical reactions are calculated from thermodynamic data. For any reaction under standard conditions (25^0C, 1 atm), the equilibrium constant (K) is related to the change in energy (ΔG_r^0) in the following way

$$\Delta G_r^0 = -RT \ln K$$

$$= -2.303\ RT \log K$$

The value of gas constant R = 1.98 x 10^{-3} kcal/deg-mol

or 8.314 x 10^{-3} kJ/deg-mol

When temperature (T) is 298.15 K (25^0C),

ΔG_r^0 in kJ = -5.706 log K

In a reaction

$\Delta G_r^0 = \sum (\Delta G_f^0)_{Product} - (\Delta G_f^0)_{Reactant}$

where ΔG_f^0 represents the standard free energy of formation of the substances taking part in the reaction.

$$\text{Therefore } \log K = \Delta G_r^0 / -2.303.\ RT$$

The logarithemic activity diagram represent the range of composition of natural waters over which the selected minerals are stable at 25^0C and 1 atm pressure. The thermodynamic stability diagrams for the behaviour of groundwater in the silicate system

(a) $CaO–Al_2O_3–SiO_2–H_2O$,

(b) $MgO–Al_2O_3–SiO_2–H_2O$

(c) $Na_2O–Al_2O_3–SiO_2–H_2O$ and

(d) $K_2O - Al_2O_3 - SiO_2 - H_2O$ at 25^0C in lowland and highland regions are given in Figures 4.6 and 4.7. These figures depicts that the all the sample points fall in the range of the stability field of kaolinite. This implies that the chemistry of the water is favourable for kaolinzation and subsequent leaching of mobile elements like alkali and alkaline earth elements. Stability in the kaolinite field suggests that infiltrating water which is enriched in soil CO_2 reacts with silicate minerals in the host rocks, particularly with feldspar minerals. The infiltrating water leaches out Ca^{2+}, Mg^{2+}, Na^+, K^+ and HCO_3^- from the host rocks which is subjected to chemical alteration and results a more silica rich clay mineral in the weathering front. In the final stage of tropical weathering, the silicate structure of clay minerals breaks down further, resulting in bauxite and laterite in the soil profiles which have high concentrations of Al and Fe hydroxides.

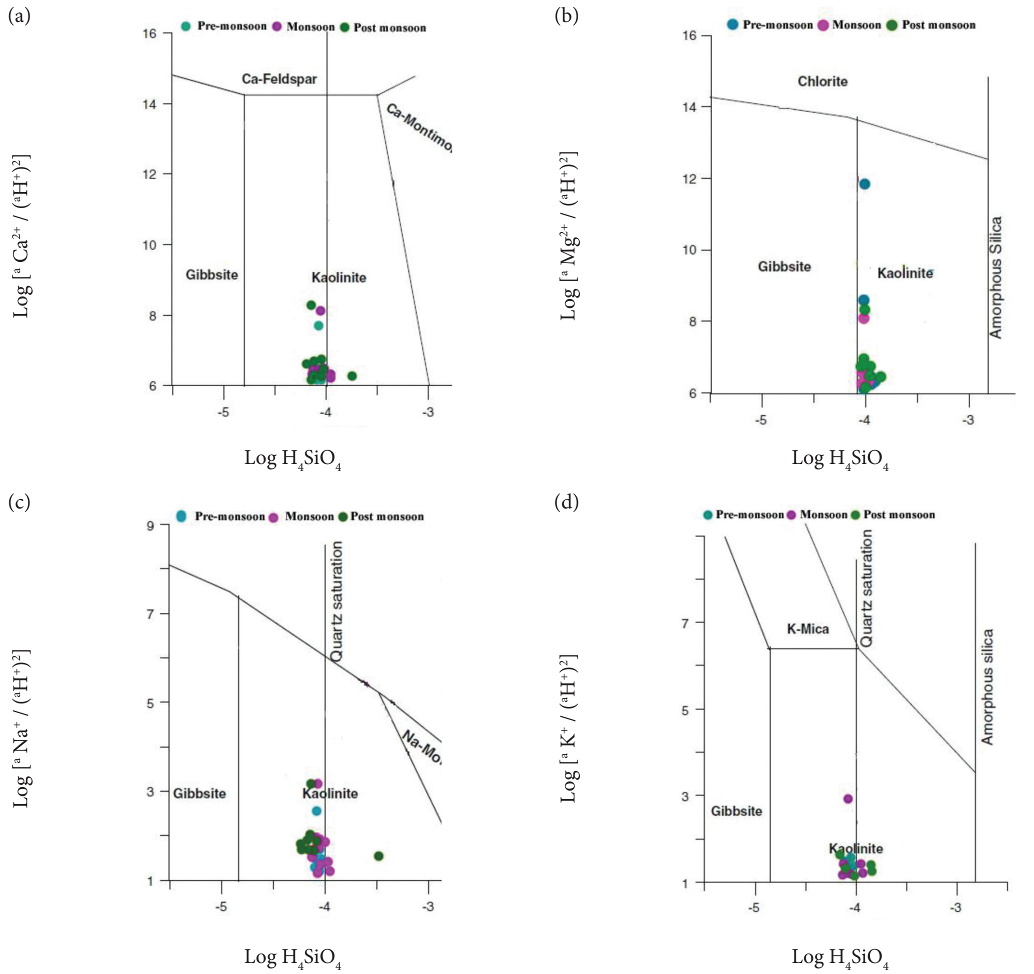

Fig. 4.6 Mineral stability diagrams for lowland springs.

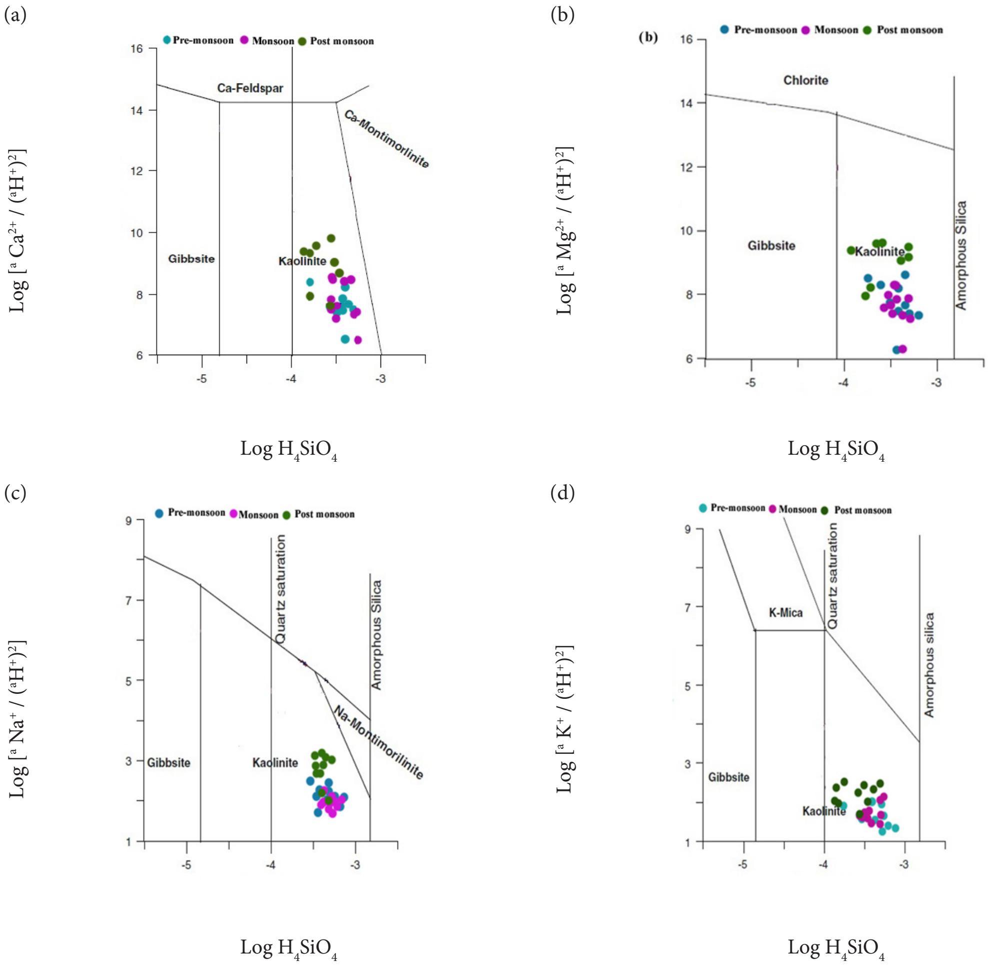

Fig. 4.7 Mineral stability diagrams for highland springs.

4.5.3 Aluminium geochemistry and solubility

Aluminum is the most abundant metal and the third most abundant element in the earth's crust, comprising about 8.8% by weight (88 g/kg). Aluminium is generally found in igneous rocks as aluminosilicate minerals (Staley and Haupin, 1992; Lide 2005). It is from the weathering of rocks and minerals Al^{3+} enters into the environment. As a major constituent of the earth's crust, the natural weathering processes far exceed its contribution from air, and human activities (Lantzy and McKenzie, 1979). The major features of the biogeochemical cycle of aluminum include leaching of aluminum from geochemical formations and soil particulates to aqueous environments, adsorption onto soil or sediment particulates, and wet and dry deposition from air to land and surface water. Concentration of aluminum vary in drinking water, between <0.001 and 1.029 mg/L (Schenk *et al.,* 1989). The use of aluminum sulfate and other aluminum compounds as coagulating agents in the treatment of raw drinking water supplies can significantly increase the total aluminum content in finished water (Miller *et al.,* 1984; USGS, 1984; Qureshi and Malmberg, 1985; Henshaw *et al.,* 1993; Cech and Montera, 2000). Canadian Environmental Protection Act, 1999 has reported that, treatment with aluminum salts may not necessarily increase the total aluminum concentration in finished drinking water, as the aluminum associated with suspended solids is removed. However, aluminum salt addition does appear to increase the concentration of low-molecular-weight, dissolved aluminum species, which may potentially present a higher bioavailability (Health Canada, 1998).

The coordination chemistry and the characteristics of the local environment, especially pH controls the behavior of aluminum in the environment. Dissolved aluminum concentrations in surface and groundwater vary with pH and the humic acid content of water (Brusewitz, 1984). High aluminum concentrations in natural water occur only when the pH is <5; therefore, concentrations in most surface water are very low. Aluminum occurs in natural waters from the weathering of aluminum-containing rocks and minerals. The element is only sparingly soluble in water between pH 6 and 8. It is reported that, aluminum concentrations in surface waters at pH levels above 5.5 will be <0.1 mg/L (Sorenson *et al.,* 1974; Brusewitz, 1984; Miller *et al.,* 1984; Taylor and Symons, 1984).

Numerous studies have shown that concentrations of Al at pH > 5 – 5.5 are regulated primarily by the pH-dependent solubility of Al-trihydroxide phases. Below pH 5, natural waters typically are undersaturated with respect to gibbsite (Helmeretal *et al.,* 1990). As per the report of Canadian Environmental Protection Act, 1999, the low pH of the gastric fluid creates a high potential for transformation of the ingested aluminium complex in human stomach. This led Reiber *et al.* (1995) to argue that the aluminium in drinking water would not be more readily assimilated than other forms of aluminium, and that regardless of the form in which the aluminium is consumed, it will likely be solubilized to monomolecular aluminium in the stomach.

The solid residue of silicate weathering forms soil profiles over bed- rock. In the final stages of weathering, there is further loss of silica from clay minerals resulting in an accumulation of $Al(OH)_3$ in bauxite profiles:

$Al_2Si_2O_5(OH)_4 + 5\ H_2O = 2Al(OH)_3 + 2\ H_4SiO_4$
kaolinite gibbsite

The basic mechanism for weathering and soil formation is the relative solubility of SiO_2 and $Al(OH)_3$ in the weathering environment.

$SiO_2 + 2H_2O = H_4SiO_4$

H_4SiO_4 represents the monomeric dissolved species and is most common in the pH range of natural waters. Al $(OH)_3$ is soluble in both acid and alkali. In low pH range $Al(OH)_3$ ionises into Al^{3+} and OH^-.

$Al\ (OH)_3 = Al^{3+} + 3\ OH^-$

The solubility of gibbsite into Al^{3+} ion is a straight line with -3:1 slope in low pH range. The solubility of $Al(OH)_3$ goes through a minimum around pH 6. Above a pH value of 4, silica is more soluble than $Al(OH)_3$. This is the condition required for the formation of a bauxite deposit over silicate bedrock. The bauxite is common in tropical climates as the high temperature takes weathering to completion and high rainfall leaches away silica. Whereas in natural water pH range $Fe(OH)_3$ is less soluble than silica (Krauskopf, 1979) and hence red (laterite) soils are also common in tropical weathering.

Comparison of pH and Al concentrations of all samples with the theoretical solubility of gibbsite indicates that all samples with pH > 5.5 are saturated with respect to gibbsite. The variation of Al *vs* pH, compared with gibbsite solubility diagram in lowland and highland region of the study area (Figures 4.8 and 4.9), shows that the spring water samples are close to equilibrium with gibbsite. The results of Al concentration in spring samples (Table 4.17) reveal that except SP9 (monsoon), all the spring samples of the study area have Al concentration well within the permissible limit of BIS (2012) of 0.2 mg/L.

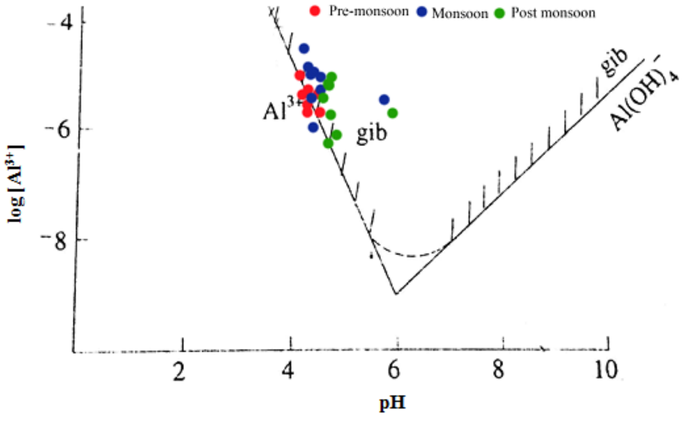

Fig.4.8. Variation diagram of total Al *vs* pH, compared with gibbsite solubility for lowland springs.

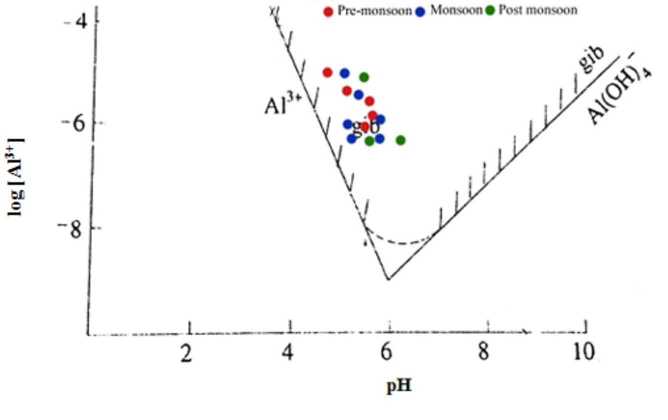

Fig.4.9. Variation diagram of total Al *vs* pH, compared with gibbsite solubility for highland springs.

Table 4.17 Aluminium concentration in spring samples of the study area.

Season	Lowland		Highland	
	Spring Code	Al	Spring Code	Al
Pre-monsoon	SP1	0.03	SP10	BDL
	SP2	0.06	SP11	BDL
	SP3	0.12	SP12	0.08
	SP4	0.06	SP13	0.04
	SP5	BDL	SP14	0.06
	SP6	0.04	SP15	BDL
	SP7	BDL	SP16	BDL
	SP8	0.06	SP17	0.02
	SP9	0.03	SP18	BDL
			SP19	0.03
Monsoon	SP1	0.09	SP10	BDL
	SP2	0.18	SP11	BDL
	SP3	0.16	SP12	0.03
	SP4	0.07	SP13	BDL
	SP5	0.19	SP14	0.10
	SP6	0.01	SP15	BDL
	SP7	0.06	SP16	0.02
	SP8	0.06	SP17	0.10
	SP9	0.74	SP18	0.01
			SP19	0.03
Post-monsoon	SP1	0.09	SP10	BDL
	SP2	0.12	SP11	BDL
	SP3	0.17	SP12	0.06
	SP4	0.03	SP13	BDL
	SP5	0.03	SP14	0.02
	SP6	0.01	SP15	BDL
	SP7	0.04	SP16	0.01
	SP8	0.02	SP17	BDL
	SP9	BDL	SP18	BDL
			SP19	BDL

All the samples are measured in ***mg/L****; BDL: Below detection level (0.01 mg/L)*

Chapter - 5

HYDROCHEMISTRY OF WELL WATERS

5.1 Introduction

Most of the countries depend on groundwater for their potable water requirements (UNECE, 1999). Groundwater is considered to be less vulnerable to climate changes compared to surface water sources and can therefore be used to sustain agricultural production and ensure food security even in undesirable situations (Moench *et al.,* 2002). Differences in climatic and hydrological conditions in the regions around the world have led to uneven distribution of water resources. The active role of groundwater in nature is its ability to interact with the ambient environment and the systematized spatial distribution of its flow (Tóth, 1999). India is one of the largest groundwater users for agriculture in the world (Shah, 2009; Shankar *et al.,* 2011; Kulkarni *et al.,* 2015; Chinnaswamy and Agoramoorthy, 2015; Mukherjee *et al.,* 2015; Patel *et al.,* 2016). It is reported that between 2000/01 and 2006/07, about 61% of irrigation in the country was from groundwater sources (Shankar *et al.,* 2011). Overexploitation of groundwater to meet its ever increasing demand for various purposes (eg: domestic uses, irrigation, agriculture, etc.) together with the degradation of top soil due to wide application of chemical fertilizers has resulted in marked changes in the quality and quantity of groundwater resources over the years. Studies reveal that groundwater in many areas of India contain residues of harmful substances, the concentration of which is directly related to human activities and /or interventions in the recharge zones of the aquifer systems (Reddy and Rao, 2001; Singhal and Gupta, 2010; Kumar *et al.,* 2011; Basavarajappa and Manjunatha, 2015; Srinivas *et al.,* 2015; Bhatti *et al.,* 2016; Tiwari *et al.,* 2016; Verma *et al.,* 2016). Contamination due to microbial pathogens and chemical residues has emerged as a serious concern in recent years (Babu *et al.,* 2007; Bundschuh *et al.,* 2010; Pandey, 2014). All these warrant the imminent need for better understanding of the quality of groundwater sources and its natural and man-made determinants for its optimal use, wise management and conservation for future generations. This is very important in densely populated areas with unique terrain characteristics and geo-environmental settings. This chapter is devoted for addressing the hydrochemistry of the well water resources of the Ithikkara and Kallada river basins.

5.2 Previous studies

Hydrogeochemical processes are responsible for the solute concentration of groundwater in an area. Groundwater has varying range of chemical composition. And, these changes are attributed to the composition of infiltrating surface water, properties of soil and rock through which groundwater moves, contact time and contact surface area between groundwater and geological constituents along its course, rate of rock-water interaction, oxidation/reduction, ion exchange, dissolution, evaporation, silicate weathering and precipitation processes. The groundwater chemically evolves due to interaction with aquifer minerals or by intermixing among the different groundwater reservoirs along the flow path in the subsurface (Domenico, 1972; Wallick and Toth, 1976). Jalali (2005) reported that the dissolution of carbonate minerals, cation exchange and weathering of silicates control the groundwater chemistry in semiarid region of western Iran.

Martinez and Bocanegra (2002) indicated that cation exchange and calcite equilibrium are the important hydrogeochemical processes that control the groundwater composition. Cireli and Miretzky (2004) have inferred that cation exchange reaction between calcium and sodium in the hydrochemical evolution of groundwater through Pampean loess is responsible for high sodium content compared to chloride content. Hydrogeochemistry of groundwater is a function of the mineral composition of the aquifer through which water flows. Mineral composition of parent rock can significantly differ over a short distance and groundwater chemistry also differs from place to place. Geochemical reactions that dissolve gases and minerals into water, changes composition of the solution and water become saturated with the constituents of secondary minerals. These secondary minerals are weathering products of the primary minerals. The weathering of primary and secondary minerals is brought about by the release of cations and silica (Jacks, 1973; Mohan *et al.,* 2000).

Groundwater quality changes are determined by the process such as dissolution, carbonate weathering and ion exchange (Kumar *et al.,* 2006). Impact of mining allied activities on groundwater quality in the upper catchment of Damodar River basin (India) is studied by Singh *et al.* (2008). Rajmohan and Elango (2004) reported that weathering of silicate minerals play an important role in determining the major ion chemistry in groundwater system. Weathering of pyroxene, amphiboles and calcic feldspar minerals that are common in basic rocks control the concentration of many ions in groundwaters (Jacks, 1973; Bartarya, 1993). The elevated concentrations of major elements are controlled by the weathering of carbonate and silicate minerals (Mikhlafi *et al.,* 2003; Yidana *et al.,* 2010).

To study the groundwater equilibrium with solid phase and its impacts on water ion chemistry, Saturation Index (SI) of minerals can be applied (Appelo and Postma, 1996).

The soil type and groundwater flow conditions have prominent effect on geochemistry and mineralogy of calcic horizons in the area. The carbonates in Vertisols are calcitic throughout whereas those in red soils in down slope positions are often dolomitic. The absence of dolomite in the Vertisols is likely to be due to the presence of large amount of calcium in charnockitic parent material in combination with the sink for magnesium in smectite formation (Jacks and Sharma, 1995). Saturation indices of calcite, dolomite, and aragonite are of positive values higher than 1, indicate the super saturation of water by these minerals (Agha and Mohammed, 2005). Ramos *et al.* (2007) reported that the SI of aragonite, calcite and dolomite are supersaturated from carbonates. Studies conducted by Jalali and Khanlari (2008) in a semi-arid aquifer of western Iran shows that the carbonate mineral phases influence the chemical composition of groundwater. Jianhua *et al.* (2008) identified that the SI values for magnesite, calcite, and dolomite for groundwater are positive, indicating that groundwater samples are oversaturated as a result of evaporation. The thermodynamic saturation states between major minerals and water samples, and mineralogical evidences indicate that the dissolution of calcite, chlorite, albite and the precipitation of clay minerals contribute groundwater chemistry in granitic gneiss of Samkwang mine area, Korea (Jeong, 2001). From saturation indices values Mikhlafi *et al*. (2003) reported that the lake water is undersaturated in calcite and dolomite during the summer period, whereas it is saturated or supersaturated in spring season. Saturation state of waters with respect to gypsum, dolomite, calcite and halite may reinforce mineralization of groundwater in continental aquifer systems (Kamel *et al.,* 2008). Jalali (2006) identified that groundwater is saturated with respect to calcite and dolomite and are undersaturated with respect to gypsum mineral in parts of mountainous region, Alvand, Hamadan, Iran. Studies indicate that coal mining drainage introduce sulfate to groundwater and decrease pH. This favours dissolution of calcite and dolomite which in turn increases the concentrations of calcium, magnesium and bicarbonate in groundwaters (Guo and Yanxin, 2005). The composition of spring waters can be explained by dolomite and anhydrite dissolution, calcite precipitation and ion exchange reactions (Leybourne, 2009). Statistical analysis like multivariate and factor analysis confirms the predominant geochemical process responsible for the various ions in the groundwater as mineral dissolution (Ganyaglo *et al.,* 2012). Majority of shallow and deep groundwater samples of the study area are oversaturated with respect to carbonate bearing minerals and under-saturated with respect to sulfur and amorphous silica bearing minerals in Pleistocene aquifers of Middle Ganga Plain, Uttar Pradesh, India (Nandimandalam, 2012). When groundwater is used for irrigation, its recycling will rapidly increase the salinity of groundwater by repeated circulation in addition to evaporation and evapotranspiration. Chourasia and Tellam (1992) reported that the groundwater in irrigated area has higher ionic concentration in hard rock terrain in central India. The quality of water plays a prominent role in promoting both the standard of agricultural production and human health (Rao *et al.,* 1997).

The chemical composition of groundwater is determined by a number of processes which include atmospheric input, interaction of water with soil and rock, and input of chemicals derived from human activities. In an urban areas the possible sources for groundwater contamination is landfill waste sites, septic tanks and cesspools, domestic and industrial effluents, leaky sewage system and gasoline stations (Jeong, 2001; Rao, 2008). Water chemistry is guided by complex weathering process, ion exchange along with influence of chloride ions from anthropogenic impact. Chemical characterization of groundwater is essential to bring out its nature and utility.

High concentration of SiO_2 and various geochemical signatures reflect the weathering of minerals. Greater ionic concentration in the groundwater of post-monsoon compared with pre-monsoon indicates the increasing addition of leachates into the groundwater from soil in the monsoon and anthropogenic activities, which leads to deteriorating quality of groundwater (Rao, 2002).

The mineralogy of coastal aquifers and marine aerosol play a significant role in the hydrogeochemistry of groundwater in the phreatic aquifer system of Al-Ain city UAE (Mohamed and Hassane, 2016). The acidification and the intrusion of contamination further lead to hydrogeochemical reactions and changed groundwater type from Ca–Mg–HCO_3 to Ca–Mg–Na–Cl in Yongxiu area, west of Poyang Lake, China (Xu and Wang, 2016). Hassen *et al.* (2016) investigated hydrochemical processes leading to mineralization and water quality with respect to agriculture and drinking for better management of groundwater resources in um Ali-Thelepte aquifer, central Tunisia. The reverse ion exchange process controls the concentration of calcium, magnesium and sodium in hard rock formations; and dissolution of carbonate and accessory minerals constitute the source of Ca and Mg, in addition to cation exchange in sedimentary formations. In general, the chemical composition of groundwater is influenced by rock–water interaction, dissolution and deposition of carbonate and silicate minerals, ion exchange, and surface water interactions (Rajmohan and Elango, 2004).

Land use is the dominant factor affecting shallow groundwater quality (Trojan *et al.,* 2003). Now the developed world faces the challenge of water conservation and the reduction of pollutant loading from both private and public point and non-point source origins. Additionally, input of chemical pollutants from permitted, non-permitted, and accidental releases of industry have contributed to many instances of human toxicity (Ettler *et al.,* 2006). Groundwater with low pH values can cause gastro-intestinal disorders, such as hyper acidity, ulcers, stomach pain and burning sensation. pH values below 6.5 cause corrosion of metal pipes, resulting in the release of toxic metals such as Zn, Pb, Cd, Cu, etc. (Trivedi and Goel, 1986). Electrical conductivity (EC) of groundwater is considered as an important parameter for irrigation and industrial purposes (Laluraj *et al.,* 2006). A Study in Guntur district, Andhra Pradesh, India, where agriculture is the main livelihood of rural people and groundwater is the main source for irrigation and drinking reveals that majority of the groundwater samples are not good for irrigation in post-monsoon compared to pre-monsoon. These conditions are caused by leaching of salts from the overlying materials by infiltrating recharge waters (Rao, 2008).

There are a number of studies carried out in Kerala with respect to hydrochemistry of groundwater (Kukillaya *et al.,* 2004; Vijith and Satheesh, 2007; Kannan and Joseph, 2009; Manjusree, 2009; Boominathan *et al.,* 2012; Maya *et al.,* 2012; Padmalal *et al.,* 2012; Sajil *et al.,* 2012; Vinayachandran, 2014; Prasanth *et al.,* 2015; Vincy *et al.,* 2015; Dhanya and Shaji, 2016; Priju *et al.,* 2016). Kumar *et al.* (2015) studied saline water intrusion into the shallow coastal aquifers of Periyar river basin (Kerala) using hydrochemical and electrical resistivity methods. It is reported that the groundwater type is Na-Cl followed by Mg-Cl. Higher values of pH and TDS are noticed in the western part of the river basin especially towards its seaward side. Many studies indicated that the coastal groundwater system of Kerala experiences setbacks in terms of the quality and quantity (Laluraj *et al*., 2005; Shaji, 2009; Harikumar and Kokkal, 2009; Prasanth *et al.,* 2012; Priju *et al.,* 2014; Dhanya and Shaji, 2016; Subin *et al.,* 2016).

5.3 Wells selected for the present study

A total of 20 perennial dug wells are selected for the present study in the Ithikkara (6 wells) and the Kallada river basins (14 wells). They are distributed in the lowland (4 samples), midland (6 samples) and highland (10 samples) regions. The locations of the wells in study area are shown in Fig. 5.1. Table 5.1 summarizes the detailed geoenvironmental features of the areas surrounding the wells chosen for the present study.

5.4 Results

5.4.1 Physico-chemical parameters

The results of the hydrochemical parameters of well water samples of Ithikkara and Kallada river basins collected during pre-monsoon, monsoon and post-monsoon seasons are given in Table 5.2. The maximum, minimum and mean with standard deviation of water quality parameters along with water quality standards set by WHO (2011) and BIS (2012) are given in Table 5.3. The temperature of the well water in lowland region varies from 26.1°C to 27°C in pre-monsoon, 25.7°C to 26.1°C in monsoon and 25.9°C to 27.1°C in post-monsoon seasons. In midland region the temperature has recorded maximum value of 27.7°C during pre-monsoon and post-monsoon seasons. During monsoon, the temperature ranges between 25.8°C and 26.7°C. In highland the temperature ranges between 26.7°C to 27.5°C, 25.7°C to 26.3°C and 25.8°C to 27.5°C respectively in pre-monsoon, monsoon and post-monsoon seasons.

The pH values of the samples vary widely between 6.7 and 8.1 in lowland, 3.6 and 7.8 in midland and 4.4 and 8.2 in highland. EC of groundwater samples varies from 101 µS/cm to 532 µS/cm in lowland, 61 µS/cm to 241 µS/cm in midland and 55 µS/cm to 430 µS/cm in highland. As per Freeze and Cherry (1979) classification, all the samples in the study area fall within the fresh water category as the TDS, is less than 1000 mg/L. In lowland, the total alkalinity varies between 8 mg/L and 115 mg/L, while in the midland, the alkalinity vary between BDL (below detection limit) and 25 mg/L. In the highland the lowest alkalinity value noticed is 4 mg/L and the highest is 150 mg/L. Among the three physiographic zones, the alkalinity values are

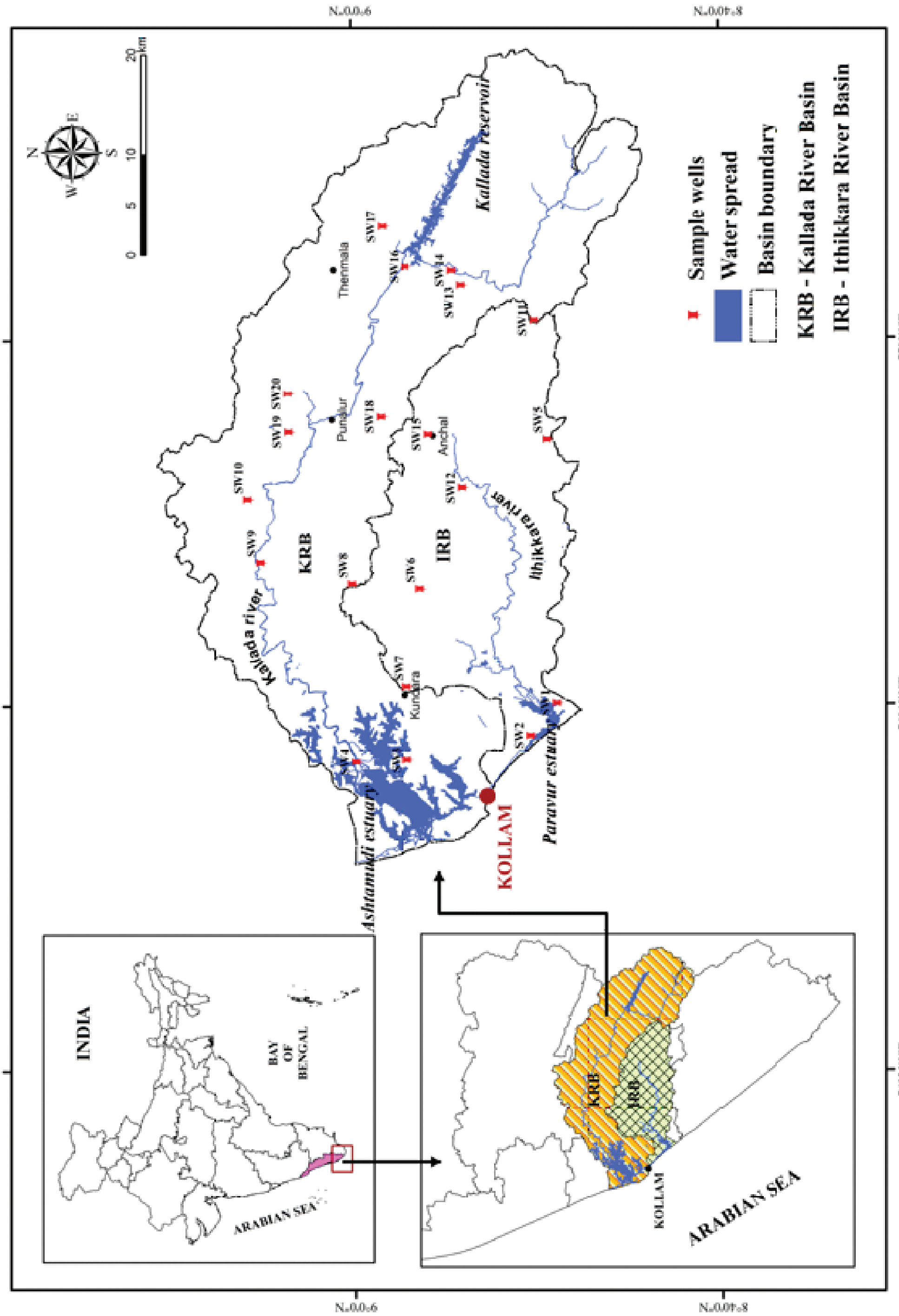

Fig. 5.1 Well water sampling locations in the Ithikkara river basin (IRB) and the Kallada river basin (KRB).

Table 5.1 Geoenvironmental settings and other relevant details of wells chosen in lowland, midland and highland region for the present study.

Well code	Block	Village	Geology	Geomorphology	Well use/Type	Watershed
LOWLAND						
SW1	Ithikkara	Poothakkulam	Laterite	Laterite upland	Monitoring (Department)	Ithikkara
SW2	Mukathala	Mayanad	Sedimentary	Alluvial plain	Monitoring (Department)	Ithikkara
SW3	Kollam	Kollam	Sedimentary	Alluvial plain	Public Supply (Private)	Kallada
SW4	Chittumala	Mantrothuruth	Laterite	Laterite upland	Monitoring (Department)	Kallada
MIDLAND						
SW5	Chadayamangalam	Kadakkal	Laterite	Laterite upland	Public Supply (PWD)	Kallada
SW6	Kottarakkara	Veliyam	Laterite	Laterite upland	Monitoring (Department)	Ithikkara
SW7	Chittumala	Kundara	Laterite	Laterite upland	Public Supply (Private)	Ithikkara
SW8	Kottarakkara	Kottarakkara	Laterite	Laterite upland	Public Supply (Government)	Kallada
SW9	Pathanapuram	Pattazhy	Laterite	Laterite upland	Monitoring (Department)	Kallada
SW10	Pathanapuram	Pathanapuram	Laterite	Laterite upland	Domestic (Private)	Kallada
HIGHLAND						
SW11	Pathnapuram	Edamon	Laterite	Laterite upland	Domestic (Private)	Kallada
SW12	Anchal	Ayoor	Laterite	Laterite upland	Domestic (Private)	Ithikkara
SW13	Anchal	Yeroor	Laterite	Laterite upland	Monitoring (Department)	Ithikkara
SW14	Anchal	Kulathupuzha	Khondalite	Laterite upland	Domestic (Private)	Kallada
SW15	Anchal	Anchal	Laterite	Laterite upland	Monitoring (Department)	Kallada
SW16	Anchal	Thenmala	Laterite	Laterite upland	Domestic (Private)	Kallada
SW17	Pathnapuram	Kazhuthuruthy	Laterite	Valley	Monitoring (Department)	Kallada
SW18	Anchal	Karavallor	Khondalite	Laterite upland	Domestic (Private)	Kallada
SW19	Pathanapuram	Piravanthur	Khondalite	Laterite upland	Public Supply (Private)	Kallada
SW20	Pathanapuram	Karavoor	Laterite	Laterite upland	Monitoring (Private)	Kallada

Source: Kerala State Groundwater department

Table 5.2 Hydro-chemical parameters estimated in the well water samples of the study area collected during pre-monsoon, monsoon and post-monsoon seasons.

Physiography/ Season	Well code	pH	EC (µS/cm)	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	TH (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	TA (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3-N (mg/L)	SiO_2 (mg/L)	Fe^{2+} (mg/L)	F^- (mg/L)	Temp.
I) LOWLAND																		
Pre-monsoon	SW1	7.3	107	64	11	1	30	8	2.4	14	17	17	BDL	3.5	18	0.5	0.04	26.2
	SW2	7.5	315	189	23.5	11.4	90	24	7.3	53	65	27	38	3.8	3	0.3	0.09	26.1
	SW3	7.9	470	282	36.8	8.3	145	50	4.88	115	140	49.7	24	6.8	3	0.27	0.04	26.7
	SW4	7.3	188	113	18	2	40	12	2.4	14.3	17.5	30.6	7.6	7	12	0.1	0.02	27
Monsoon	SW1	7.6	131	79	14	1.2	40	12	2.4	32	39	21	1	0.5	14	BDL	0.05	25.8
	SW2	7.7	351	211	25	18	95	22	9.7	46	56	63	36	1.8	4	BDL	0.06	25.7
	SW3	8.1	532	319	39.1	7.5	170	48	12.2	96	117	67	41	5.6	6	BDL	BDL	26.1
	SW4	7.5	160	96	24	BDL	25	6	2.4	8	9.8	38	1	3	15.5	BDL	0.07	25.9
Post-monsoon	SW1	7.1	180	108	16	0.5	45	14	2.4	8	9.8	25	22.9	3.8	3	0.31	0.4	26.2
	SW2	6.7	310	186	30	3.2	80	22	6.1	30	37	51	54	4.1	1.5	0.25	BDL	25.9
	SW3	8.1	510	306	32	7	175	52	11	105	128	57	36	8.3	5.2	0.04	BDL	27.1
	SW4	6.7	110	66	15	2.4	20	8.4	2.4	4	4.9	26	1	1.9	9.5	3.3	BDL	25.9
II) MIDLAND																		
Pre-monsoon	SW5	6.5	68	41	4	0.2	25	6	2.4	20	24.4	6	0.6	1	13	2.7	0.12	27.2
	SW6	7.3	64	38	4	3	20	6	1.2	21	25	7.2	BDL	0.6	6	0.76	0.14	27.7
	SW7	3.6	135	81	18.5	3.6	25	6	1.22	BDL	BDL	29	4	6.8	7	0.08	0.12	26.9
	SW8	6	200	120	19.3	7.3	45	12	3.7	4	4.9	41	6	5	11.5	3.4	0.55	26.8
	SW9	6.7	65	39	5.8	2.6	15	6	BDL	6	7.3	11	0.6	2.3	7	0.3	0.06	26.5
	SW10	7	161	97	18.4	14	30	8	2.4	12	14.6	27	10	6.8	8	8.6	0.05	26.3

Contd...

Physiography/ Season	Well code	pH	EC (µS/cm)	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	TH (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	TA (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^-N (mg/L)	SiO_2 (mg/L)	Fe^{2+} (mg/L)	F^- (mg/L)	Temp.
Monsoon	SW5	6.8	95	57	5.2	0.2	35	6	4.9	18	22	12.4	1	3.5	21	BDL	BDL	26.1
	SW6	7.3	61	37	6	1	15	2	2.4	12	15	10	1	BDL	11.5	BDL	0.06	25.8
	SW7	3.8	154	92	19	3.3	30	8	2.4	BDL	BDL	35	BDL	6.1	4	BDL	0.08	26.1
	SW8	7.1	241	145	30	8	45	12	3.7	4	5	54	30	3.1	12	BDL	BDL	26.2
	SW9	7.3	74	44	9	2.9	15	6	BDL	12	15	16	1	0.3	5.5	0.15	BDL	25.8
	SW10	7.8	110	66	14	12	15	4	1.2	12.5	15.3	30	2	BDL	13	BDL	0.1	26.7
Post-monsoon	SW5	6.7	90	54	11	0.5	20	6	1.2	15	18	17.5	1	1.2	11.5	BDL	BDL	26.7
	SW6	7.1	98	58.8	16	2	10	6	1.2	2	2.4	25	BDL	2.7	13	BDL	0.08	27.7
	SW7	6.4	115	69	11	0.5	30	8	2.4	25	31	17	6	0.6	3	BDL	BDL	26
	SW8	6.2	230	138	30	4	50	14	3.7	4	4.9	55	BDL	10.5	4.5	0.27	0.04	26.4
	SW9	6.7	70	42	6	1.5	20	4	2.4	8	10	13	0.6	2.2	3	0.1	0.2	27.3
	SW10	7.7	115	69	14.8	5.5	15	4	1.2	8	9.8	27	7	0.95	7	0.07	BDL	27.1
III) HIGHLAND																		
Pre-monsoon	SW11	7.2	165	99	13.3	1.5	50	14	3.7	22	27	21	20	2.9	14	1.8	0.05	27.1
	SW12	7	117	70	12.6	4.4	25	6	2.4	4	4.9	20.7	BDL	7	20	BDL	0.02	26.9
	SW13	7.2	430	258	49	10	95	38	BDL	62	76	58.5	33	6.8	28	0.16	0.12	27
	SW14	4.5	240	144	28	11	40	4	7.3	4	4.9	54	BDL	6.8	10	0.35	0.24	27.2
	SW15	7.6	320	192	18.6	1.4	110	26	11	139	170	17	4	BDL	12	0.62	0.2	27.4
	SW16	7	55	33	5.5	1.1	15	4	1.2	8.2	10	11	BDL	1.3	13	1.25	0.05	27.5
	SW17	7.1	400	240	38	12	90	30	3.7	88	107	48	21	2.6	16	0.44	0.06	26.8
	SW18	7.1	265	159	34	9.4	45	10	4.9	32	39	52.9	12	7	18	0.3	0.09	26.7
	SW19	6.7	148	89	6.5	12	40	10	3.7	28	34	15.3	10	1.5	22	0.5	0.2	27.4
	SW20	7	320	192	25	17	85	22	4.9	70	85	37.8	15.7	5	9	0.61	0.09	27.3

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Physiography/ Season	Well code	pH	EC (µS/cm)	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	TH (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	TA (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3-N (mg/L)	SiO_2 (mg/L)	Fe^{2+} (mg/L)	F^- (mg/L)	Temp.
Monsoon	SW11	7.4	85	51	8	4.3	20	4	2.4	25	31	12	1	BDL	23	0.12	0.09	25.9
	SW12	7.2	85	51	9	3.1	20	2	3.7	26	32	17	2	0.9	16	BDL	0.12	26.3
	SW13	6.4	428	257	71	6.6	45	10	4.9	6	7.3	105	21	6.9	19	0.1	0.14	26.1
	SW14	4.4	265	159	36	12	45	10	4.9	4	5	64	20	4.5	5.5	BDL	0.11	25.7
	SW15	8.2	302	181	20	1.6	100	22	11	124	151	19	1	BDL	16	BDL	0.08	25.7
	SW16	6.9	70	42	8	1.3	15	6	BDL	10	12	17	1	BDL	17	0.16	0.12	26.2
	SW17	8.2	345	207	36	8.3	80	26	3.7	120	146	35	2	BDL	9	0.13	0.08	26
	SW18	7.6	210	126	27.6	7	35	12	1.2	20	24.4	39	11	5	8	BDL	0.08	26.1
	SW19	7.9	200	120	10	4.7	65	20	3.7	56	68	15	22	BDL	13	BDL	0.09	26.3
	SW20	7.5	280	168	23	18	70	16	7.3	48	59	34	20	4.5	14	BDL	0.11	25.9
Post-monsoon	SW11	7.5	78	47	7.5	2	20	6	1.2	12	15	12.8	2	1.8	11	BDL	BDL	25.9
	SW12	7.4	170	102	24	1	25	6	2.4	6	7.3	36	3.3	4.1	19	0.2	0.25	26.5
	SW13	5.4	290	144	35	5.4	35	12	1.2	18	12.2	65	1.5	9.1	17	BDL	BDL	26.7
	SW14	4.5	235	141	27	6.3	45	16	6.1	4	4.9	60	0.4	9.2	8	0.2	BDL	25.8
	SW15	8.1	380	228	17	0.9	150	28	20	150	183	22	6.9	0.9	11	0.23	BDL	26.3
	SW16	7.1	92	55	9	1.6	25	6	2.4	12	14.6	19	2	1.8	10.5	BDL	0.25	27.4
	SW17	7.9	395	237	38	3.8	95	26	7.3	76	93	60	22	1.1	11	0.08	0.15	27.5
	SW18	7.4	240	144	35	5.4	35	12	1.2	18	22	42	9	7	7.5	BDL	0.5	27.1
	SW19	6.7	105	63	10	3.5	25	8	1.2	20	24	14	4	2.3	5	BDL	BDL	26.9
	SW20	7.3	265	159	15	8	90	32	2.4	38	46	25	37	4.4	6.5	2.6	0.2	26.9

TH, TA estimated as $CaCO_{3;}$ Detection Limit and Accuracy: SO_4:0.5mg/L ± 0.97; NO_3-N: 0.01 mg/L,Fe: 0.01 mg/L, ,± 0.024, F: 0.02 mg/L, ± 0.04, BDL: Below detection limit.

Table 5.3 Ranges and mean with standard deviation (given in parenthesis) of water quality parameters of the present study with that of WHO (2011) and BIS (2012).

Parameters	Pre-monsoon			Monsoon			Post-monsoon			WHO (2011)	BIS (2012)	
	Lowland	Midland	Highland	Lowland	Midland	Highland	Lowland	Midland	Highland		AL	PL
pH	7.3-7.9 (7.5,±0.28)	3.6–7.3 (6.2,±1.34)	4.5-7.6 (6.8,±0.9)	7.1-8.1 (7.7,±0.26)	3.8-7.8 (6.9,±1.5)	4.4-8.2 (7.2,±1.5)	6.7-8.1 (7.2,±0.8)	6.2-7.7 (6.8,±0.5)	4.5-8.1 (6.9,±1.2)	6.5-8.5	6.5-8.5	NR
EC(µS/cm)	107–470 (270,±158.5)	64-200 (116,±58.4)	55-430 (246,±124)	131–532 (294,±187)	61-241 (123,±66)	70-428 (227,±120)	110–510 (276,±176)	70-230 (120,±57)	78-380 (225,±113)	1500	-	-
TDS (mg/L)	64.2–287 (162,±95.1)	38-120 (69,±35)	33-258 (147,±74.3)	78.6–319 (176,±112)	37-145 (73.4,±40)	42-257 (136,±72.2)	66–306 (167,±105)	42-138 (72,±34)	47-237 (132,±67)	500	500	2000
Na (mg/L)	11-36.8 (22.3,±10.9)	4-19.3 (11.7,±7.8)	5.5-49 (23,±14.3)	14-39.1 (25.5,±10)	5.2-30 (13.9,±10)	8-71 (24.8,±19)	15–32 (23.2,±9)	6-30 (14.8,±8)	7.5-38 (21.7,±12)	200	-	-
K (mg/L)	1-11.4 (5.7,±5)	0.2-14 (5,±4.9)	1.5-17 (7.9,±5.5)	BDL–18 (6.7,±8.2)	0.2-12 (4.6,±4.5)	1.3-18 (6.9,±5.1)	0.5–7 (3.3,±2.7)	0.5-5.5 (2.3,±2)	0.9-8.0 (3.7,±2.4)	12	-	-
TH (mg/L)	40–145 (76.3,±52.8)	15-45 (26.7,±10)	15-110 (60,±32.6)	25–170 (82.5,±66)	15-45 (25.8,±13)	20-100 (50,±29)	20–175 (80,±68)	10-50 (24,±14.2)	20-150 (55,±43)	-	200	600
Ca (mg/L)	8–50 (23.5,±18.9)	6-12 (7.3,±2.4)	4-38 (16.4,±12)	6–48 (22,±18.6)	2-12 (6.3,±3.5)	2-26 (12.8,±8)	8.4–52 (24,±19.4)	4-14 (7,±3.7)	6-28 (15.2,±10)	75	75	200
Mg (mg/L)	2.4-7.3 (4.2,±0.28)	BDL-3.7 (1.8,±1.3)	BDL-11.0 (4.3,±3.1)	2.4-12.2 (6.7,±5)	BDL-4.9 (2.4,±1.7)	BDL-7.3 (4.3,±3.1)	2.4–11 (5.5,±4.1)	1.2-3.7 (2,±1.01)	1.2-20 (4.5,±5.8)	50	30	100

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Parameters	Pre-monsoon			Monsoon			Post-monsoon			WHO (2011)	BIS (2012)	
	Lowland	Midland	Highland	Lowland	Midland	Highland	Lowland	Midland	Highland		AL	PL
TA (mg/L)	14–115 (49.1,±47.6)	BDL-21 (11,±8.7)	4-70 (45.7,±44)	8–96 (46,±37.1)	BDL-18 (9.8,±6.5)	4-124 (44,±45)	4–105 (36.7,±47)	2-25 (10.3,±9)	4-150 (35.4,±45)	-	200	600
HCO_3 (mg/L)	17–140 (59.9,±57.9)	BDL-25 (12.7,±10)	4.9-107 (55.8,±54)	9.8–117 (55.5,±45)	BDL-22 (12,±8)	5-146 (52,±50.1)	4.9–128 (45,±57)	2.4-31 (12.6,±10)	4.9-183 (42.2,±56)	500	-	-
Cl (mg/L)	17-49.7 (31,±13.9)	6-41 (20,±14.2)	11-58.5 (33.6,±19)	21–67 (47.3,±22)	10-54 (26.2,±17)	12-105 (36,±29)	25–57 (40,±16.6)	13-55 (25.8,±15)	12.8-65 (36,±20)	250	250	1000
SO_4 (mg/L)	BDL–38 (17.4,±16.9)	0.6-10 (3.5,±3.9)	BDL-33 (11.6,±11)	1–41 (19.8,±22)	BDL-30 (5.8,±12)	1-22 (10,±9.6)	1–54 (28.4,±22.3)	BDL-7.0 (2.4,±3.2)	0.4-37 (8.8,±11.8)	250	200	400
NO_3-N (mg/L)	3.5–7 (5.3,±1.9)	0.6-6.8 (3.7,±2.8)	BDL-7.0 (4.09,±2.8)	0.5–5.6 (2.7,±2.2)	BDL-6.1 (2.2,±2.5)	BDL-6.9 (2.2,±3)	1.9-8.3 (4.5,±2.7)	0.6-10.5 (3.03,±4)	0.9-9.2 (4.2,±3.2)	45	45	NR
SiO_2 (mg/L)	3–18 (9,±7.4)	6–13 (8.8,±2.8)	9–28 (16.2,±5.9)	4–15.5 (9.8,±5.7)	4–21 (11.2,±6.1)	5.5–23(14.1,±5.3)	1.5–9.5 (4.8,±3.5)	3–13 (7,±4.3)	5–19 (10.7,±4.4)	-	-	-
Fe (mg/L)	0.1-0.5 (0.3,±0.16)	0.08-8.6 (2.6,±3.2)	BDL-1.25 (0.6,±0.5)	BDL (-)	BDL-0.15 (0.03,±0.1)	BDL-0.16 (0.1,±0.06)	0.04-3.3 (1,±1.6)	BDL-0.27 (0.1,±0.1)	BDL-2.6 (0.3,±0.8)	0.3	0.3	NR
F (mg/L)	0.02-0.09 (0.05,±0.03)	0.05-0.55 (0.2,±0.2)	0.02-0.24 (0.1,±0.07)	BDL-0.07 (0.05,±0.03)	BDL-0.1 (0.04,±0.05)	0.08-0.14 (0.1,±0.02)	BDL-0.4 (0.1,±0.2)	BDL-0.2 (0.1,±0.1)	BDL-0.5 (0.1,±0.2)	-	1	1.5
Temp ^{0}C	26.1-27 (26.5,±0.4)	26.3–27.7 (26.9,±0.5)	26.7–27.5 (27.1,±0.3)	25.7–26.1 (25.9,±0.2)	25.8–26.7 (26.1,±0.3)	25.7–26.3 (26,±0.2)	25.9–27.1 (26.3,±0.6)	26–27.7 (26.9,±0.6)	25.8–27.5 (26.7,±0.6)			

TH, TA estimated as $CaCO_3$; AL: Acceptable Limit, PL: Permissible Limit in the absence of alternate source, BDL: Below Detection Limit., NR: No Relaxation.

comparatively high in lowland and highland whereas the values are substantially low in midlands. However, the sample SW7 in the midland the alkalinity is not detected as the sample shows anomalous pH value with high level of acidity during pre-monsoon (pH=3.6) and monsoon (pH=3.8) seasons. During post-monsoon, the situation has improved (pH=6.4) due to continued dilution effect caused by rain water infiltration, which initiated with the onset of monsoon.

The ranges of chloride concentration in lowland, midland and highland are 17 - 67 mg/L, 6 - 55 mg/L and 11 - 105 mg/L respectively. All the samples of the study area are noticed to have a remarkable regional and seasonal variation in sulphate concentration. The sulphate value ranges from BDL to 54 mg/L in lowland, BDL to 30 mg/L in midland and BDL to 37 mg/L in the highland. In the case of midland the highest value of 30 mg/L is observed for the well number. SW8 during the monsoon season whereas in all the other samples sulphate concentrations are found to be low and ranges between BDL and 10 mg/L.

The content of nitrate in the well water samples shows significant spatial as well as seasonal variations. The minimum and maximum concentrations of NO_3-N are 0.6 - 7 mg/L, BDL - 6.9 mg/L and 0.6 - 10.5 mg/L in pre-monsoon, monsoon and post-monsoon seasons, respectively. The respective concentration ranges of nitrate in lowland, midland and highland are 0.5 - 8.3 mg/L, BDL - 10.5 mg/L and BDL - 9.2 mg/L. All the samples of pre-monsoon, 80% of monsoon and 45% of post-monsoon samples recorded the presence of fluoride.

Calcium and magnesium are the most abundant elements in surface and groundwater, and exist mainly as bicarbonates and to a lesser degree as sulphates and chlorides (Vincy *et al.,* 2015). Calcium and magnesium are the dominant cations in the groundwater sources of the study area which is followed by sodium and potassium.

On an average, 52% of total cation during pre-monsoon, 59% of monsoon and 58% of post-monsoon are contributed by alkaline earths. Ranges of calcium are 6 - 50 mg/L, 2 - 14 mg/L and 2 - 38 mg/L respectively in lowland, midland and highland regions. The content of calcium in pre-monsoon samples ranges from 4 mg/L to 50 mg/L, and that of monsoon and post-monsoon periods from 2 mg/L to 48 mg/L and 4 mg/L to 52 mg/L, respectively. The ranges of magnesium in the pre-monsoon, monsoon and post-monsoon seasons are BDL - 11 mg/L, BDL - 12.2 mg/L and 1.2 mg/L - 20 mg/L, respectively. In the lowland region, content of sodium varies from 11mg/L to 39.1 mg/L whereas in midland and highland the variations are 4mg/L to 30 mg/L and 5.5mg/L to 71 mg/L, respectively. The observed ranges of sodium are 4 to 49 mg/L in pre-monsoon, 5.2 to 71 mg/L in monsoon and 6 to 38 mg/L in post-monsoon seasons, respectively. Compared to sodium, potassium is present only in marginal concentrations throughout the year. The spatial variation of potassium as observed in the study are BDL to 18 mg/L in lowland, 0.2 mg/L to 14 mg/L in midland and 0.9 mg/L to 18 mg/L in highland samples. The concentration of potassium in different seasons are 0.2 - 17 mg/L in pre-monsoon, BDL - 18 mg/L in monsoon and 0.5 - 8 mg/L in post-monsoon seasons.

The content of iron in groundwater shows marked seasonal variations. About 80% of the pre-monsoon samples record iron values above the permissible limit of drinking water standard. And, it is found that there is decrease in iron concentration during monsoon season and in 75% of the samples iron was undetectable while the rest of the samples have iron values within the prescribed limit of drinking water standards. The ferric ion (Fe^{3+}) has a restricted field of stability at high redox potential (Eh) and low pH values. On the other hand the main dissolved species in natural waters is the ferrous ion (Fe^{2+}). This shows dilution of well water during the monsoon season. About 90% of post-monsoon samples fall within the safe limit whereas 10% of the samples exceed the limit with the reported values ranging from BDL to 3.3 mg/L. The highest iron concentration is observed in the sample number SW10 of midland during pre-monsoon season.

The SiO_2 values for pre- monsoon, monsoon and post-monsoon seasons in lowland part of the study area vary between 3-18 mg/L, 4-15.5 mg/L, and 1.5-9.5 mg/L respectively. In midland the content of SiO_2 ranges between 6 and 13 mg/L, 4 and 21 mg/L, and 3 and 13 mg/L during the pre-monsoon, monsoon and post-monsoon seasons. In highland region the vales are 9 and 28 mg/L during pre-monsoon, 5.5 and 23 mg/L during monsoon, and 5 and 19 mg/L during post-monsoon seasons.

5.4.2 Bacteriological analysis

Bacteriological analysis revealed that 75% samples in the lowland has the presence of total and faecal coliform during pre-monsoon season. The well SW3 which is used exclusively for domestic purpose is free from bacterial contamination during pre-monsoon since it is disinfected by chlorination. During monsoon and post-monsoon seasons all the samples exhibited bacterial contamination. *E.coli* is detected in 33% of pre-monsoon, 75% of monsoon and 50% of post-monsoon samples. Table 5.4 depicts the bacteriological parameters of the well water samples of the study area during pre-monsoon, monsoon and post-monsoon seasons. About 83% well water samples of pre-monsoon, 100% of monsoon and 67% of post-monsoon seasons of the midland region show incidence of bacterial pollution. *E.coli* was found to be positive in 50% of pre-monsoon samples. 83% of monsoon samples and 33% of post-monsoon samples confirmed the presence of *E.coli*. In highland, 60% of pre-monsoon samples were contaminated, whereas the entire samples of monsoon had bacterial count. About 90% of post-monsoon samples recorded total coliform, of which only 60% were polluted by feacal coliform. *E.coli* showed positive response in 10% of pre-monsoon samples whereas it is 50% in monsoon season. 30% of post-monsoon samples were positive to *E.coli*.

Table 5.4 Bacteriological parameters of the well water samples of the study area collected during pre-monsoon, monsoon and post-monsoon seasons.

Physiography	Well code	Pre-monsoon			Monsoon			Post-monsoon		
		TC*	FC#	*E.coli*	TC*	FC#	*E.coli*	TC*	FC#	*E.coli*
Lowland	SW1	140	110	-ve	300	240	+ve	90	90	-ve
	SW2	350	350	-ve	1600	1600	+ve	900	500	+ve
	SW3	Nil	Nil	-ve	90	80	-ve	60	50	-ve
	SW4	900	900	+ve	1600	1600	+ve	900	500	+ve
Midland	SW5	1600	1600	+ve	1600	1600	+ve	1600	900	+ve
	SW6	500	300	+ve	900	900	+ve	350	240	-ve
	SW7	22	26	-ve	900	500	+ve	12	9	-ve
	SW8	220	33	-ve	14	14	-ve	Nil	Nil	-ve
	SW9	1600	900	+ve	1600	1600	+ve	900	500	+ve
	SW10	Nil	Nil	-ve	240	130	+ve	Nil	Nil	-ve
Highland	SW11	Nil	Nil	-ve	170	140	-ve	70	Nil	-ve
	SW12	Nil	Nil	-ve	900	500	+ve	33	Nil	-ve
	SW13	350	280	-ve	1600	1600	+ve	1600	900	+ve
	SW14	170	140	-ve	900	500	+ve	110	80	-ve
	SW15	500	300	-ve	1600	900	+ve	900	900	+ve
	SW16	Nil	Nil	-ve	300	240	-ve	500	Nil	-ve
	SW17	900	900	+ve	1600	1600	+ve	1600	900	+ve
	SW18	50	30	-ve	220	170	-ve	40	23	-ve
	SW19	Nil	Nil	-ve	70	50	-ve	Nil	Nil	-ve
	SW20	50	23	-ve	140	110	-ve	34	33	-ve

** TC –Total Coliform, # FC – Faecal Coliform; All values in MPN/100ml*
+ve : Positive, -ve: Negative.

5.5 Discussion

5.5.1 Hydrochemical processes

An organized scientific study report containing the natural and man-made determinants of the quality of water resources of a region is very essential for developing plans for its better management and wise use. The procedures include simple comparisons and inspection of analytical data to more extensive statistical analysis and the preparation of graphs and maps that show significant relationships and allow for exploration of available data to an extent, sufficient to be most practical and useful. The following sections give a detailed evaluation of the results of the hydrochemical data generated in the study.

5.5.1.1 Major ion chemistry

The ionic ratios of the study area are given in Table 5.5. Mean Ca^{2+} + Mg^{2+} / Na^{+} + K+ ratios during pre-monsoon (PRM), monsoon (MON) and post-monsoon (POM) seasons are 1.17, 1.06 and 1.15 respectively suggesting significant contribution of ions from sources other than weathering of silicates. The mean HCO_3^- / Ca^{2+} + Mg^{2+} ratio during PRM, MON and POM are 0.57, 0.67 and 0.46 respectively. The HCO_3^- / Ca^{2+}ratios (due to higher concentration of HCO_3^-) during monsoon are comparatively higher than that of post-monsoon season, which could be attributed to higher dissolution of atmospheric CO_2 during rains. About 55% of pre-monsoon, 72% of monsoon and 75% post- monsoon samples have Ca^{2+}/ Mg^{2+} ratio equal or greater than 2. All these indicate the effect of silicate minerals in contributing Ca^{2+} and Mg^{2+} ions to the well waters (Katz *et al.,* 1998). Hren *et al.* (2007) used Ca^{2+}/ Na^{2+} and Mg^{2+} / Na^{+} ratios are used to calculate the relative proportions of Ca^{2+} and Mg^{2+} ions derived from carbonate and silicate weathering fronts. Mean Ca^{2+} / Na^{2+} ratios for pre-monsoon, monsoon and post-monsoon are 0.99, 0.77 and 0.87, respectively.

Table 5.5 Ionic ratios existing among the major cations and anions.

Ionic ratio	Pre-monsoon		Monsoon		Post- monsoon	
	Average	Range	Average	Range	Average	Range
*Ca^{2+}+Mg^{2+}/Na^{+}+K^{+}	1.17	0.45–2.71	1.06	0.28–3.03	1.15	0.38–3.99
*HCO_3^-/Ca^{2+}+Mg^{2+}	0.57	0.93–1.27	0.67	0.09–1.49	0.46	0.06–0.99
**HCO_3^-/Ca^{2+}	2.66	0.14-6.54	3.97	0.42–16	2.09	0.31–6.54
*Ca^{2+}/Na^{+}	0.99	0.16–1.77	0.77	0.16–2.30	0.87	0.29–2.45
*Mg^{2+}/Na^{+}	0.44	0.12–1.13	0.47	0.08–1.78	0.41	0.06–2.22
*Ca^{2+}/Mg^{2+}	2.40	0.33–6.25	1.99	0.33–6.10	2.97	0.85–8.13
*Ca^{2+}/SO_4^{2-}	6.66	1.52-24	10.86	0.96–52.80	12.09	0.98-96
*Mg^{2+}/Ca^{2+}	0.58	0.16–2.99	0.74	0.16–3.03	0.46	0.12–1.17
*HCO_3^-/HCO_3^-+SO_4^{2-}	0.75	0.39–1.00	0.74	0.12–0.99	0.76	0.25–1.00

** Ratios are derived from meq/L values ** ratios derived from molar values*

The respective ratios (average) Mg^{2+} / Na^{+} are 0.44, 0.47 and 0.41. The average Ca^{2+} / Na^{2+} and Mg^{2+} / Na^{+} are relatively higher during pre-monsoon, which reflects either an enrichment of Ca^{2+} and Mg^{2+} or depletion in Na^{+} . The ratio of Ca^{2+} / SO_4^{2-} is greater than unity in all the three seasons indicating supply of protons to enable chemical weathering by H_2CO_3 (Stallard and Edmond, 1987). The Na/Cl ratio is used to identify the source of salinity in groundwater. Na/Cl molar ratio > 1 reflects Na^{+} released from silicate weathering (Stallard and Edmond, 1983; Meybeck, 1987; Srinivasamoorthy *et al.,* 2012) is resulted from rock water interaction. About 35% of pre-monsoon, 15% of monsoon and 20% of post-monsoon samples reflect the release of sodium due to silicate weathering in the study area. It is also noted that all post-monsoon samples of lowland and midland, and 60% of highland have Na/Cl ratio < 1. The remaining samples, irrespective of seasons, show the dominance of chloride ion concentration. The chloride content exceeding the concentration of Na in the samples could be attributed to base exchange phenomena or to pollution from anthropogenic activities (Jones *et al.,* 1999). The plots of $Ca^{2+} + Mg^{2+}$ *vs*. HCO_3^{-} (Fig. 5.2), for pre-monsoon, monsoon and post-monsoon samples of the study area shows that majority of data points in the plot fall above the equiline (1:1) suggesting an excess of alkaline earth metals ($Ca^{2+} + Mg^{2+}$) over HCO_3^{-} reflecting additional sources of Ca^{2+} and Mg^{2+} to be balanced by Cl^{-} and SO_4^{2-} and/or supplied by silicate weathering (Zhang *et al.,* 1995).

During pre-monsoon 70% of samples fall below equiline, though some points fall close to the theoretical 1:1 trend line, showing a calcium dominance over HCO_3^{-} + SO_4^{2-} (See Fig 5.2). Similar trend is observed in monsoon and post-monsoon samples of midland region as well as post-monsoon samples of highland. On the contrary, most of the monsoon and post-monsoon lowland samples have excess of $HCO_3^{-} + SO_4^{2}$ over $Ca^{2+} + Mg^{2+}$. In highland region the monsoon samples g*et al*igned more towards the

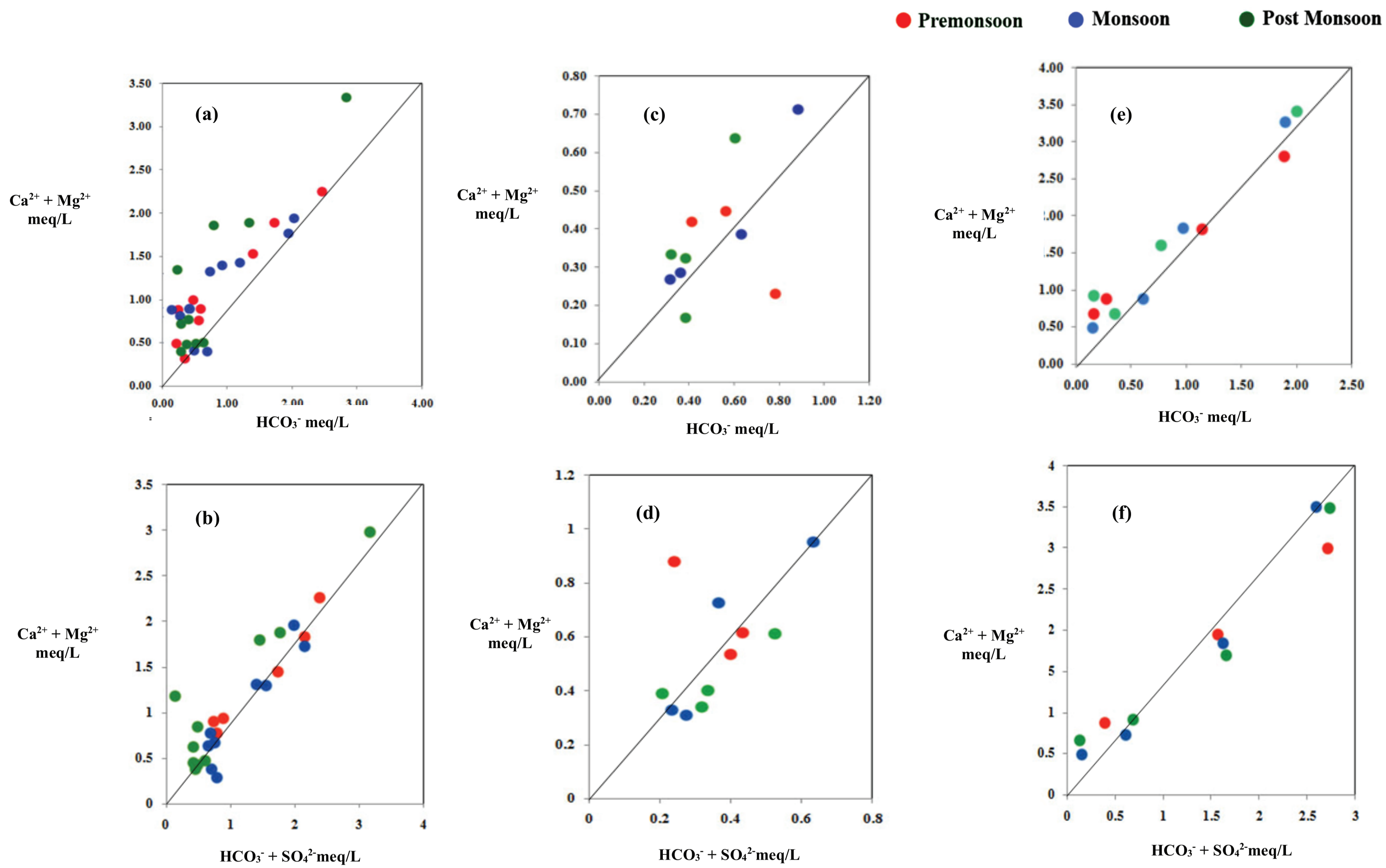


Fig. 5.2 Plots of ($Ca^{2+} + Mg^{2+}$) vs HCO_3^- and ($Ca^{2+} + Mg^{2+}$) vs ($HCO_3^- + SO_4^{2-}$) in the well samples of (a) & (b) highland, (c) & (d) midland and (e) & (f) lowland regions of the study area.

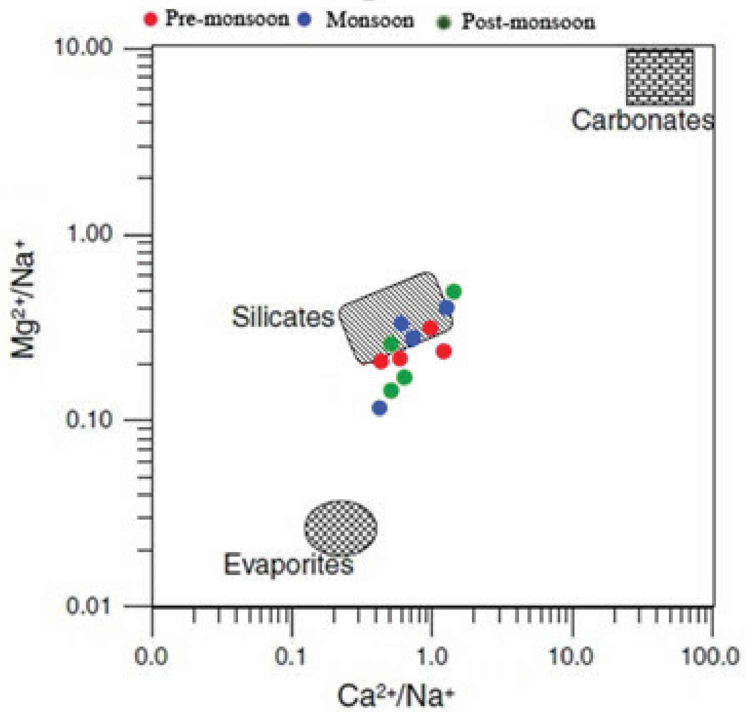
equiline, due to the dissolution of calc-plagioclase feldspars and other silicates from the weathering front.

The geochemical data plotted on bivariate diagrams of HCO_3^-/Na^+ *vs.* Ca^{2+}/Na^+ and Ca^{2+}/Na^+ *vs* Mg^{2+}/Na in lowland, midland and highland regions (Figs 5.3, 5.4 & 5.5) relating carbonate and silicate end members shows that weathering of alumino-silicate minerals is the major lithogenic contributor along with minor addition of atmospheric dissolution (Refer Chapter IV, Section 4.5.2). The molar ratio HCO_3^-/SiO_2 is computed to study the influence of silicate dissolution in well water samples. The ratio shows that 70% of the well water samples have a molar ratio value < 5 indicating the predominance of silicate weathering (Hounslow, 1995). 15% of the samples have molar ratio value between 5 to 10 and the rest 15% have the ratio above 10.

High quality kaolin is produced in the vicinity of locations like Kundara, Chathanoor and Quilon of the study area. According to Ghosh (1986), kaolin occurs in two beds separated by sandstone, and the lower bed is purer than the upper bed. Kaolinite makes up 25 percent of the lower bed and is derived from the weathering of the underlying pre-cambrian crystalline rocks (Arogyaswamy, 1968, Ghosh, 1986).

5.5.1.2 Hydro-chemical facies

The data plots on the Piper diagram belonging to the lowland of the study area shows that majority of the sample points are clustered in the non-dominant zone. The plots of hydrochemical data on the central diamond shaped field which relates the cation and anion triangles reveal that in 25% samples alkaline earth elements (Ca2+ + Mg2+) exceed alkalis and strong acids ($Cl^- + SO_4^{2-}$) exceeds weak acids (HCO_3^-). The water types of lowland fall under ($Ca^{2+} + Mg^{2+}$) - ($Cl^- + SO_4^{2-}$) type of water and 50% of pre-monsoon samples are found to be calcium dominant. The piper plot for midland reveals that majority of samples irrespective of seasons, fall in the no dominant facies



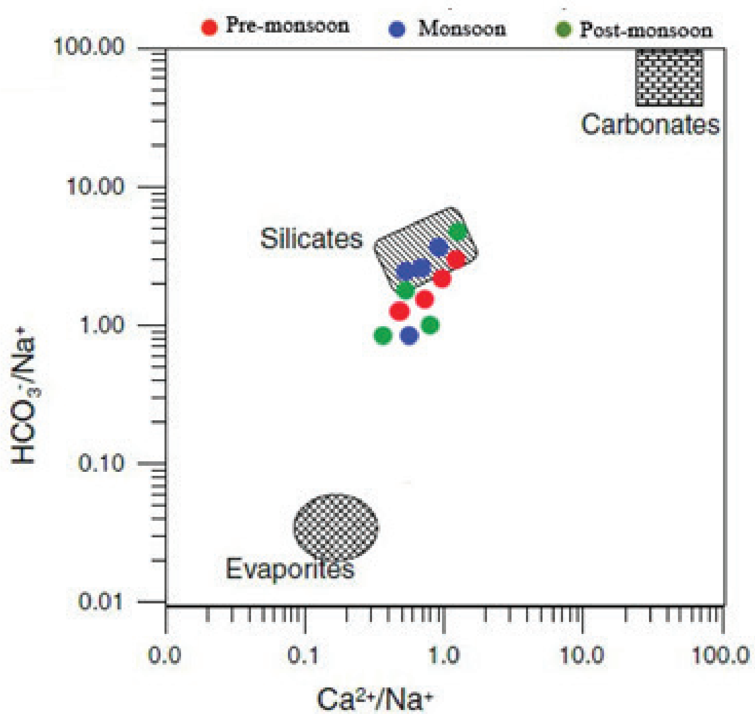


Fig. 5.3 Scatter plot of Mg^{2+} / Na^+ vs Ca^{2+} / Na^+ and HCO_3^- / Na^+ vs Ca^{2+} / Na^+ relating carbonate and silicate members in lowland well water samples.

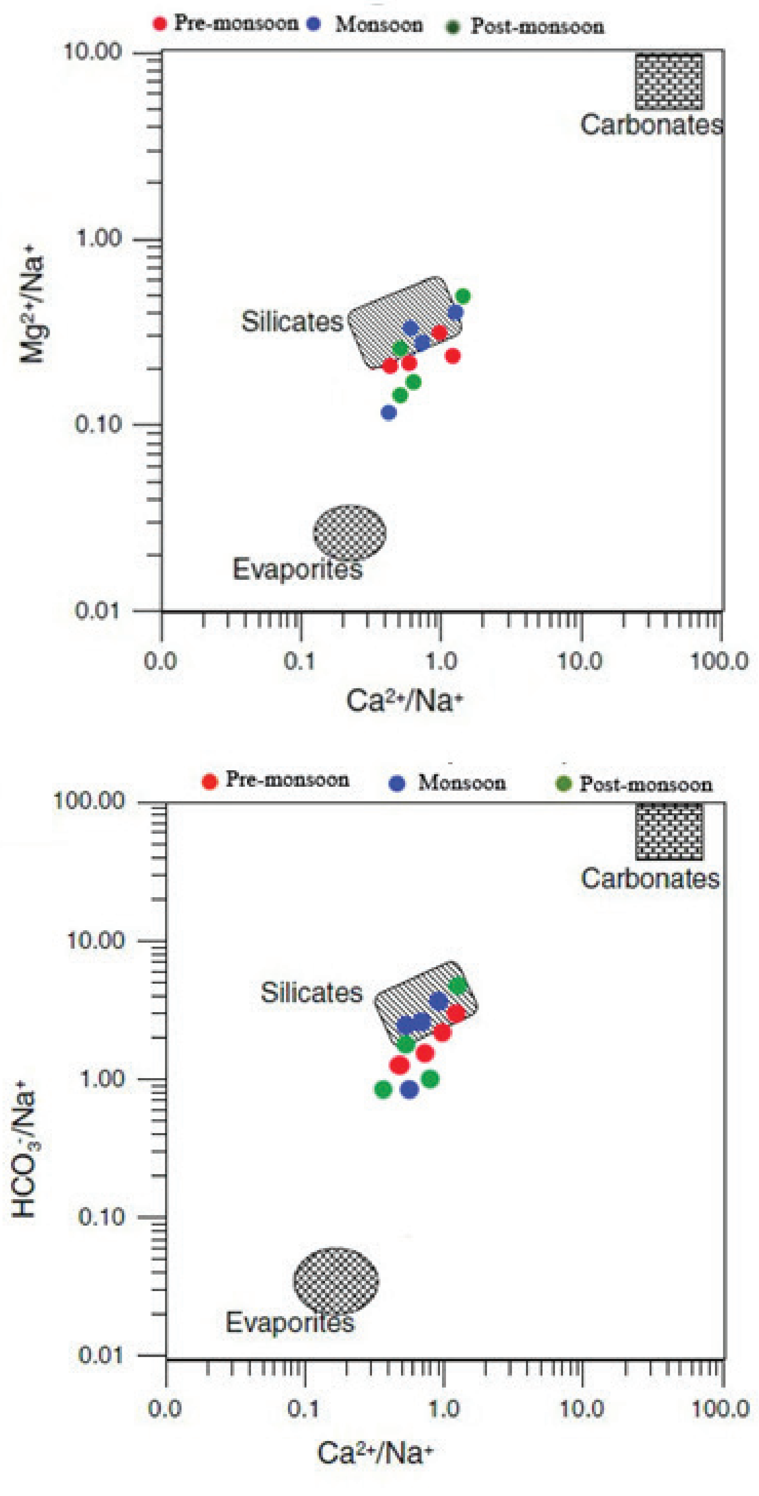
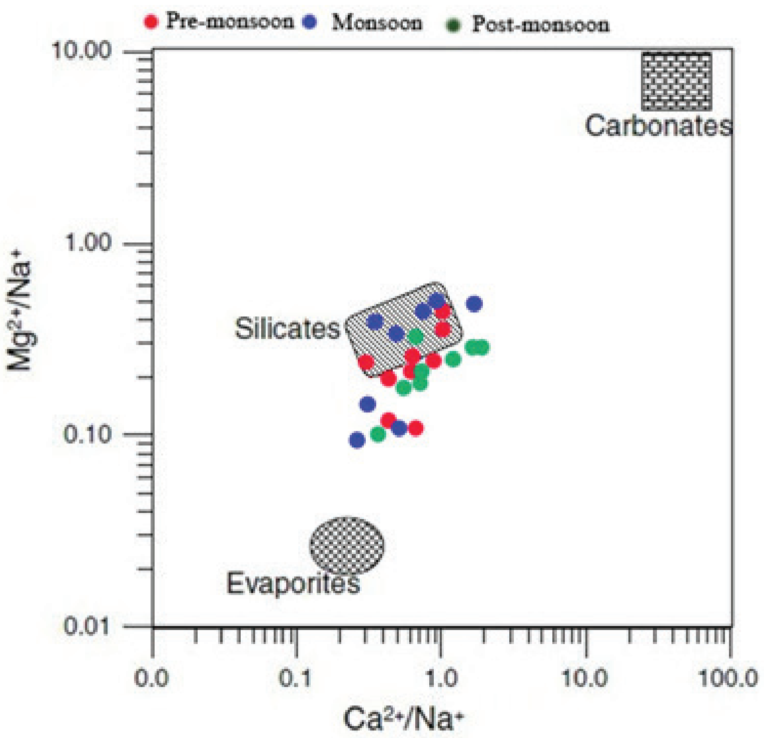


Fig. 5.4 Scatter plot of Mg^{2+} / Na^{+} vs Ca^{2+} / Na^{+} and HCO_3^{-} / Na^{+} vs Ca^{2+} / Na^{+} relating carbonate and silicate members in midland well water samples.



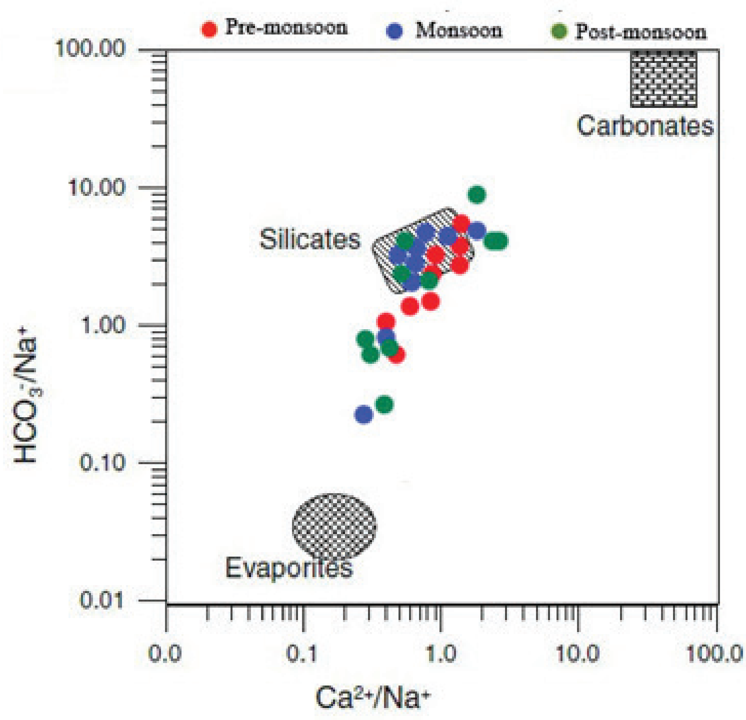


Fig. 5.5 Scatter plot of Mg^{2+} / Na^+ vs Ca^{2+} / Na^+ and HCO_3^- / Na^+ vs Ca^{2+} / Na^+ relating carbonate and silicate members in highland well water samples.

and a few samples in the $Na^+ + K^+$ cation facies. The predominant anion species is that of Cl^-. It is also clear from piper trilinear diagram (Fig. 5.6) that non-carbonate alkalinity (primary salinity) exceeds 50% and in 17 % of the samples carbonate hardness exceeds 50% , i.e.; in the samples of midland regions, alkali exceeds alkaline earth and strong acid exceeds weak acids in about 83% of the samples without any significant seasonal variation. In short, midland samples contain Na-Cl (water type) dominant groundwater with subordinate $Ca^{2+} + Mg^{2+}$ - HCO_3^-.

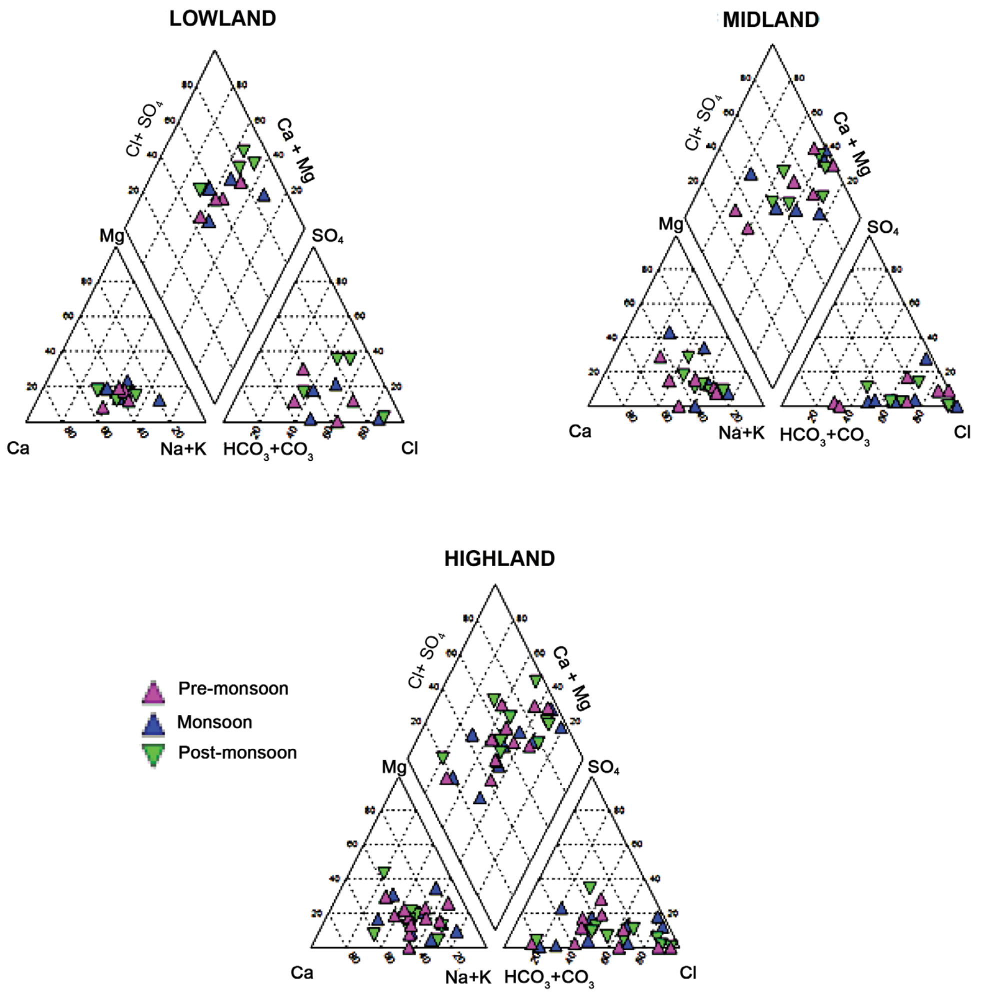


Fig. 5.6 Piper diagram showing the relationship between dissolved ions in the well water samples of the lowland, midland and highland regions of Ithikkara and Kallada river basins.

The trilinear diagram of the analytical results of groundwater samples in highland shows that majority of the sample plots fall into the $Na^+ + K^+$ field showing dominance of alkalis ($Na^+ + K^+$) over alkaline earths ($Ca^{2+} + Mg^{2+}$) and strong acid ($Cl^- + SO_4^{2-}$) over weak acid (HCO_3^-) and the water can be categorized in Na-Cl and mixed type.

5.5.1.3 Data analysis using correlation matrix

The Pearson correlation matrix done for the lowland region is given in Table 5.6 and their corresponding P values is shown in Table 5.7. pH records a strong correlation with EC (r = 0.71), Ca^{2+} (r = 0.73), TH (r = 0.76), HCO_3^- (r = 0.80) and have a moderate correlation with Mg^{2+} (r = 0.64) at a significant P value < 0.05. EC and TDS are strongly correlated to Na^{2+} (r = 0.93), TH (r = 0.99), Ca^{2+} (r = 0.96) and HCO_3^- (r = 0.93). A strong correlation is noticed between EC and Mg^{2+} (r= 0.88), Cl^- (r = 0.86) and SO_4^{2-} (r = 0.76) and a moderate correlation between K^+ (r = 0.62) and NO_3-N (r = 0.64). This indicates that these are the ions involved in the geochemical process regulating water quality in lowland region. Na^+ is strongly correlated with TH (r = 0.88), Ca^{2+} (r = 0.87), Mg^{2+} (r = 0.75), HCO_3^- (r = 0.83), Cl^- (r = 0.88), SO_4^{2-} (r= 0.71) and moderately correlated with NO_3-N (r = 0.58). The strong positive correlation of Na^+ and Cl^- with EC and also with each other reflects a common source for these ions (Okeke *et al.,* 2015). K^+ is strongly correlated with Mg^{2+} (r=0.72) and moderately correlated with TH (r = 0.58), Cl^- (r = 0.61) and SO_4^{2-} (r = 0.58) which specifies a possible ion exchange processes in the aquifer system. The moderate correlation between Ca^{2+} - SO_4^2 and Mg^{2+} - SO_4^2 confirms the existence of magnesium calcareous materials in the lowland province of the study area (Singh *et al.,* 2011). TH has a strong correlation with Ca^{2+} (r = 0.98), HCO_3^- (r = 0.98), and exhibits a strong correlation with Mg^{2+} (r = 0.87), Cl^- (r = 0.80) and SO_4^{2-} (r=0.71). A moderate correlation is noticed between TH and NO_3-N (r = 0.64). Correlation of TH with these ions indicates that hardness in well water samples of lowland region is mainly due to the salts like HCO_3^-, SO_4^{2-}, Cl^- and nitrates of Ca^{2+} and Mg^{2+}. Mg^{2+} shows a strong correlation between HCO_3^- (r = 0.74), Cl^- (r = 0.84) and SO_4^{2-} (r=0.78). TA is moderately correlated with Cl^- (r = 0.68) and

Table 5.6 Correlation matrix (Pearson) for lowland well water samples

Variables	pH	EC	TDS	Na^+	K^+	TH	Ca^{2+}	Mg^{2+}	TA	HCO_3^-	Cl^-	SO_4^{2-}	NO_3-N	SiO_2	Fe^{2+}	F^-
pH	**1.00**															
EC	**0.71**	**1.00**														
TDS	**0.71**	**1.00**	**1.00**													
Na^+	0.57	**0.93**	**0.93**	**1.00**												
K^+	0.45	**0.62**	**0.62**	0.48	**1.00**											
TH	**0.76**	**0.99**	**0.99**	**0.88**	**0.58**	**1.00**										
Ca^{2+}	**0.73**	**0.96**	**0.96**	**0.87**	0.49	**0.98**	**1.00**									
Mg^{2+}	**0.64**	**0.88**	**0.88**	**0.75**	**0.72**	**0.87**	**0.77**	**1.00**								
TA	**0.80**	**0.93**	**0.93**	**0.84**	0.54	**0.96**	**0.98**	**0.74**	**1.00**							
HCO_3^-	**0.80**	**0.93**	**0.93**	**0.84**	0.54	**0.96**	**0.98**	**0.74**	**1.00**	**1.00**						
Cl^-	0.54	**0.86**	**0.86**	**0.88**	**0.61**	**0.80**	**0.73**	**0.84**	**0.68**	**0.68**	**1.00**					
SO_4^{2-}	0.21	**0.76**	**0.76**	**0.71**	**0.59**	**0.71**	**0.63**	**0.78**	0.54	0.54	**0.71**	**1.00**				
NO_3-N	0.47	**0.64**	**0.64**	**0.58**	0.06	**0.64**	**0.69**	0.38	**0.61**	**0.61**	0.41	0.35	**1.00**			
SiO_2	-0.08	**-0.65**	**-0.65**	**-0.60**	-0.57	**-0.60**	**-0.58**	-0.55	-0.49	-0.49	-0.54	**-0.86**	-0.30	**1.00**		
Fe^{2+}	-0.56	-0.38	-0.38	-0.35	-0.20	-0.37	-0.30	-0.32	-0.34	-0.34	-0.33	-0.34	-0.29	0.08	**1.00**	
F^-	-0.20	-0.26	-0.26	-0.32	-0.19	-0.26	-0.25	-0.30	-0.31	-0.32	-0.34	-0.04	-0.16	-0.22	-0.13	**1.00**

Values in bold are with a significance level alpha=0.05

Table 5.7 P values for lowland well water samples

Variables	pH	EC	TDS	Na^+	K^+	TH	Ca^{2+}	Mg^{2+}	TA	HCO_3^-	Cl^-	SO_4^{2-}	NO_3-N	SiO_2	Fe^{2+}	F^-
pH	**0.00**															
EC	**0.01**	**0.00**														
TDS	**0.01**	**<0.0001**	**0.00**													
Na^+	0.05	**<0.0001**	**<0.0001**	**0.00**												
K^+	0.14	**0.03**	**0.03**	0.12	**0.00**											
TH	**0.00**	**<0.0001**	**<0.0001**	**0.00**	**0.05**	**0.00**										
Ca^{2+}	**0.01**	**<0.0001**	**<0.0001**	**0.00**	0.11	**<0.0001**	**0.00**									
Mg^{2+}	**0.02**	**0.00**	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**								
TA	**0.00**	**<0.0001**	**<0.0001**	**0.00**	0.07	**<0.0001**	**<0.0001**	**0.01**	**0.00**							
HCO_3^-	**0.00**	**<0.0001**	**<0.0001**	**0.00**	0.07	**<0.0001**	**<0.0001**	**0.01**	**<0.0001**	**0.00**						
Cl^-	0.07	**0.00**	**0.00**	**0.00**	**0.03**	**0.00**	**0.01**	**0.00**	**0.01**	**0.01**	**0.00**					
SO_4^{2-}	0.51	**0.00**	**0.00**	**0.01**	**0.04**	**0.01**	**0.03**	**0.00**	0.07	0.07	**0.01**	**0.00**				
NO_3-N	0.13	**0.03**	**0.03**	**0.05**	0.84	**0.02**	**0.01**	0.23	**0.04**	**0.04**	0.19	0.27	**0.00**			
SiO_2	0.81	**0.02**	**0.02**	**0.04**	0.05	**0.04**	**0.05**	0.06	0.11	0.11	0.07	**0.00**	0.35	**0.00**		
Fe^{2+}	0.06	0.22	0.22	0.27	0.54	0.24	0.34	0.31	0.28	0.28	0.30	0.27	0.36	0.80	**0.00**	
F^-	0.54	0.41	0.41	0.31	0.56	0.41	0.43	0.34	0.32	0.32	0.28	0.91	0.62	0.50	0.69	**0.00**

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

NO_3-N (r = 0.61). A moderate correlation coefficient is also observed between NO_3-N with Ca^{2+} (r = 0.69). SO_4^{2-} is correlated moderately with K^+ (r = 0.59) indicating input from similar source. SiO_2 has a strong negative correlation with SO_4^{2-} (r = -0.8. HCO_3^- is moderately correlated to NO_3-N (r = 0.61).

The following inferences are reached from the Pearson correlation matrix (Table 5.8) generated along with P values (Table 5.9) at a significant level of $P < 0.05$ for the water quality parameters of dug well samples in the midland region of the study area. pH does not show any significant positive correlation with any of the parameters. EC and TDS are correlated strongly to Na^+ (r =0.95) and Cl^- (r = 0.96). K^+ is moderately correlated to Cl^- (r = 0.52) and Fe^{2+} (r = 0.59) and weakly to SO_4^{2-} (r = 0.47). HCO_3^- shows a negative moderate correlation with Cl^- (r = -0.63) and NO_3-N (r =-0.57). Negative correlation between bicarbonate and nitrate is a strong indicator of microbial denitrification process (Chkirbene *et al.,* 2009).TH is strongly correlated to Ca^{2+} and Mg^{2+} (r =0.89, 0.80) and moderately to Cl^- and NO_3-N (r =0.69, 0.67) which indicates that chloride and nitrates of Ca^{2+} and Mg^{2+} regulate the alkalinity character of groundwater (Das and Nag, 2015). Ca^{2+} and Cl^- are strongly correlated (r = 0.78) and Ca^{2+} and NO_3-N is moderately correlated (r = 0.68).

The Pearson correlation matrix prepared for the highland region is given in Table 5.10 and their corresponding P values is shown in Table 5.11. pH shows a moderate correlation with HCO_3^- (r = 0.58) and weak correlation to TH (r = 0.38). EC and TDS are strongly correlated to TH, Ca^{2+} (r = 0.78) and moderately to HCO_3^- (r= 0.59), SO_4^{2-} (r =0.54), Cl^- (r= 0.67) and weakly to Mg^{2+} (r = 0.46). Na^+ and Cl^- are strongly correlated to each other (r = 0.93). Na is correlated moderately to NO_3-N (r = 0.54) and weakly to SO_4^{2-} (r = 0.41) and K (r =0.37). K is weakly correlated to Cl^-, SO_4^{2-} and NO_3-N (r = 0.39, 0.45 and 0.39 respectively). A strong correlation exist between TH

Table 5.8 Correlation matrix (Pearson) for midland well water samples

Variables	pH	EC	TDS	Na^+	K^+	TH	Ca^{2+}	Mg^{2+}	TA	HCO_3^-	Cl^-	SO_4^{2-}	NO_3-N	SiO_2	Fe^{2+}	F^-
pH	**1.00**															
EC	-0.28	**1.00**														
TDS	-0.28	**1.00**	**1.00**													
Na^+	-0.28	**0.95**	**0.95**	**1.00**												
K^+	0.17	**0.51**	**0.51**	**0.51**	**1.00**											
TH	-0.31	**0.84**	**0.84**	**0.64**	0.20	**1.00**										
Ca^{2+}	-0.26	**0.87**	**0.87**	**0.76**	0.25	**0.89**	**1.00**									
Mg^{2+}	-0.12	**0.55**	**0.56**	0.34	0.03	**0.80**	**0.52**	**1.00**								
TA	0.46	**-0.49**	**-0.49**	**-0.62**	-0.25	-0.15	-0.29	0.02	**1.00**							
HCO_3^-	0.46	**-0.49**	**-0.49**	**-0.62**	-0.25	-0.15	-0.29	0.03	**1.00**	**1.00**						
Cl^-	-0.24	**0.96**	**0.96**	**0.98**	**0.52**	**0.69**	**0.78**	0.40	**-0.63**	**-0.63**	**1.00**					
SO_4^{2-}	0.12	**0.62**	**0.62**	**0.57**	**0.47**	0.45	0.43	0.32	-0.16	-0.16	**0.54**	**1.00**				
NO_3-N	**-0.59**	**0.71**	**0.71**	**0.69**	0.26	**0.67**	**0.68**	0.43	**-0.57**	**-0.57**	**0.66**	0.07	**1.00**			
SiO_2	0.28	-0.06	-0.05	-0.13	0.01	0.04	-0.12	0.38	0.15	0.14	-0.09	0.10	-0.18	**1.00**		
Fe^{2+}	0.05	0.22	0.22	0.10	**0.59**	0.23	0.22	0.16	0.09	0.09	0.04	0.17	0.32	0.03	**1.00**	
F^-	-0.21	0.18	0.18	0.03	0.17	0.26	0.24	0.20	-0.24	-0.24	0.14	-0.10	0.16	0.02	0.28	**1.00**

Values in bold are with a significance level alpha=0.05

Table 5.9 P values for midland well water samples

Variables	pH	EC	TDS	Na^+	K^+	TH	Ca^{2+}	Mg^{2+}	TA	HCO_3^-	Cl^-	SO_4^{2-}	NO_3-N	SiO_2	Fe^{2+}	F^-
pH	**0.00**															
EC	0.26	**0.00**														
TDS	0.27	**<0.0001**	**0.00**													
Na^+	0.26	**<0.0001**	**<0.0001**	**0.00**												
K^+	0.49	**0.03**	**0.03**	**0.03**	**0.00**											
TH	0.20	**<0.0001**	**<0.0001**	**0.00**	0.42	**0.00**										
Ca^{2+}	0.29	**<0.0001**	**<0.0001**	**0.00**	0.31	**<0.0001**	**0.00**									
Mg^{2+}	0.63	**0.02**	**0.02**	0.17	0.90	**<0.0001**	**0.03**	**0.00**								
TA	0.05	**0.04**	**0.04**	**0.01**	0.32	0.54	0.24	0.92	**0.00**							
HCO_3^-	0.05	**0.04**	**0.04**	**0.01**	0.31	0.54	0.24	0.91	**<0.0001**	**0.00**						
Cl^-	0.33	**<0.0001**	**<0.0001**	**<0.0001**	**0.03**	**0.00**	**0.00**	0.10	**0.01**	**0.01**	**0.00**					
SO_4^{2-}	0.62	**0.01**	**0.01**	**0.01**	**0.05**	0.06	0.07	0.20	0.51	0.52	**0.02**	**0.00**				
NO_3-N	**0.01**	**0.00**	**0.00**	**0.00**	0.29	**0.00**	**0.00**	0.07	**0.01**	**0.01**	**0.00**	0.78	**0.00**			
SiO_2	0.25	0.83	0.83	0.60	0.96	0.87	0.65	0.12	0.56	0.57	0.73	0.69	0.49	**0.00**		
Fe^{2+}	0.83	0.38	0.38	0.68	**0.01**	0.36	0.38	0.53	0.71	0.73	0.86	0.50	0.20	0.90	**0.00**	
F^-	0.40	0.47	0.48	0.90	0.50	0.31	0.34	0.42	0.34	0.33	0.59	0.70	0.52	0.95	0.26	**0.00**

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

Table 5.10 Correlation matrix (Pearson) for highland well water samples

Variables	pH	EC	TDS	Na^+	K^+	TH	Ca^{2+}	Mg^{2+}	TA	HCO_3^-	Cl^-	SO_4^{2-}	NO_3-N	SiO_2	Fe^{2+}	F^-
pH	**1.00**															
EC	0.06	**1.00**														
TDS	0.09	**1.00**	**1.00**													
Na^+	-0.22	**0.80**	**0.79**	**1.00**												
K^+	-0.30	**0.40**	**0.41**	**0.37**	**1.00**											
TH	**0.38**	**0.78**	**0.79**	0.27	0.17	**1.00**										
Ca^{2+}	0.35	**0.78**	**0.78**	0.35	0.24	**0.89**	**1.00**									
Mg^{2+}	0.17	**0.46**	**0.47**	0.04	-0.05	**0.72**	0.35	**1.00**								
TA	**0.58**	**0.59**	**0.60**	0.08	-0.01	**0.88**	**0.74**	**0.69**	**1.00**							
HCO_3^-	**0.58**	**0.59**	**0.60**	0.08	0.00	**0.89**	**0.75**	**0.69**	**1.00**	**1.00**						
Cl^-	**-0.49**	**0.67**	**0.65**	**0.93**	**0.39**	0.10	0.16	0.01	-0.16	-0.16	**1.00**					
SO_4^{2-}	0.10	**0.54**	**0.55**	**0.41**	**0.45**	**0.44**	**0.62**	-0.06	0.11	0.13	0.35	**1.00**				
NO_3-N	**-0.61**	0.26	0.23	**0.54**	**0.39**	-0.18	-0.06	-0.21	**-0.47**	**-0.47**	**0.68**	0.15	**1.00**			
SiO_2	0.16	0.02	0.02	0.11	-0.02	-0.09	-0.03	-0.16	-0.04	-0.05	0.05	0.03	0.02	**1.00**		
Fe^{2+}	0.04	-0.03	-0.02	-0.21	-0.01	0.18	0.27	-0.05	0.01	0.02	-0.19	**0.41**	-0.04	-0.15	**1.00**	
F^-	0.04	0.03	0.05	0.14	0.05	-0.08	-0.06	-0.12	-0.12	-0.11	0.08	0.11	0.08	-0.07	0.04	**1.00**

Values in bold are with a significance level alpha=0.05

Table 5.11 P values for highland well water samples

Variables	pH	EC	TDS	Na^+	K^+	TH	Ca^{2+}	Mg^{2+}	TA	HCO_3^-	Cl^-	SO_4^{2-}	NO_3-N	SiO_2	Fe^{2+}	F^-
pH	**0.00**															
EC	0.74	**0.00**														
TDS	0.65	**<0.0001**	**0.00**													
Na^+	0.25	**<0.0001**	**<0.0001**	**0.00**												
K^+	0.11	**0.03**	**0.03**	**0.04**	**0.00**											
TH	**0.04**	**<0.0001**	**<0.0001**	0.15	0.36	**0.00**										
Ca^{2+}	0.06	**<0.0001**	**<0.0001**	0.06	0.20	**<0.0001**	**0.00**									
Mg^{2+}	0.36	**0.01**	**0.01**	0.82	0.80	**<0.0001**	0.06	**0.00**								
TA	**0.00**	**0.00**	**0.00**	0.68	0.95	**<0.0001**	**<0.0001**	**<0.0001**	**0.00**							
HCO_3^-	**0.00**	**0.00**	**0.00**	0.68	1.00	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**0.00**						
Cl^-	**0.01**	**<0.0001**	**0.00**	**<0.0001**	**0.03**	0.60	0.39	0.96	0.40	0.40	**0.00**					
SO_4^{2-}	0.58	**0.00**	**0.00**	**0.02**	**0.01**	**0.01**	**0.00**	0.77	0.56	0.50	0.06	**0.00**				
NO_3-N	**0.00**	0.17	0.22	**0.00**	**0.03**	0.35	0.75	0.26	**0.01**	**0.01**	**<0.0001**	0.41	**0.00**			
SiO_2	0.40	0.90	0.93	0.57	0.92	0.65	0.88	0.40	0.84	0.80	0.80	0.86	0.90	**0.00**		
Fe^{2+}	0.83	0.89	0.92	0.27	0.97	0.35	0.16	0.81	0.98	0.94	0.31	**0.02**	0.85	0.43	**0.00**	
F^-	0.84	0.87	0.80	0.45	0.77	0.68	0.76	0.53	0.53	0.56	0.66	0.57	0.69	0.72	0.82	**0.00**

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

and Ca^{2+} (r = 0.89). Mg^{2+} (r = 0.72), HCO_3^- (r = 0.89) and a weak correlation with SO_4^{2-} (r = 0.44). HCO_3^- is strongly correlated to 0.75 and moderately to Mg^{2+} (r = 0.69). In highland samples also HCO_3^- shows a negative correlation NO_3-N (r = -0.47). Cl^- and NO_3-N are moderately correlated (r = 0.68) and Fe^{2+} and SO_4^{2-} are weakly correlated (r = 0.41). From the results it is clear that the bicarbonate of Ca^{2+} and Mg^{2+} impart alkalinity to water.

5.5.1.4 Ion exchange

Ion-exchange is an important factor that determines the geochemical processes responsible for changes in groundwater quality (Refer Chapter IV, Section 4.5.1). The positive value of CAI indicates that there is exchange between sodium and potassium in water with calcium and magnesium in the rocks by a type of base-exchange reactions. The negative value of CAI represents the absence of base-exchange reactions and existence of cation-anion exchange type of reactions. In lowland, samples 75% of samples of pre-monsoon season exhibit negative CAI values indicating prevalence of cation anion exchange reaction whereas in monsoon and post-monsoon season exchange of sodium and potassium in water with calcium and magnesium from host rock or soil occurs.

In the midland region 78% of the samples have positive CAI values. In well water samples of the highlands of Ithikkara and Kallada river basins, 75% of the samples have negative CAI values indicating chloro-alkaline disequilibrium and prevalence of cation - anion exchange reaction (Table 5.12). During this process, the host rock is the primary source of dissolved solids in water. In about 25% of the samples, the values are positive indicating the prevalence of Base Exchange reaction. Hence it is evident that pre-monsoon water samples of lowland and highland region are subjected to similar types of geochemical processes.

Table 5.12. Total ions concentration, CAI, SAR, % Na, RSC, Kelly Index, Permeability Index and Magnesium Hazard values for lowland, midland and highland well water samples of the study area.

Physiography/ Season	Well code	TZ-	TZ+	CAI - I	CAI-II	SAR	% Na	RSC	KI	PI	MH
I) LOWLAND											
Pre-monsoon	SW1	1.01	1.10	-0.05	-0.05	0.88	45.87	-0.32	0.80	93.61	32.97
	SW2	2.88	3.11	-0.73	-0.26	1.08	42.19	-0.73	0.57	72.82	33.27
	SW3	4.69	4.71	-0.29	-0.13	1.33	38.47	-0.60	0.55	69.22	13.79
	SW4	1.81	1.63	0.03	0.03	1.24	51.06	-0.51	0.98	83.44	24.69
Monsoon	SW1	1.29	1.44	-0.08	-0.07	0.97	44.58	-0.16	0.77	100.20	24.69
	SW2	3.57	3.45	0.13	0.13	1.12	45.02	-0.98	0.58	68.61	41.96
	SW3	5.01	5.29	0.00	0.00	1.30	35.76	-1.48	0.50	60.49	29.41
	SW4	1.47	1.54	0.03	0.07	2.09	67.68	-0.34	2.09	93.76	39.60
Post-monsoon	SW1	1.61	1.61	-0.01	0.00	1.05	44.29	-0.74	0.78	68.94	21.94
	SW2	3.45	2.99	0.03	0.02	1.45	46.35	-0.99	0.81	71.68	31.25
	SW3	5.05	5.07	0.02	0.01	1.05	30.95	-1.40	0.40	58.03	25.75
	SW4	0.97	1.11	0.03	0.08	1.17	53.57	-0.54	1.05	73.69	31.90
II) MIDLAND											
Pre-monsoon	SW5	0.65	0.68	-0.06	-0.02	0.34	26.07	-0.10	0.97	113.24	39.60
	SW6	0.67	0.65	-0.24	-0.11	0.38	38.27	0.01	0.69	133.98	24.69
	SW7	1.39	1.40	-0.10	-0.14	1.79	69.05	-0.04	0.90	74.54	25.00
	SW8	1.72	1.93	0.11	0.23	1.25	53.21	-0.82	0.82	55.03	33.58
	SW9	0.61	0.62	-0.03	-0.03	0.65	51.35	-0.18	0.79	110.55	-
	SW10	1.69	1.76	-0.52	-0.43	1.46	66.01	-0.36	0.69	72.99	32.97
Monsoon	SW5	0.98	0.93	0.34	0.19	0.39	25.10	-0.34	0.98	82.49	57.24
	SW6	0.54	0.59	-0.02	-0.02	0.68	49.05	-0.05	0.91	127.76	66.30
	SW7	1.42	1.51	0.08	0.17	1.52	60.52	-0.60	0.91	63.86	32.97
	SW8	2.45	2.41	0.01	0.01	1.93	62.49	-0.82	0.86	53.36	33.58
	SW9	0.73	0.77	-0.03	-0.05	1.01	60.75	-0.05	0.84	115.57	-
	SW10	1.14	1.22	-0.08	-0.24	1.58	75.46	-0.05	0.66	102.14	32.97
Post-monsoon	SW5	0.90	0.89	0.00	0.00	1.08	55.30	-0.10	0.97	100.23	24.69
	SW6	0.94	0.95	-0.06	-0.18	1.57	65.35	-0.36	0.93	78.28	24.69
	SW7	1.15	1.09	-0.03	-0.02	0.88	45.23	-0.09	0.97	92.32	32.97
	SW8	2.38	2.41	0.09	0.17	1.84	58.30	-0.92	0.93	51.01	30.23
	SW9	0.70	0.70	0.18	0.20	0.58	42.93	-0.23	0.87	99.14	49.59
	SW10	1.13	1.08	-0.03	-0.06	1.66	72.36	-0.14	0.82	95.36	32.97

Contd....

Physiography/ Season	Well code	TZ-	TZ+	CAI - I	CAI-II	SAR	% Na	RSC	KI	PI	MH
III) HIGHLAND											
Pre- monsoon	SW11	1.66	1.62	-0.04	-0.02	0.82	38.07	-0.56	0.94	78.63	30.23
	SW12	1.16	1.16	-0.13	-0.13	1.10	57.08	-0.42	0.83	79.58	39.60
	SW13	4.06	4.29	-0.45	-0.31	2.19	55.68	-0.65	0.89	80.55	-
	SW14	2.10	2.30	0.01	0.04	1.93	65.26	-0.72	0.81	74.45	74.95
	SW15	3.34	3.04	-0.76	-0.13	0.77	27.73	0.59	0.96	82.32	40.95
	SW16	0.57	0.57	0.14	0.17	0.62	47.26	-0.13	0.89	119.82	32.97
	SW17	3.74	3.76	-0.45	-0.26	1.74	52.08	-0.05	0.84	86.14	16.82
	SW18	2.88	2.62	-0.15	-0.16	2.20	65.60	-0.26	0.86	95.71	44.55
	SW19	1.31	1.39	-0.37	-0.18	0.45	42.36	-0.25	0.48	94.78	37.76
	SW20	3.15	3.22	-0.43	-0.22	1.25	50.35	-0.11	0.71	87.59	26.75
Monsoon	SW11	0.86	0.86	-0.36	-0.23	0.78	53.59	0.11	0.76	142.46	49.59
	SW12	1.04	0.87	0.02	0.01	0.87	53.86	0.12	0.83	140.40	75.20
	SW13	4.01	4.16	-0.10	-0.28	4.60	78.31	-0.78	0.95	86.07	44.55
	SW14	2.62	2.77	-0.04	-0.09	2.33	67.50	-0.82	0.84	75.06	44.55
	SW15	3.04	2.91	-0.70	-0.17	0.87	31.27	0.16	0.95	81.52	45.05
	SW16	0.70	0.68	0.20	0.45	0.90	55.96	-0.10	0.91	122.16	0.00
	SW17	3.43	3.38	-0.80	-0.33	1.75	52.58	0.79	0.88	98.23	18.92
	SW18	2.08	2.08	-0.26	-0.28	2.03	66.39	-0.30	0.87	96.53	14.08
	SW19	2.00	1.86	-0.31	-0.08	0.54	29.88	-0.19	0.78	85.76	23.27
	SW20	2.66	2.86	-0.53	-0.30	1.20	51.10	-0.43	0.68	82.70	42.79
Post-monsoon	SW11	0.77	0.78	-0.05	-0.04	0.73	48.65	-0.15	0.86	113.46	24.69
	SW12	1.50	1.57	-0.05	-0.11	2.09	68.28	-0.38	0.98	90.21	39.60
	SW13	2.87	2.36	0.09	0.19	2.58	70.39	-0.50	0.92	88.69	14.08
	SW14	2.44	2.24	0.21	0.48	1.46	50.67	-1.22	0.88	58.91	38.46
	SW15	3.83	3.76	-0.23	-0.04	0.60	20.05	-0.04	0.97	65.40	53.94
	SW16	0.95	0.93	0.19	0.25	0.79	46.53	-0.26	0.91	99.16	39.60
	SW17	3.75	3.65	-0.04	-0.03	1.70	47.96	-0.37	0.94	81.31	31.52
	SW18	2.23	2.36	-0.40	-0.46	2.58	70.39	-0.34	0.92	95.59	14.08
	SW19	1.04	1.02	-0.33	-0.20	0.87	51.28	-0.10	0.83	113.81	19.74
	SW20	2.55	2.66	-0.22	-0.08	0.69	30.28	-1.04	0.84	62.09	10.95

TZ^- - Total Anions, TZ^+ - Total Cations, CAI– Chloro Alkali Index, SAR – Sodium Adsorption Ratio, % Na – Percent Sodium, RSC – Residual Sodium Carbonate, KI –Kelly Index, , PI- Permeability Index, MH-Magnesiun Index (All concentrations expressed in meq/L)

5.6 Saturation indices (SI) of well water samples

The calculated SI values with respect to various mineral phases such as anhydrite ($CaSO_4$), aragonite (CaCO3), calcite (CaCO3), chalcedony (SiO2), dolomite ($CaMg(CO_3)_2$), fluorite (CaF_2), gypsum ($CaSO_42H_2O$), halite (NaCl) quartz (SiO_2), talc ($Mg_3Si_4O_{10}(OH)_2$), geothite (FeOOH) and hematite (Fe_2O_3) by PHREEQC software (Parkhust and Appolelo, 1999) of the well water samples in lowland regions with their respective water types is given in Table 5.13. The majority of lowland well water samples are having negative SI values which show undersaturation, with respect to all the above mentioned minerals except quartz, goethite and hematite. The samples SW1 and SW4 are supersaturated with respect to quartz in all seasons, whereas the samples in which iron is detected are supersaturated with goethite and hematite. In midland waters, the minerals having positive saturation indices are quartz, goethite and hematite (Table 5.14). The monsoon sample of SW7 and post-monsoon samples of SW7, SW8 and SW9 and in undersaturation with quartz i.e. further dissolution of mineral phase is possible. All the other samples during three seasons are supersaturated with respect to this mineral.

In the highland region, the calculated SI values with respect to various mineral phases as mentioned above are illustrated in Table 5.15. The well water samples of highlands are found to be supersaturated with respect to the minerals chalcedony, quartz, goethite and hematite with positive SI values. The phase controlling the mineral silica concentrations is quartz. Samples SW12 and SW13 in highland region are supersaturated with respect to chalcedony whereas all the other samples are in undersaturation during all the seasons. The saturation index values for the minerals goethite and hematite reflects that the samples in highland for which iron is detected are supersaturated with respect to these minerals, suggesting that these phases control Fe concentration in solution (Sracek *et al.,* 2010).

Table 5.13 Saturation Index (SI) of mineral phases worked out for the lowland well water samples.

Season	Well code	Water type	SI anhydrite	SI aragonite	SI calcite	SI dolomite	SI fluorite	SI gypsum	SI halite	SI calcedony	SI quartz	SI goethite	SI hematite
Pre-monsoon	SW1	Na-Ca-Mg-Cl-HCO_3	-	-2.12	-1.97	-4.18	-4.50	-	-8.24	0.09	0.53	8.15	18.29
	SW2	Ca-Na-Mg-HCO_3-SO_4-Cl	-2.58	-0.94	-0.79	-1.82	-3.42	-2.34	-7.74	-0.69	-0.25	8.16	18.30
	SW3	Ca-Na-HCO_3-Cl	-2.52	0.08	0.23	-0.27	-3.84	-2.28	-7.29	-0.70	-0.25	8.28	18.55
	SW4	Na-Ca-Cl	-3.48	-1.95	-1.80	-4.02	-4.96	-3.24	-7.78	-0.09	0.36	7.44	16.87
Monsoon	SW1	Na-Ca-HCO_3-Cl	-4.35	-1.29	-1.15	-2.71	-4.15	-4.11	-8.05	-0.03	0.42	-	-
	SW2	Ca-Na-Mg-Cl-HCO_3-SO_4	-2.65	-0.85	-0.70	-1.47	-3.83	-2.42	-7.35	-0.57	-0.12	-	-
	SW3	Ca-Na-HCO_3-Cl	-2.33	0.17	0.31	0.31	-	-2.10	-7.14	-0.40	0.05	-	-
	SW4	Na-Ca-Cl	-4.64	-2.29	-2.14	-4.40	-4.16	-4.40	-7.56	-0.02	0.47	-	-
Post-monsoon	SW1	Ca-Na-Cl-SO_4	-2.95	-2.35	-2.20	-4.88	-2.30	-2.71	-7.92	-0.69	-0.25	7.51	17.01
	SW2	Na-Ca-Cl-SO_4	-2.47	-2.03	-1.88	-4.03	-	-2.23	-7.36	-0.99	-0.55	6.26	14.50
	SW3	Ca-Na-HCO_3-Cl	-2.35	0.43	0.58	0.77	-	-2.12	-7.30	-0.46	-0.018	7.46	16.90
	SW4	Na-Ca-Cl	-4.49	-3.24	-3.10	-6.45	-	-4.25	-7.93	-0.19	0.25	7.46	16.90

Table 5.14 Saturation Index (SI) of mineral phases worked out for the midland well water samples.

Season	Well code	Water type	SI anhydrite	SI aragonite	SI calcite	SI dolomite	SI fluorite	SI gypsum	SI halite	SI calcedony	SI quartz	SI goethite	SI hematite
Pre-monsoon	SW5	Ca-Mg-Na-HCO_3-Cl	-4.83	-2.87	-2.73	-5.57	-3.66	-4.59	-9.13	-0.05	0.39	6.78	15.55
	SW6	Ca-Na-HCO_3-Cl	-	-2.06	-1.91	-4.24	-3.52	-	-9.05	-0.39	0.05	8.34	18.66
	SW7	Na-Ca-Cl	-4.03	-	-	-	-3.93	-3.80	-7.79	-0.32	0.12	-3.44	-4.90
	SW8	Na-Ca-Cl	-3.60	-3.80	-3.66	-7.54	-2.09	-3.36	-7.63	-0.11	0.34	5.37	12.72
	SW9	Ca-Na-Cl-HCO_3	-4.80	-3.18	-3.04	-	-4.25	-4.56	-8.70	-0.32	0.12	6.44	14.86
	SW10	Na-Ca-K-Cl	-3.54	-2.53	-2.39	-5.01	-4.34	-3.31	-7.83	-0.27	0.18	8.70	19.39
Monsoon	SW5	Mg-Ca-Na-HCO_3-Cl	-4.62	-2.62	-2.48	-4.76	-	-4.38	-8.71	-0.15	0.60	-	-
	SW6	Na-Mg-Cl-HCO_3	-5.06	-2.75	-2.60	-4.84	-4.73	-4.82	-8.73	-0.10	0.33	-	-
	SW7	Na-Ca-Cl	-	-	-	-	-4.08		-7.70	-0.56	0.12	-	-
	SW8	Na-Ca-Cl	-2.93	-2.73	-2.58	-5.38	-	-2.69	-7.32	-0.08	0.36	-	-
	SW9	Na-Ca-Cl-HCO_3	-4.59	-2.28	-2.13		-	-4.35	-8.35	-0.42	0.02	7.64	17.26
	SW10	Na-K-Cl-HCO_3	-4.49	-1.97	-1.82	-3.88	-4.01	-4.25	-7.89	-0.06	0.39	-	-
Post-monsoon	SW5	Na-Ca-Cl-HCO_3	-4.60	-2.81	-2.66	-5.73	-	-4.37	-8.23	-0.11	0.34	-	-
	SW6	Na-Ca-Cl	-	-3.28	-3.14	-6.69	-4.02	-	-7.91	-0.05	0.39	-	-
	SW7	Na-Ca-HCO_3-Cl	-3.73	-2.76	-2.61	-5.47	-	-3.49	-8.25	-0.69	-0.24	-	-
	SW8	Na-Ca-Cl	-	-3.54	-3.39	-7.08	-4.30	-	-7.31	-0.52	0.07	4.86	11.71
	SW9	Na-Ca-Mg-Cl-HCO_3	-4.99	-3.23	-3.08	-6.10	-3.39	-4.75	-8.62	-0.69	-0.25	5.95	13.89
	SW10	Na-Cl	-3.95	-2.26	-2.12	-4.47	-	-3.71	-7.92	-0.33	0.12	7.66	17.31

Table 5.15 Saturation Index (SI) of mineral phases worked out for the highland well water samples.

Season	Well code	Water type	SI anhydrite	SI aragonite	SI calcite	SI dolomite	SI fluorite	SI gypsum	SI halite	SI chalcedony	SI quartz	SI goethite	SI hematite
Pre-monsoon	SW11	Ca-Na-Cl-HCO_3-SO_4	-3.01	-1.81	-1.67	-3.63	-4.11	-2.78	-8.08	-0.23	0.42	8.50	18.98
	SW12	Na-Ca-Cl	-	-3.07	-2.93	-5.97	-5.22	-	-8.10	0.13	0.58	-	-
	SW13	Na-Ca-Cl-HCO_3	-2.46	-0.98	-0.83	-2.98	-2.98	-2.23	-7.09	0.27	0.72	7.40	16.78
	SW14	Na-Mg-Cl	-	-5.63	-5.49	-10.43	-3.32	-	-7.35	-0.17	0.28	-0.12	1.74
	SW15	Ca-Mg-Na-HCO_3	-3.53	-0.38	-0.24	-0.56	-2.70	-3.29	-8.04	-0.09	0.35	8.54	19.06
	SW16	Na-Ca-Cl-HCO_3	-	-2.93	-2.78	-5.80	-4.58	-	-8.73	-0.05	0.39	7.90	17.79
	SW17	Na-Ca-HCO_3-Cl	-2.75	-1.03	-0.88	-2.38	-3.68	-2.51	-7.28	0.03	0.50	7.59	17.17
	SW18	Na-Cl-HCO_3	-3.40	-1.91	-1.76	-3.54	-3.77	-3.16	-7.28	0.09	0.53	7.48	16.94
	SW19	Ca-K-Mg-Na-HCO_3-Cl	-3.43	-2.34	-2.19	-4.53	-3.04	-3.20	-8.52	0.17	0.62	6.61	15.21
	SW20	Ca-Na-HCO_3-Cl	-2.98	-1.34	-1.20	-2.76	-3.44	-2.74	-7.56	-0.21	0.23	7.50	16.98
Monsoon	SW11	Na-Ca-Mg-HCO_3-Cl	-4.78	-2.05	-1.90	-3.74	-4.09	-4.54	-8.53	-0.13	0.32	7.68	17.34
	SW12	Na-Mg-HCO_3-Cl	-4.79	-2.54	-2.39	-4.23	-4.15	-4.55	-8.33	0.11	0.55	-	-
	SW13	Na-Cl	-3.20	-3.36	-3.21	-6.45	-3.41	-2.96	-6.67	0.06	0.51	5.00	11.98
	SW14	Na-Cl	-3.19	-5.32	-5.18	-10.38	-3.64	-2.95	-7.17	-0.26	0.18	-	-
	SW15	Ca-Mg-Na- HCO_3	-4.19	0.22	0.37	0.73	-3.56	-3.95	-7.96	-0.13	0.31	-	-
	SW16	Na-Ca-Cl- HCO_3	-4.59	-2.77	-2.63		-3.65	-4.35	-8.38	-0.15	0.30	-4.35	15.44
	SW17	Na-Ca- HCO_3-Cl	-3.82	0.14	0.29	0.02	-3.48	-3.58	-7.44	-0.13	0.31	7.98	17.94
	SW18	Na-Ca-Cl- HCO_3	-3.33	-1.52	-1.37	-3.45	-3.76	-3.09	-7.50	-0.30	0.16	-	-
	SW19	Ca-Na- HCO_3-SO_4-Cl	-2.84	-0.57	-0.42	-1.30	-3.46	-2.61	-8.36	-0.46	0.03	-	-
	SW20	Na-Ca-Mg- HCO_3-Cl	-3.00	-1.14	-0.99	-2.04	-3.40	-2.76	-7.64	-0.35	0.09	-	-

Contd...

Season	Well code	Water type	SI anhydrite	SI aragonite	SI calcite	SI dolomite	SI fluorite	SI gypsum	SI halite	SI chalcedony	SI quartz	SI goethite	SI hematite
Post-monsoon	SW11	Na-Ca-Cl- HCO_3	-4.30	-2.08	-1.93	-4.29	-4.06	-8.53	-	-0.11	0.56	-	-
	SW12	Na-Ca-Cl	-4.12	-2.52	-2.38	-4.87	-3.05	-3.88	-7.58	0.06	0.32	7.90	17.78
	SW13	Na-Ca-Cl	-4.20	-4.00	-3.86	-8.43	-3.96	-7.17	-	0.23	0.18	-	-
	SW14	Na-Ca-Mg-Cl	-4.67	-5.05	-4.90	-9.93	-	-4.44	-7.32	-0.14	0.26	-0.37	1.24
	SW15	Mg-Ca- HCO_3	-3.30	0.34	0.49	1.12	-	-3.07	-7.98	-0.15	0.38	8.22	18.42
	SW16	Na-Ca-Mg-Cl- HCO_3	-4.31	-2.50	-2.35	-4.82	-3.03	-4.07	-8.28	-0.13	0.26		-
	SW17	Na-Ca-Cl- HCO_3	-2.79	-0.36	-0.21	-0.69	-2.95	-2.56	-7.19	-0.30	0.15	7.76	17.50
	SW18	Na-Ca-Cl	-3.42	-1.76	-1.61	-3.95	-2.17	-3.18	-7.36	-0.50	0.12		-
	SW19	Na-Ca-Cl- HCO_3	-3.89	-2.56	-2.42	-5.37	-	-3.65	-8.37	-0.40	0.13	-	-
	SW20	Ca-Na-SO4- HCO_3-Cl	-2.45	-1.16	-1.01	-2.87	-2.59	-2.21	-7.96	-0.36	0.26	8.83	19.64

5.7 Water - mineral equilibria

The thermodynamic stability diagrams for the behaviour of groundwater in the silicate systems are:

(a) $CaO–Al_2O_3–SiO_2–H_2O$

(b) $MgO–Al_2O_3–SiO_2–H_2O$

(c) $Na_2O–Al_2O_3–SiO_2–H_2O$ and

(d) $K_2O –Al_2O_3–SiO_2–H_2O$.

The thermodynamic stability diagrams (at 25^0C) are plotted for lowland, midland and highland regions (and are given in Figures 5.7, 5.8 & 5.9). These figures depict that all the sample points fall in the range of the stability field of kaolinite. This implies that the chemistry of water is favoring kaolinzation and subsequent leaching of mobile elements as in the case of spring samples discussed in Chapter 4. Stability in the kaolinite field suggests that infiltrating water that is enriched in soil CO_2 reacts with silicate minerals contained in the host rock, particularly in plagioclase feldspar, and breakdown to soluble elements like alkali (Na, K) and alkaline earth (Ca, Mg) elements and insoluble kalonite left *in situ* in the weathering front. Although there is a minor deviation in the phase of kalonisation as indicated in the spread of the plots, all the sample points are in the kaolinite field.

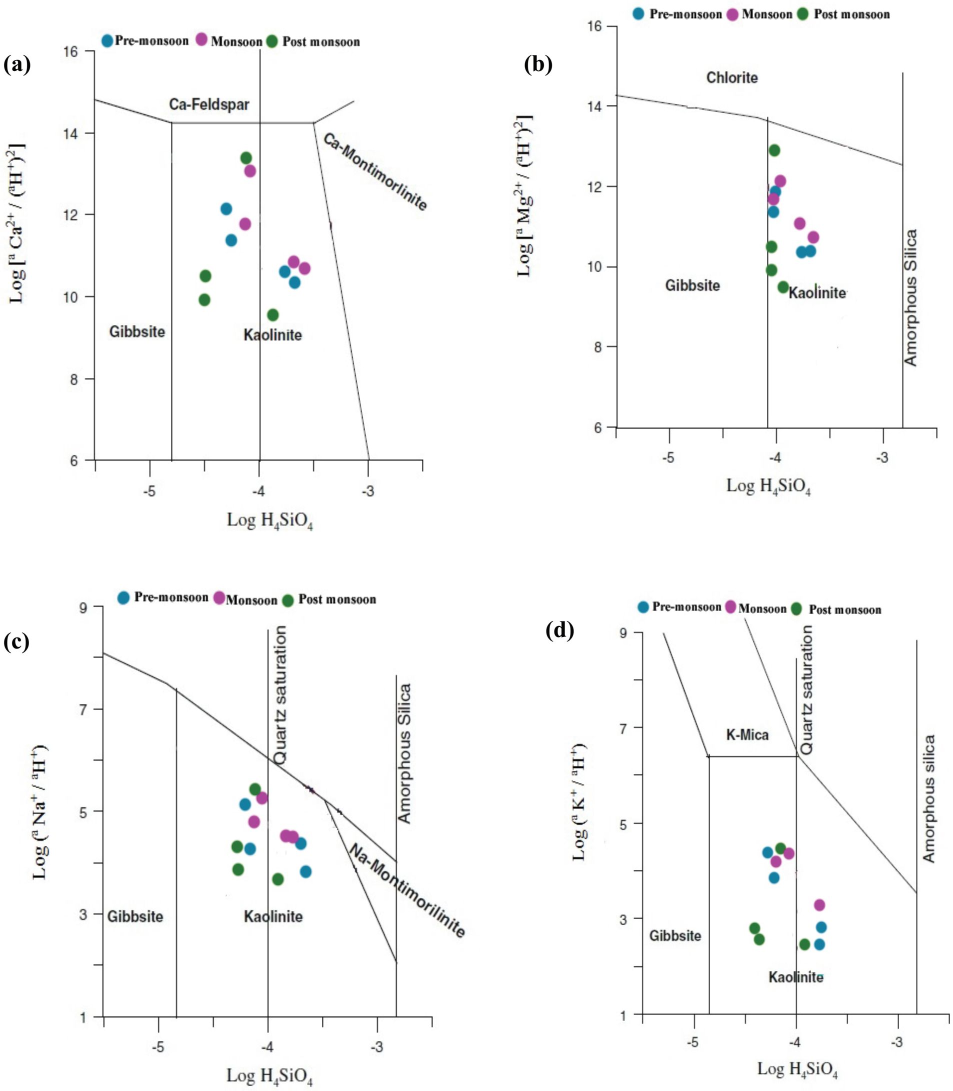


Fig. 5.7 Mineral stability diagrams for lowland well water samples.

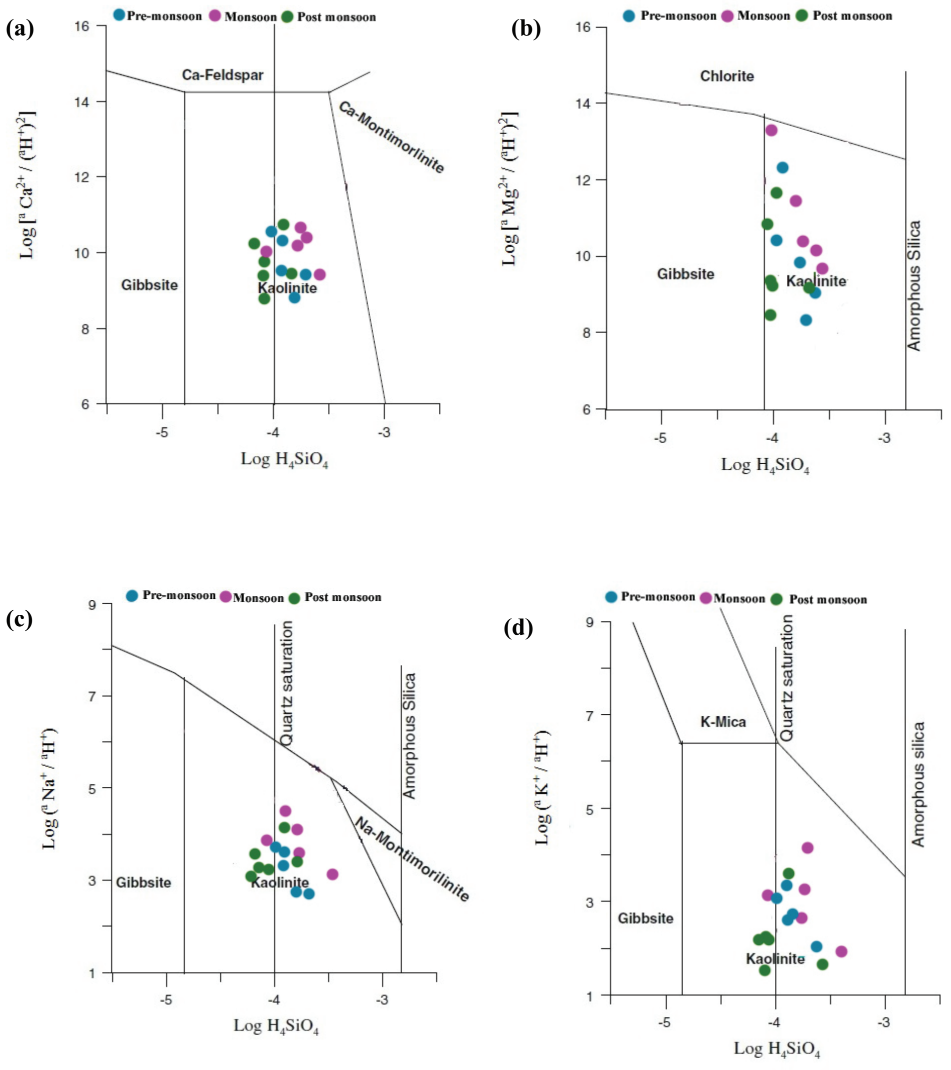


Fig. 5.8 Mineral stability diagrams for midland well water samples.

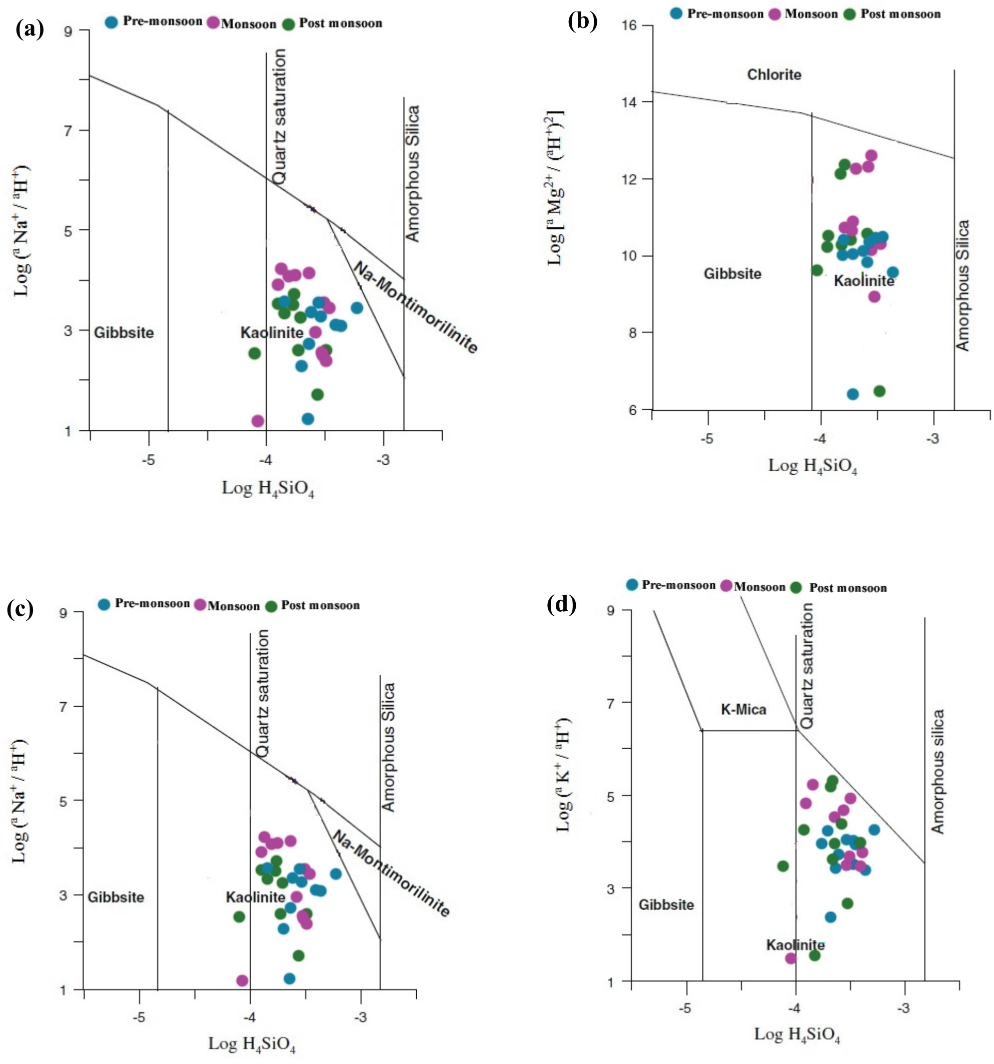


Fig. 5.9 Mineral stability diagrams for highland well water samples.

Chapter - 6

ASSESSMENT OF WATER QUALITY AND GROUNDWATER POTENTIAL

6.1 Introduction

Groundwater quality assessment for drinking and irrigation has become a necessity for present and future groundwater quality management programmes. A number of studies have addressed the groundwater quality monitoring and evaluation for domestic and agricultural activities around the world (Mitra *et al.,* 2007; Hakim *et al.,* 2009; Nagarajan *et al.,* 2010; Alam *et al.,* 2012; Rao *et al.,* 2012; Shi *et al.,* 2013; Alaya *et al.,* 2014; Annapoorna and Janardhana, 2015; Hema *et al.,* 2015; Shanmughasundaram *et al.,* 2015; Golchin *et al.,* 2016; Kumar *et al.,* 2016). However systematic studies in this angle in the small catchment river basins in the south-western side of Western Ghats are scarce. Therefore an attempt has been made to assess the groundwater quality (drinking water suitability and irrigation water quality) and potential of spring and well water sources of the Ithikkara and Kallada river basins in the southern Western Ghats.

6.2 Assessment of spring water quality

The hydrochemical characteristics of spring water sources of Ithikkara and Kallada river basins have already been discussed in Chapter 4. This section deals with water quality assessment (drinking and irrigation water quality) of the spring water sources of the Ithikkara and Kallada river basins.

6.2.1 Drinking water suitability

The cold water springs in the Ithikkara and Kallada river basins have high water resource potential. Because of the peculiar rainfall pattern and climatic conditions of the region, people use some of these springs for meeting their domestic water requirements. As the water requirements of the area are steadily increasing over the years due to increase in population, there is an imminent need for finding additional sources of potable water in the area. The present study in the Ithikkara and Kallada river basins discloses that springs can offer a viable source of fresh water. With the exception of pH and bacteriological contents, all the other water quality parameters satisfy the quality standards set by WHO (2011) and BIS (2012) for drinking water (Refer Table 4.3). A comparative evaluation of the chemical quality of spring waters of the study area with other reported springs in India (Refer Table 4.14) shows that the water quality of the studied springs is far better. Fluoride is present in most of the samples in pre-monsoon and a few samples in monsoon and post-monsoon seasons, but the values are well within desirable limits. Fluoride in the study area originates mainly from weathering of fluoride bearing minerals like flourapatite [$Ca_5(PO_4)_3(F,OH,Cl)$] and biotite [$K(Mg_2Fe)(AlSi_3)O_{10}(OH,F)_2$] that are present in accessory amounts in the khondalite suite of rocks and associated pegmatite intrusives that forms the major host rock in the spring catchments (Rajesh and Santosh, 1996).

Nitrate and chloride ions in the lowland exhibit a good positive correlation indicating anthropogenic sources. The overuse of nitrogenous fertilizers in agricultural areas, leakage of sewerage canals and septic tanks in the nearby urban agglomerations, application of livestock manure in agricultural lands, etc., are some of the sources of NO_3^- and Cl^- in underground waters (Reddy *et al.,* 2011), which is later transformed into spring waters. As per the classification of CPCB (2008), most of the spring water samples of the present study fall within the category ‘C’ i.e., drinking water that require conventional treatment and disinfection.

Water Quality Index: The quality of the spring water samples is determined using Water Quality Index (WQI) method (Singh *et al.,* 2015; Boateng *et al.,* 2016; Krishnan *et al.,* 2016). The relative weight assigned to the hydro chemical quality parameters based on their relative importance for drinking purpose is given in Table 6.1. The water quality indexing is performed for all the three seasons (Table 6.2). During pre-monsoon, 90% of the samples fall in 'Excellent' category as per the water quality classification based on WQI. One sample each falls in the category, 'Good' (SP15) and 'Poor' (SP7) during pre-monsoon season. In monsoon, 90% of samples are in the category 'Excellent' and the rest belongs to category, 'Good'. During post-monsoon season, about 78% of samples are 'Excellent' and hence suitable for drinking purpose and 12 % falls in the category 'Good'.

Table 6.1 Relative weight of physico-chemical parameters based on their importance on water quality for drinking purposes (after Gebrehiwot *et al*., 2011).

Chemical parameters	BIS (2012)	WHO 2011	Weight (wi)	Relative Weight $Wi = wi / \sum_{i=1}^{n} wi$
pH	6.5 - 8.5	8.5	4	0.2
EC (µS/cm)	500	500	4	0.2
TDS (mg/L)	500	500	5	0.2
Na^+ (mg/L)	-	200	2	0.1
K^+ (mg/L)	-	12	2	0.1
TH (mg/L)	200 - 600	-	3	0.15
Ca^{2+} (mg/L)	75-200	75	2	0.15
Mg^{2+} (mg/L)	30 - 100	50	2	0.1
HCO_3^- (mg/L)	-	500	3	0.15
Cl^- (mg/L)	250 - 1000	250	3	0.15
SO_4^{2-} (mg/L)	200 - 400	250	4	0.2
NO_3^-N (mg/L)	45	45	5	0.25
Fe^{2+} (mg/L)	0.3	0.3	4	0.2
F^- (mg/L)	1	1	4	0.2

Table 6.2 Water quality index (WQI) worked out for spring water samples collected during pre-monsoon, monsoon and post-monsoon seasons.

Spring code	WQI Pre-monsoon	Classification type	WQI Monsoon	Classification type	WQI Post-monsoon	Classification type
SP1	32.41	Excellent	18.97	Excellent	22.28	Excellent
SP2	33.32	Excellent	23.62	Excellent	25.64	Excellent
SP3	33.98	Excellent	26.19	Excellent	33.80	Excellent
SP4	33.70	Excellent	25.08	Excellent	37.07	Excellent
SP5	31.31	Excellent	26.25	Excellent	28.71	Excellent
SP6	40.68	Excellent	21.89	Excellent	30.70	Excellent
SP7	158.92	Poor	87.86	Good	85.03	Good
SP8	29.42	Excellent	21.94	Excellent	27.11	Excellent
SP9	26.93	Excellent	43.46	Excellent	22.72	Excellent
SP10	36.25	Excellent	28.26	Excellent	48.01	Excellent
SP11	41.21	Excellent	43.05	Excellent	42.84	Excellent
SP12	27.73	Excellent	35.22	Excellent	54.04	Good
SP13	34.81	Excellent	43.61	Excellent	45.34	Excellent
SP14	30.89	Excellent	25.83	Excellent	31.32	Excellent
SP15	63.99	Good	60.94	Good	31.85	Excellent
SP16	45.82	Excellent	33.47	Excellent	34.14	Excellent
SP17	40.85	Excellent	21.80	Excellent	30.32	Excellent
SP18	33.52	Excellent	42.42	Excellent	51.53	Good
SP19	36.84	Excellent	25.24	Excellent	30.26	Excellent

< 50 : Excellent water, 50 – 100 : Good water, 100 – 200 : Poor water, 200-300 : Very poor water, > 300 : Unsuitable for drinking

6.2.2 Irrigation water suitability

In irrigation suitability assessment, many conventional tests are applied. The Residual Sodium Carbonate (RSC) measurement is one among such tests to evaluate the effect of carbonate or bicarbonate suitability for irrigation. RSC can be calculated using the formula,

$$RSC = (CO_3^{2-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+}).$$

The estimated RSC values of the spring water samples of the Ithikkara and Kallada river basins are less than 0.5 meq/L indicating that the spring water in the study area is safe for irrigation, as well (Eaton, 1950).

Total salt concentration, Sodium Absorption Ratio (SAR), and Sodium Percentage (%Na) are also used to assess the quality of water for irrigation uses (Refer: Tables 4.9 and 4.10, Chapter IV). The sodium or alkali hazard expressed in terms of SAR is estimated using the formula, (Chow, 1964):

$SAR = Na/\sqrt{(Ca + Mg)/2}$; where all concentrations are in meq/L

The SAR computed for the spring waters of the Ithikkara and Kallada river basins ranges between 0.8 and 2.3 in lowland samples and 0.35 and 1.04 in highland samples. About 90% of the samples are good for irrigation purpose as it won't create any salinity hazard to the crops. As per the US salinity diagram (Richards, 1954), the water samples from all the three seasons clusters within the field C1S1 (Figs. 6.1 & 6.2), indicating low salinity - low sodium water. The %Na is calculated using the formula of Wilcox (1955)

$$\% Na = \{(Na^{+} + K^{+}) / (Ca^{2+} + Mg^{2+} + K^{+} + Na^{+})\} \times 100$$

(where all ionic concentrations are expressed in meq/L).

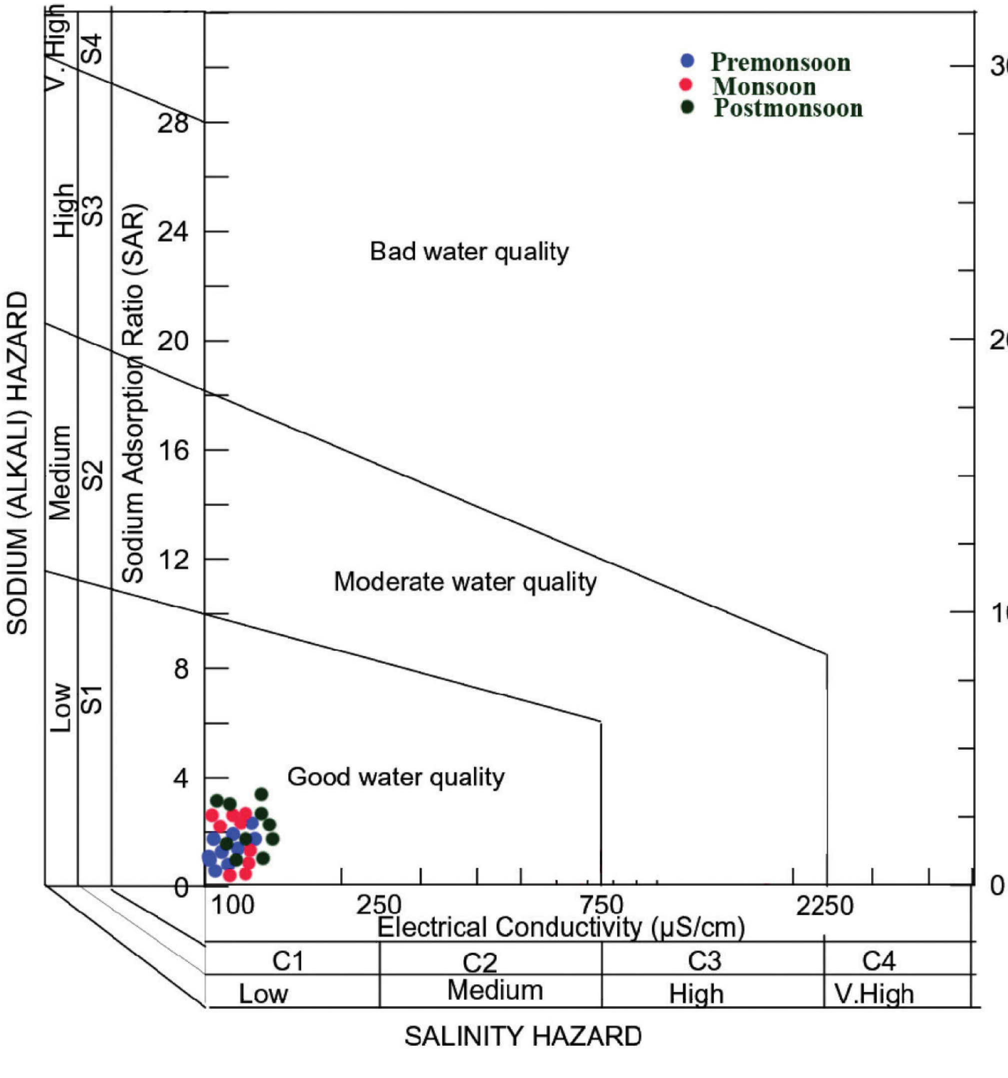


Fig. 6.1 Irrigation water quality of lowland springs (Richards, 1954).

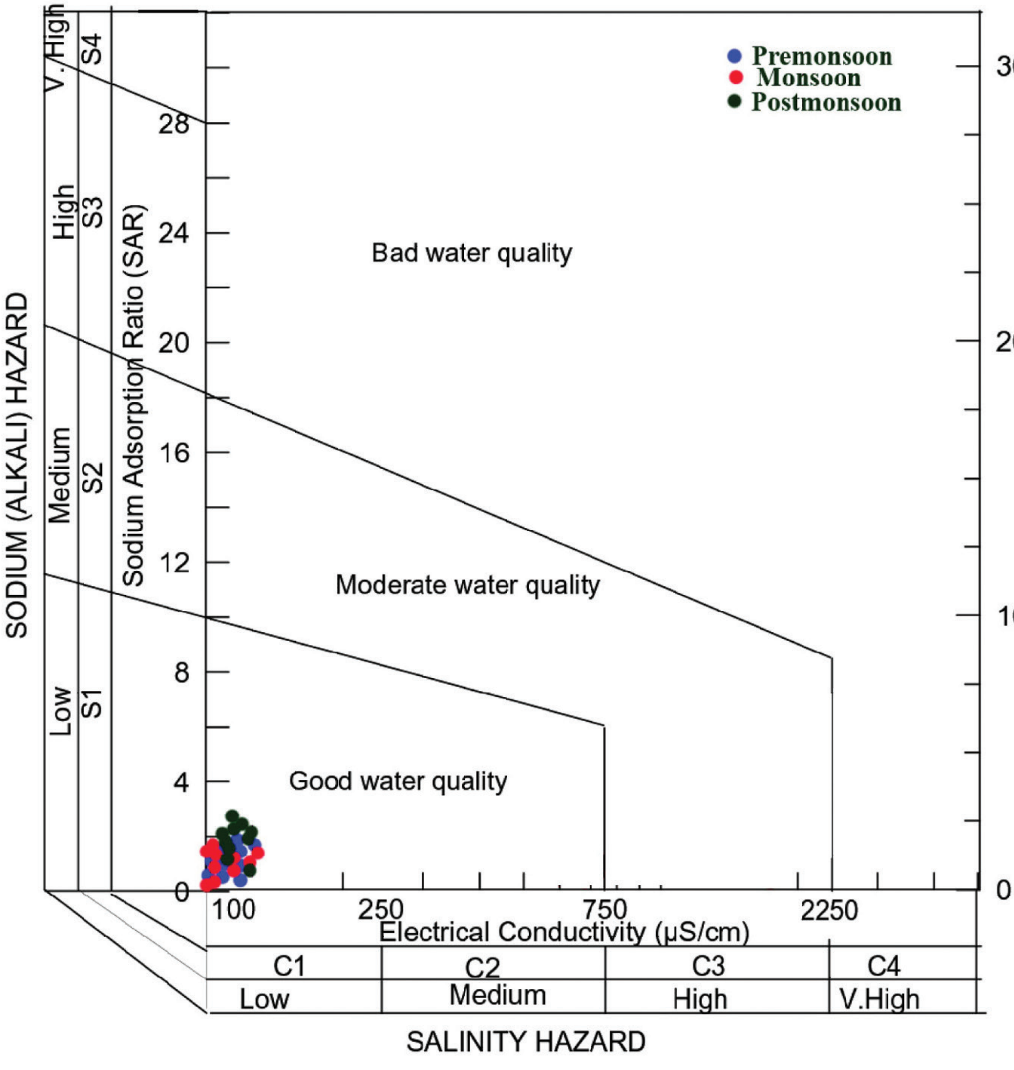


Fig. 6.2 Irrigation water quality of highland springs (Richards, 1954).

Plots of analytical data on the Wilcox (1955) diagram show that the spring water samples of the highland and lowland regions of Ithikkara and Kallada river basins fall in 'Excellent' to 'Good' category (Figs. 6.3 & 6.4) Therefore, the spring waters of the study area can be used for irrigation in almost all type of soils with little danger of exchangeable sodium and/or salinity.

6.3 Assessment of well water quality

The groundwater quality of aquifers is generally area specific and time variant. The composition of different litho-units, permeability of soils, intensity and the kind of weathering etc., are some of the natural factors determining the fate and dispersal of hydrochemical signals (especially cations and anions) in well water samples. The quality of well water is the outcome of many natural and man-made processes. In addition to this, agricultural practices, drainage characteristics and irrigation also have a decisive role in influencing the hydrochemical makeup of well waters. In the present study, the well water samples of the study area are evaluated for its drinking and irrigation suitabilities based on the quality and quantity of hydrochemical components in well waters.

6.3.1 Drinking water suitability

Table 6.3 shows a comparative evaluation of the averages and ranges of physico-chemical parameters of the present study with that of the reported results from the adjoining areas. An overall evaluation shows that about 75% of the samples of pre-monsoon, 90% of monsoon and 85% of post-monsoon seasons fall within the limit of drinking water standard suggested by WHO (2011) and BIS (2012); (Refer: Table 5.3, Chapter V). The pH, strength of the water to react with acidic or alkaline materials in water, is controlled mainly by carbon dioxide, carbonate and bicarbonate equilibrium (Hem, 1985). The midland and highland areas show acidic to alkaline water, whereas

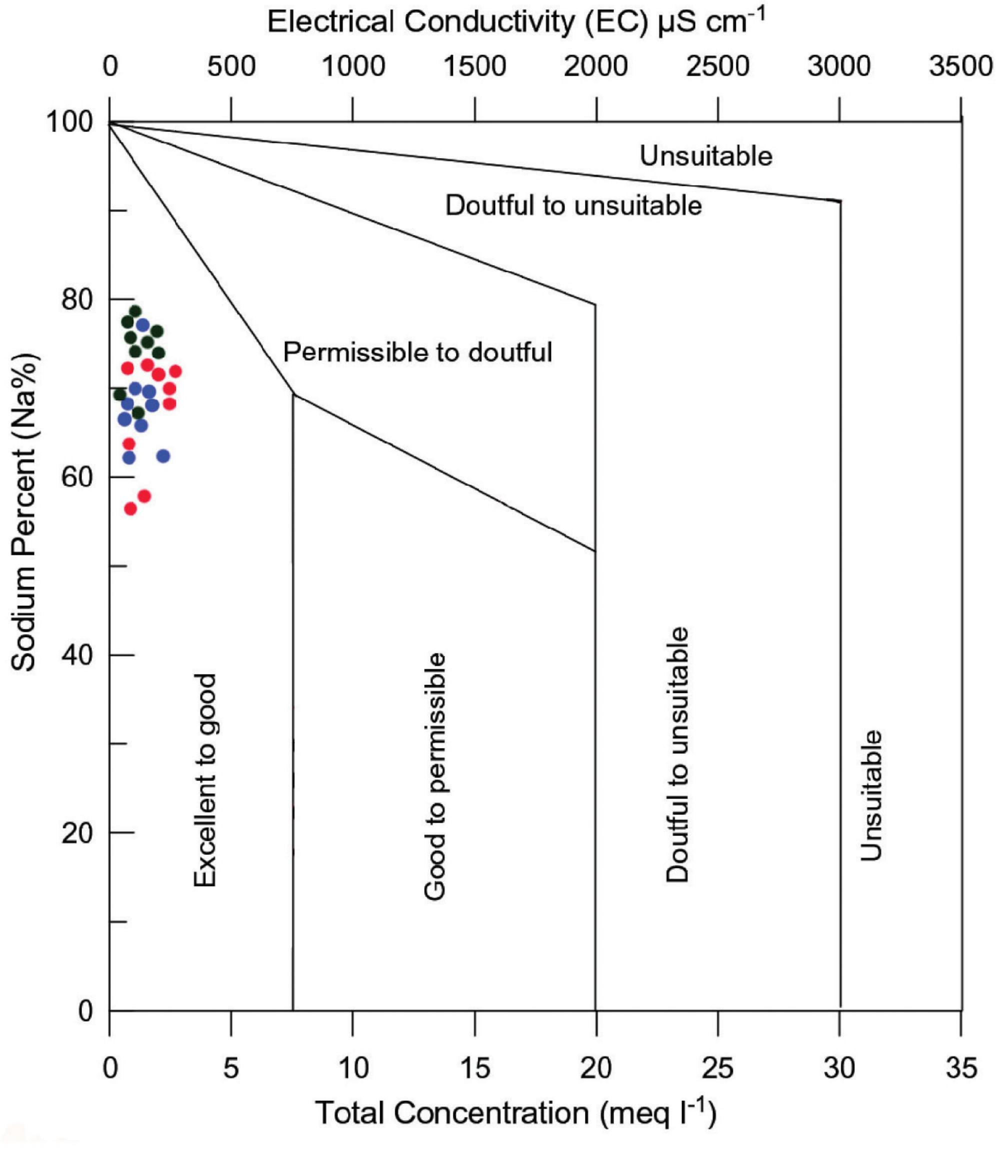


Fig. 6.3 Quality of lowland springs as per Wilcox (1955) classification. Samples codes are similar to that of Fig. 6.1.

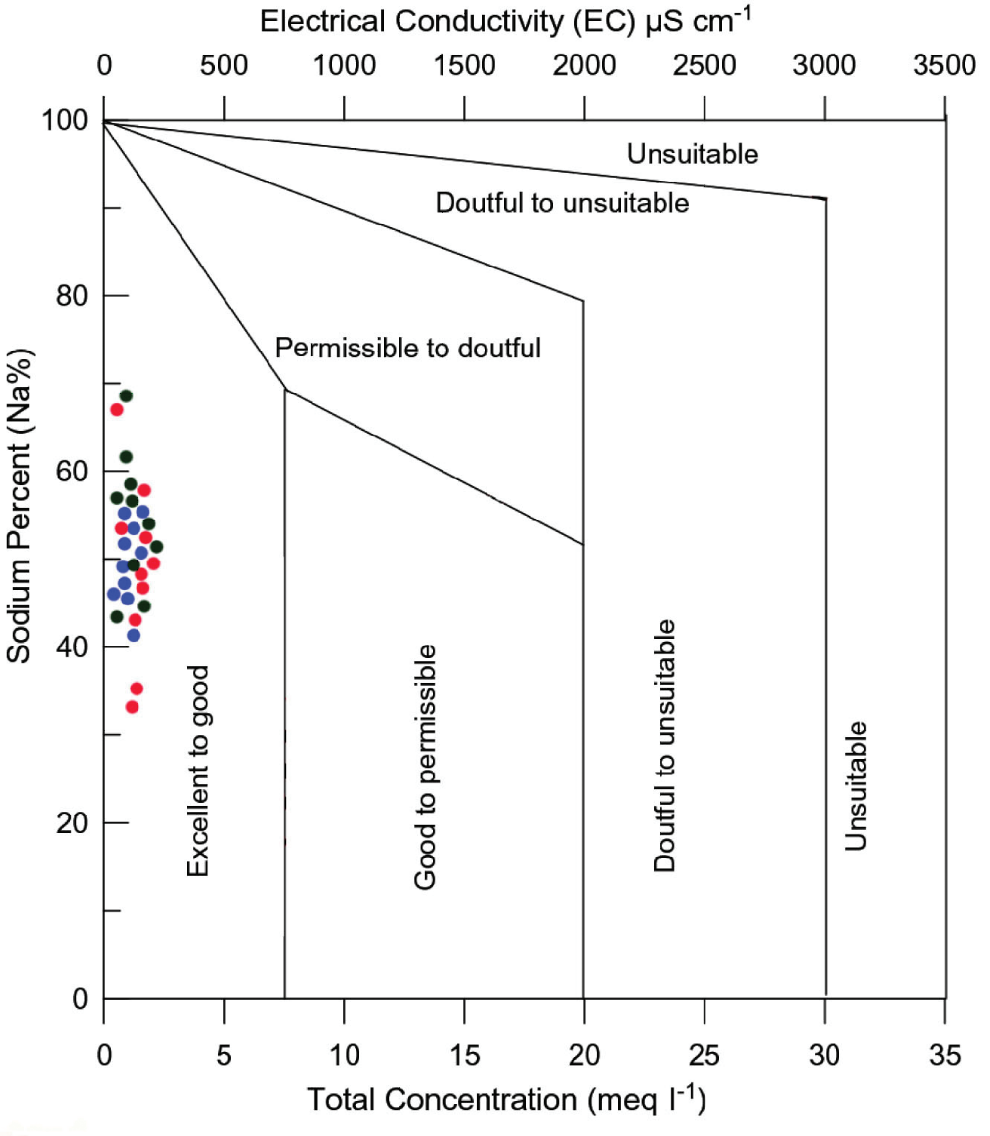


Fig. 6.4 Quality of highland springs of the study area as per Wilcox (1955). Sample codes are similar to that of Fig. 6.3.

Table 6.3 Comparison of the hydro-chemical parameters in the well water samples of the study area with other published works.

Parameters	Present Study Area Ithikkara &Kallada River Basin	Spring waters Ithikkara & Kallada River Basin (Hema *et al*., 2015)	Kallada River Basin(GW samples), South Kerala, India (Harikumar and Kokkal, 2013)	Coastal Phreatic Aquifers of Alleppey District, Kerala (Shaji *et al*., 2009)	Coastal stretch of Alappuzha District, Kerala, India (GW samples) (Prasanth *et al*; 2012)	Meenachil River Basin, Kerala (GW samples) (Vincy *et al*; 2015)	Neyyar River Basin,Kerala (GW samples) (Maya *et al*;2013)	Vamanapuram River Basin, South Kerala, India (GW samples) (Veena and Binoj Kumar, 2013)
pH	3.6-8.4	3.6–7.2	4.64–8.38	6.17–9.27	5.2–6.8	5.46–7.02	4.92-6.46	4.5-7.8
EC(µS/cm)	55-510	17-121	45.60–972.96	88-1519	64-2200	81.95-504	42.06-296.3	31.6-4600
TDS (mg/L)	33-319	19-73	37.63-690.80	56-972	94-1898	24.65–499.98	30.04-211.64	16.7-3800
Na (mg/L)	4-49	3.6–18.4	2.43-210	3.60-154	1.8–272.5	2.50–23.50	2.7-18.8	1-3600
K (mg/L)	BDL-17	0.2–4.1	0.20-161	0.80-58	0.4–11.2	1.10–8.70	0.3-5.5	1-800
TH (mg/L)	10-175	5-25	4-400	-	70-544	9.45–66.70	8-88	-
Ca (mg/L)	2-52	0.8-6	1.6-80	3.20–152.30	17.6-1147	5.3–56.7	1.6-27.25	2.01-218.3
Mg (mg/L)	BDL-20	0–4.9	0–48.6	0.50-24	1.5–106.4	2.91–25.11	0.48-13.12	1.2-127.6
TA (mg/L)	BDL-124	-	4.15–124.50	-	-	22.25–156.4	4-86	-
HCO_3 (mg/L)	BDL-183	0-36.6	-	1.04-207	60-490	30.40–93.10	-	10–165
Cl (mg/L)	6-105	4.8–28.8	8.02–284.40	8.50–468.60	12-540	17.02–36.16	0.29-1.33	7.1-1700
SO_4 (mg/L)	BDL-54	0.51–4.2	0.24–38.80	0.60–275.50	0–0.76	BDL–74.14	1.49-47.65	0-50
NO_3-N (mg/L)	BDL–6.9	0–4.02	0.02–1.960	0.70–304.2	-	0.44–3.68	144.68-1381.61	0-5.12
Fe (mg/L)	BDL-8.6	0–1.9	-	-	-	-	-	-
F (mg/L)	BDL-0.24	0.01-1	-	0.02–0.28	-	-	-	-

BDL: Below Detection Limit

the pH values in lowland are within the limits of BIS (2012). Samples SW7, SW8 of midland, post-monsoon sample of SW13 and SW14 have low pH values and are below the acceptable limit as the samples are acidic. In the case of electrical conductivity, it is observed that the samples have wide seasonal as well as spatial variation. EC exhibits an increasing trend during monsoon season. Conductivity increases with increasing concentrations of salts, acids and bases where these concentrations also depend on factors such as rainfall and size of catchment area. Larger catchments yield higher conductivity values due to increase in evapotranspiration as well as longer contact of runoff with rock and soil (Walling, 1980; Kalff, 2002). Almost all analyzed parameters in the samples of the region with the exception of pH and Fe^{2+} in a few samples are found to be within the permissible limit of drinking water quality standards. About 80% of the pre-monsoon samples contain iron above the acceptable limit. This may be due to the higher residence time of well water which gives more time to dissolve Fe^{2+} from the host rocks. However, monsoon showers have significant effect in controlling the iron contents in well water samples. During monsoon, the content of Fe^{2+} is found to be below 0.3 mg/L in all samples. About 15% of post-monsoon season samples record Fe^{2+} value above the prescribed limit of WHO (2011) and BIS (2012). The main dissolved iron species in natural waters is the ferrous ion. Fe^{2+} on in normal groundwater is mostly in the form of inorganic complexes derived from laterites and other type of ferruginous soils (Rajmohan and Elango, 2004). In a typical aquifer, the upper part in contact with the atmosphere will have oxidized iron minerals in equilibrium with high Eh (Redox potential, Eh= 0.30 - 0.074 pH) of water. On the other hand, in deeper layers, particularly in presence of organic matter, Fe may occur in reduced forms like pyrites under low Eh conditions. A pumping well under such condition can cause mixing of waters of different Eh values and impose oxidizing conditions at deeper levels due to the cone of dewatering. Hem (1967) pointed out that this process is a major factor for precipitation of Fe $(OH)_3$ along with $CaCO_3$ as encrustation on tube well pipes.

Compared to alkaline earths, the concentration of alkali metals, especially sodium is high in many of the samples subjected to the present study. This is due to the geological influence of sodium and potassium feldspar rich minerals in the host rock of the study area. Among the lowland samples, 50% of the samples fall in the soft (0-75 as $CaCO_3$ mg/L), and the rest in moderately hard to hard category (75 – 150 as $CaCO_3$ mg/L, 150 – 300 mg/L) categories (Sawyer and McCarthy, 1967). The samples of the midland region have substantially low calcium and magnesium than the rest of the area. In the case of samples of the midland area, water remains soft during all the seasons where the values vary between 15 - 50 (as $CaCO_3$) mg/L. About 60% of pre-monsoon, 80% of monsoon and 70% of post-monsoon samples of the upland renders soft water and the rest of the samples fall in moderately hard category.

The chloride ion concentration is higher in lowland and highland samples compared to that of midland. Monsoon and post-monsoon samples have higher concentration of chloride than pre-monsoon samples. Among lowland water samples in study area, sample SW3 has the highest chloride concentration during all three seasons. This may be due to sea water intrusion in the area. Midland sample SW8 and highland sample SW13 also showed substantially high values of chloride, presumably due to seepage of polluted water from the nearby urban centers (Yamamoto *et al.,* 2014).

The sulphate concentrations in midland and highland were lower in post-monsoon than in pre-monsoon and monsoon, which indicate higher enrichment in pre-monsoon and monsoon than post-monsoon due to breakdown of organic material and agricultural runoff carrying unutilized sulphate (Anderson, 1979). As per Madison and

Brunett (1985), nitrate concentration greater than 3 mg/L indicates contamination of water sources. A recent study by Dubrovsky *et al.* (2010) revealed that concentrations over 1 mg/L nitrate indicate human activity. In the study area, the well water samples show varying concentration of nitrate nitrogen. Bacteriological contamination in well water samples can enhance nitrate-nitrogen content. Fluoride concentration is considerably low in the water samples of the study area as fluoride bearing minerals are meagre in host rocks. But certain minerals like hornblende, biotite etc., of the granulite rocks of the study area contains marginal amounts of fluoride in mineral lattices which upon chemical weathering can impart traces of fluoride in the well water sources (Hema *et al.,* 2015).

An overall evaluation of the bacteriological analysis between lowland, midland and highland reveals that 70% of the samples during the pre-monsoon show incidence of bacterial contamination- both by total coliform and faecal coliform. Almost all the samples collected from highland and midland confirm the presence of total coliform and faecal coliform bacteria during monsoon and post-monsoon seasons. Studies show that in Kerala 70% of open wells are contaminated with bacteria (Harikumar and Madhava, 2013). In the study area, domestic wells which are disinfected occasionally using bleaching powder registers either nil or reduction in bacterial count. Indeed the impact of the on-site sanitation system has a pronounced effect on shallow unconfined aquifers in lateritic and hard rock areas as compared to the confined aquifer. The situation is same for both chemical and bacteriological contaminant estimated in the well water samples of the study area.

There are a number of conventional methods used in Kerala to purify water in domestic wells. Plants like Brahmi, Lagenandra (Kinar vazha) and fishes like Carp, Channa, Tilapia etc., were used to purify and treat water. The seeds of *Strychnos* *potatorum* also known as Clearing-Nut Tree were commonly used for purifying water in India. The studies revealed that it can remove all dissolved constituents from water and destroy bacteria like *E.coli* and Faecal streptococci from water (Ushakumari, 2008). Hardness of water can also be reduced using this nut. The results of the experiments conducted on conventional water treatment methods using Panchamukhi Rudraksham showed that pH was neutralised irrespective of the nature of water taken (acidic or alkaline). The conductivity, hardness, alkalinity and chloride values were found to be reduced and there was reduction in MPN index, *E.coli* and Faecal streptococci within a one hour period (Ushakumari, 2008).

One of the widely used tools for water quality assessment is determination of Water Quality Index (WQI). The relative weight assigned to the hydrochemical quality parameters based on their relative importance for drinking purpose is same as the case of spring samples. Water quality index is prepared for all the three seasons (Table 6.4). During pre-monsoon, 20% of the samples fall in excellent category as per WQI estimation. About 50% samples fall in good quality water category, 15% in poor category and 10% in very poor category. The very high value of WQI for sample SW10 reveal its unsuitability for domestic purpose. During monsoon, 55% of samples are in excellent category and the rest 45% belongs to good category. During post-monsoon season, 45% of samples are excellent for drinking purposes and another 45% samples falls in good category. Two samples (SW4 in lowland and SW20 in highland) exhibit very poor water quality. The spatial distribution of water quality indices for all the three seasons is given in Fig. 6.5.

Table 6.4 Water Quality Index (WQI) of well water samples and their categories/type.

Well Code	WQI Pre-monsoon	Categories/ Type	WQI Monsoon	Categories/ Type	WQI Post-monsoon	Categories/ Type
SW1	65.71	Good	35.85	Excellent	68.45	Good
SW2	87.13	Good	77.01	Good	75.36	Good
SW3	99.96	Good	92.57	Good	94.9	Good
SW4	49.47	Excellent	37.34	Excellent	251	Very poor
SW5	206.66	Very Poor	30.13	Excellent	27.27	Excellent
SW6	81.79	Good	26.73	Excellent	32.36	Excellent
SW7	37.64	Excellent	31.96	Excellent	29.1	Excellent
SW8	281.5	Very Poor	51.84	Good	66.53	Good
SW9	47.25	Excellent	37.79	Excellent	37.07	Excellent
SW10	622.34	Unsuitable	41.63	Excellent	40.05	Excellent
SW11	160.28	Poor	40.37	Excellent	29.12	Excellent
SW12	36.12	Excellent	32.46	Excellent	56.1	Good
SW13	90.34	Good	77.57	Good	49.36	Excellent
SW14	74.77	Good	53.96	Good	60.05	Good
SW15	99.84	Good	58.32	Good	83.87	Good
SW16	108.55	Poor	38.28	Excellent	34.64	Excellent
SW17	99.97	Good	75.21	Good	75.71	Good
SW18	78.05	Good	50.45	Good	60.4	Good
SW19	80.01	Good	48.97	Excellent	31.62	Excellent
SW20	111.16	Poor	68.92	Good	236.42	Very poor

< 50 : Excellent water, 50 – 100 : Good water, 100 – 200 : Poor water, 200-300 : Very poor water, > 300 : unsuitable for drinking

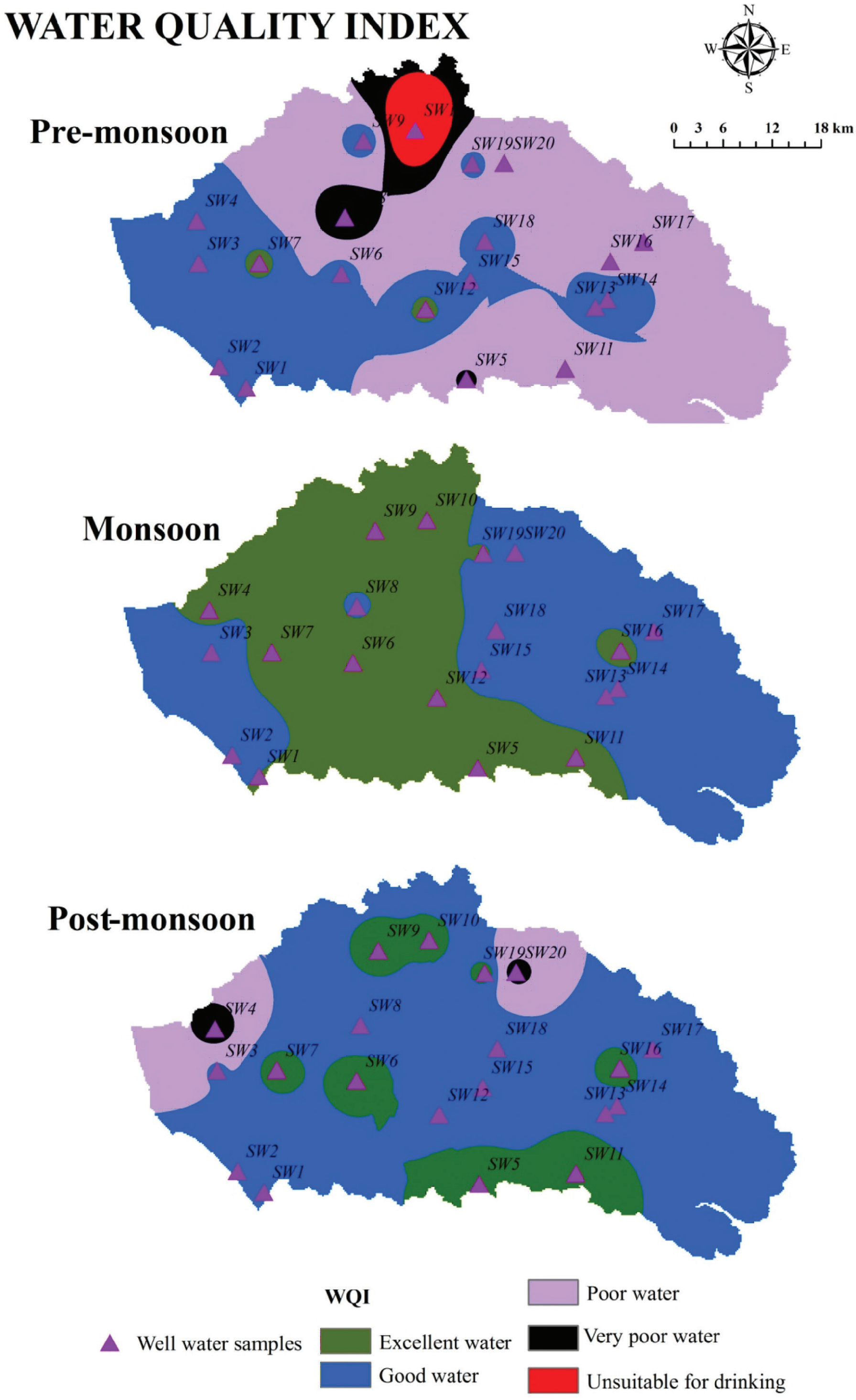


Fig. 6.5 Spatial distribution of Water Quality Indices worked out for the well water samples of the study area.

6.3.2 Irrigation suitability

Well water carries chemical constituents dissolved from natural and anthropogenic sources. The nature and concentration of these constituents determine the quality of water (Wilcox, 1955). As water quality is one of the essential determinants of the kind of cropping practices, its estimation and suitability assessments are of paramount importance in planning sustainable agricultural practices in a given region (Singh *et al.,* 2013). The different methods like Total Salt Concentration (EC), Sodium Adsorption Ratio (SAR), Sodium percentage (Na%), Residual Sodium Carbonate (RSC), Kelly Index (KI), Permeability Index (PI) and Magnesium Hazard (MH) are the commonly used parameters for assessing irrigation suitability of water (Ayers and Westcot, 1994). Therefore, all these parameters are estimated in this investigation to assess irrigation suitability of the study area (Refer Table 5.7, Chapter 5). The results of these analyses are tabulated (Table 6.5) for their better evaluation of irrigation suitability of well waters of the Ithikkara and Kallada river basins.

The high salt content in water could result in gradual accumulation of salts in the root zone of plants which in turn imparts salinity hazard and toxicity to plants (Jalali, 2011). U.S. salinity diagram used for testing irrigation suitability considers two important parameters such as EC and SAR (Richards, 1954) for evaluation. In this diagram, the irrigation water is classified as low (EC< 250 µS/cm), medium (250- 750 µS/cm), high (750- 2250 µS/cm) and very high (2250- 5000 µS/cm) salinity classes. Sodium Adsorption Ratio (SAR), also expressed as Alkali Hazard, is another important tool to examine irrigation water of a region. Osmotic activity of plants gets reduced by high salinity and prevents water reaching the leaves and branches of plants (Deepali *et al.,* 2010). Moreover, if water used for irrigation is high in sodium and low in calcium, the cation exchange become affected as it is saturated with sodium. This in turn destroys the soil structure due to dispersion of clay particles (Todd, 1980).

Table 6.5 Irrigation suitability of the well waters of Ithikkara and Kallada river basins using different methods.

Sl. No.	Method	Irrigation suitability
1	EC and Sodium Adsorption Ratio (SAR)	Majority of water samples of lowland and highland regions cluster around the good water quality field in C1S1 and C2S1 zones indicating low salinity- low alkalinity and medium salinity - low alkalinity water. In midland, 94% of samples are clustered in the C1S1 zone indicating low salinity- low alkalinity water. The well water of the area can be used for irrigation in most soil and crops with little danger of development of exchangeable sodium and salinity.
2	Percentage Sodium (% Na)	The percent sodium values of the study area ranges between 35% and 684% for lowland region, 27% and 69% for midland and 20% and 78% for highland region. As per this method, the well water of the study area comes under excellent to good category. The effect of dilution is well observed in post- monsoon samples by an increase in number of samples tending more towards excellent category.
3	Residual Sodium Carbonate (RSC)	The RSC values for samples from lowland, midland and highland areas have RSC values < 1.25 meq/l indicating the groundwater is safe for irrigation.
4	Kelly Index (KI)	Kelly Index of the well waters varies from 0.4 to 2.09 in lowland samples, 0.46 to 0.98 in midland and 0.48 to 0.97 in highland samples. The sample SW4 in the lowland during monsoon and post monsoon season has an increased concentration of sodium as per Kelly's ratio.
5	Permeability Index (PI)	About 33% of lowland, 67% of midland and 87% of highland samples comes under class I category whereas the rest fall in class II category. None of the samples go to class III making sure that all the samples are good for irrigation.
6	Magnesium Hazard (MH)	About 83% of lowland, 89% of midland and 90% of highland samples have low MH values (>50) and hence suitable for irrigation. The sample SW1, SW5, SW6 and SW12 of monsoon season and SW14 of pre-monsoon and SW15 of post-monsoon seasons are found to be unfit for irrigation as per this method.

The analytical data plotted on the U.S. salinity diagram reveals that (Figs. 6.6, 6.7 & 6.8) majority of water samples during all the three seasons in lowland and highland are clustered in the good water quality sector. The concentration of sodium ion is also used for the classification and evaluation of water suitability for irrigation purposes. High sodium water causes exchange of sodium in water for calcium and magnesium and reduces the permeability and results in soil with poor internal drainage (Collins and Jenkins, 1966). The percent sodium values of the area under study ranges between 35% to 68% for lowland region, 27% to 69% for midland and 20 to 78% for highland region, respectively. As per Wilcox diagram (Figs. 6.9, 6.10 & 6.11), the groundwater of the study area comes under excellent to good category. The effect of dilution is well observed in post-monsoon samples by an increase in the number of samples which are more tending towards excellent category.

The carbonate and bicarbonate concentration over the sum of calcium and magnesium in water influences its fitness for irrigation. The content of $CO_3^{2-} + HCO_3^-$ over $Ca^{2+} + Mg^{2+}$ may cause complete precipitation of the latter as carbonate (Karanth, 1989). The effect of carbonate and bicarbonate, and suitability for irrigation can be assessed by computing the Residual Sodium Carbonate (RSC) values. A high value of RSC in water leads to an increase in the adsorption of sodium on soil (Eaton, 1950). Irrigation waters having RSC values > 5 meq/L have been considered harmful to the growth of plants and waters with RSC values above 2.5 meq/L are unsuitable for irrigation. Water having RSC values < 1.25 is safe for irrigation. The RSC value of the samples satisfies the safe limit, making it suitable for irrigation.

Kelly (1946) proposed an index to classify water for irrigation uses. Water with Kelly Index (KI) <1.0 is considered suitable for irrigation (Sundaray *et al*., 2009), whereas water with KI>1 shows excess of sodium in water which makes water unsuitable for agriculture.

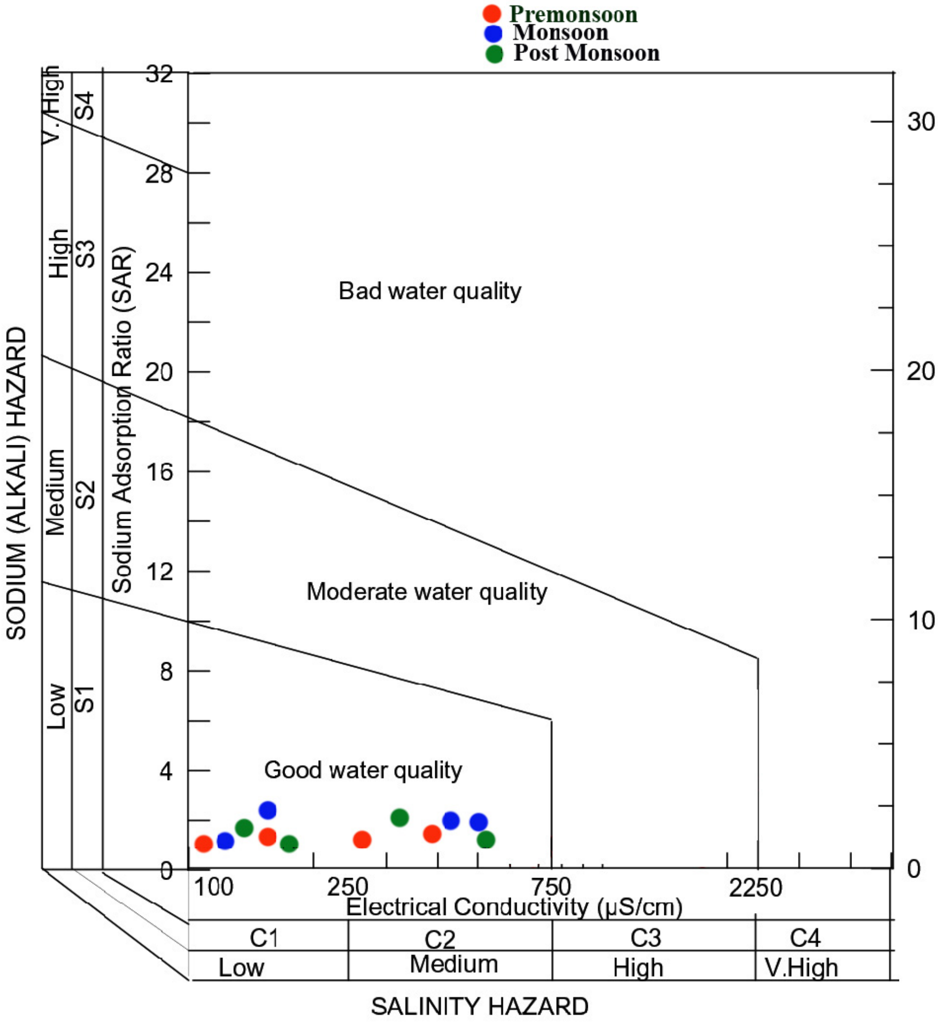


Fig. 6.6 Irrigation water quality of lowland well water samples (Richards, 1954).

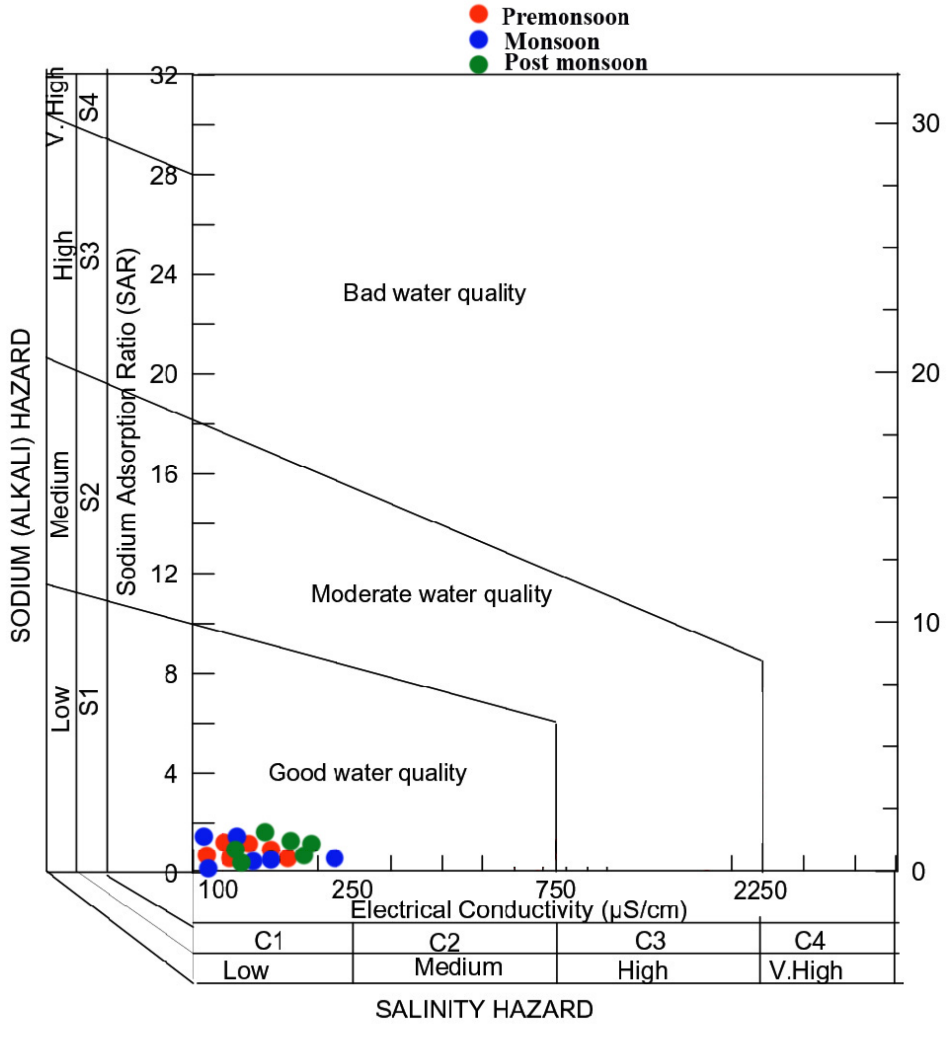


Fig. 6.7 Irrigation water quality of midland well water samples (Richards, 1954).

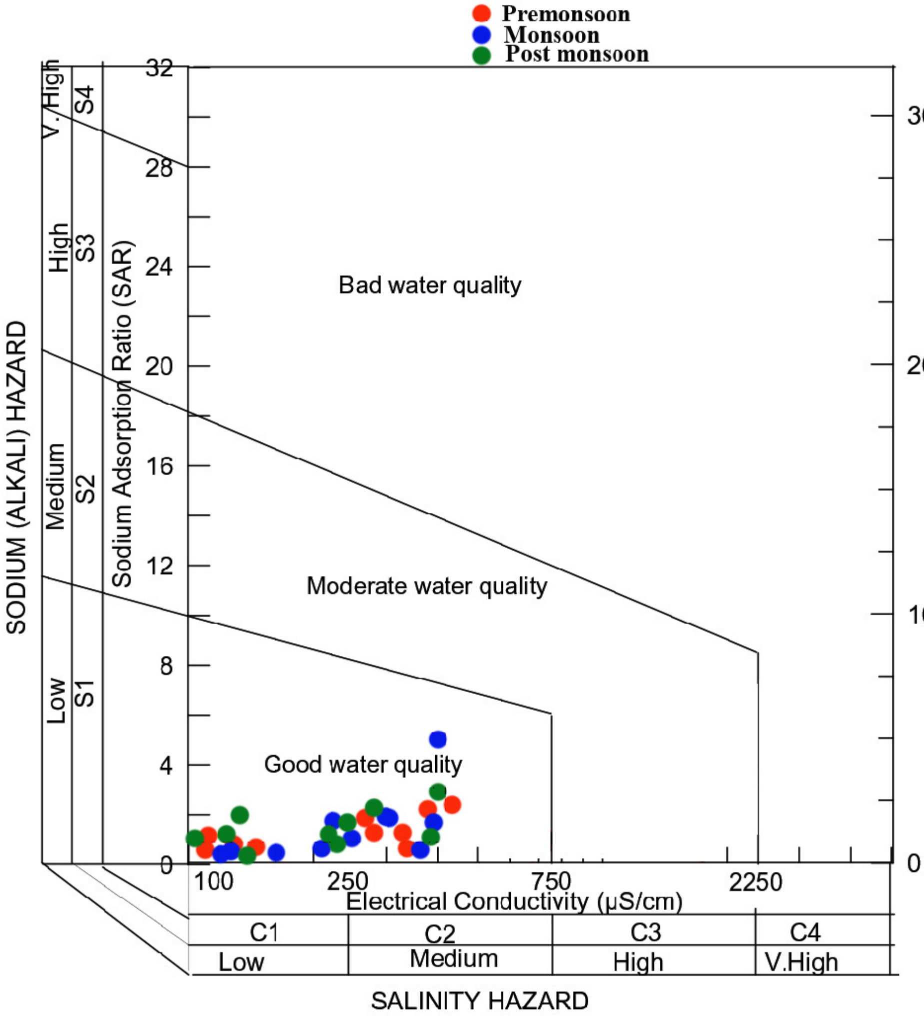


Fig. 6.8 Irrigation water quality of highland well water samples (Richards, 1954).

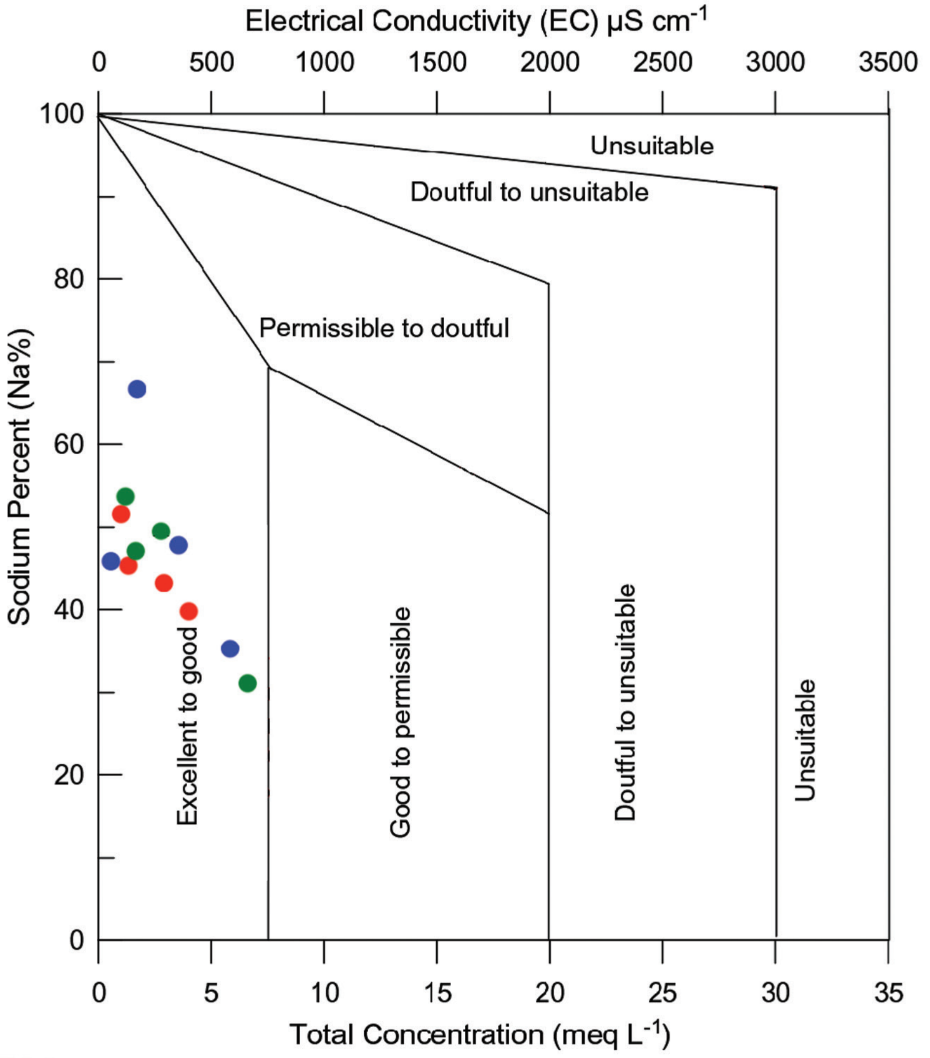


Fig. 6.9 Quality of lowland well water samples as per Wilcox (1955).
Refer Fig. 6.6 for colour codes of samples.

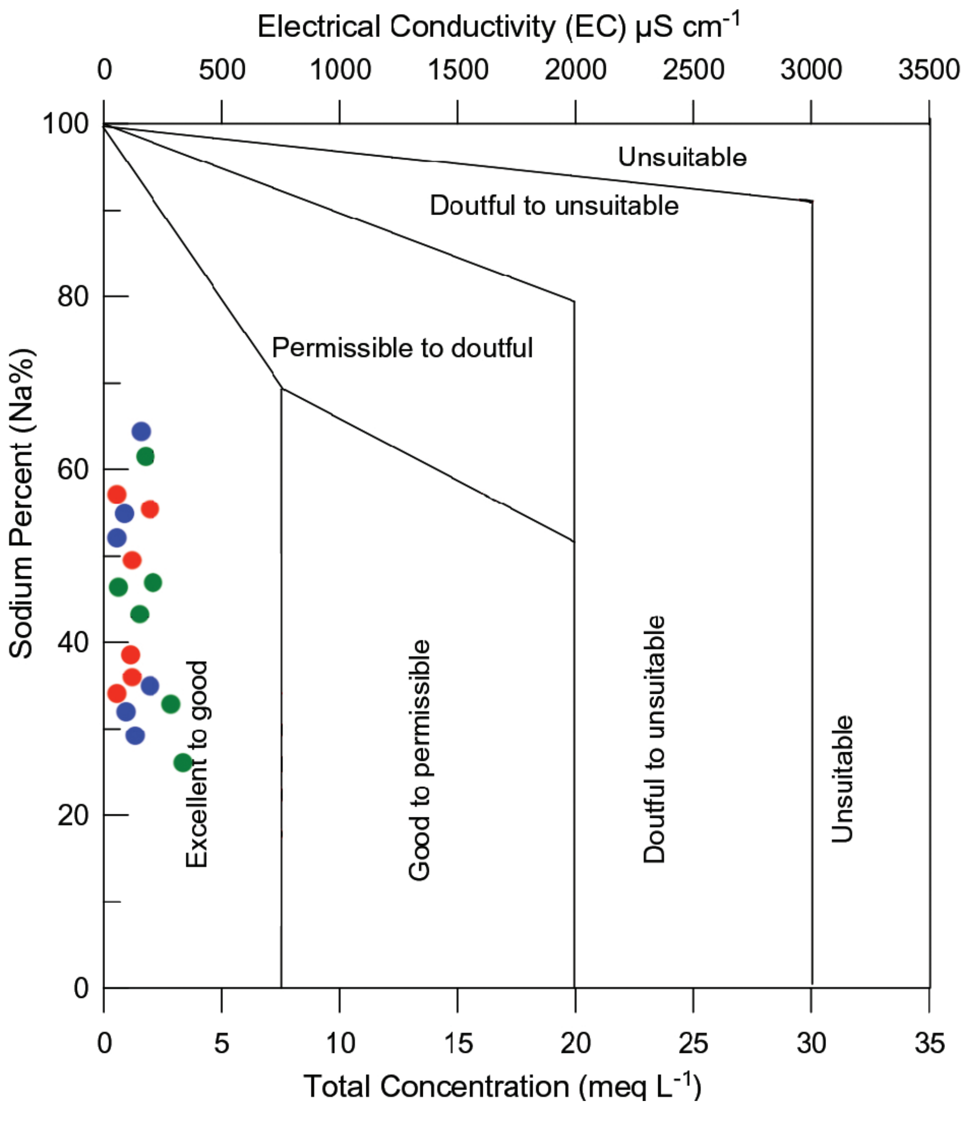


Fig. 6.10 Quality of midland well water samples as per Wilcox (1955). Refer Fig. 6.6 for colour codes of samples.

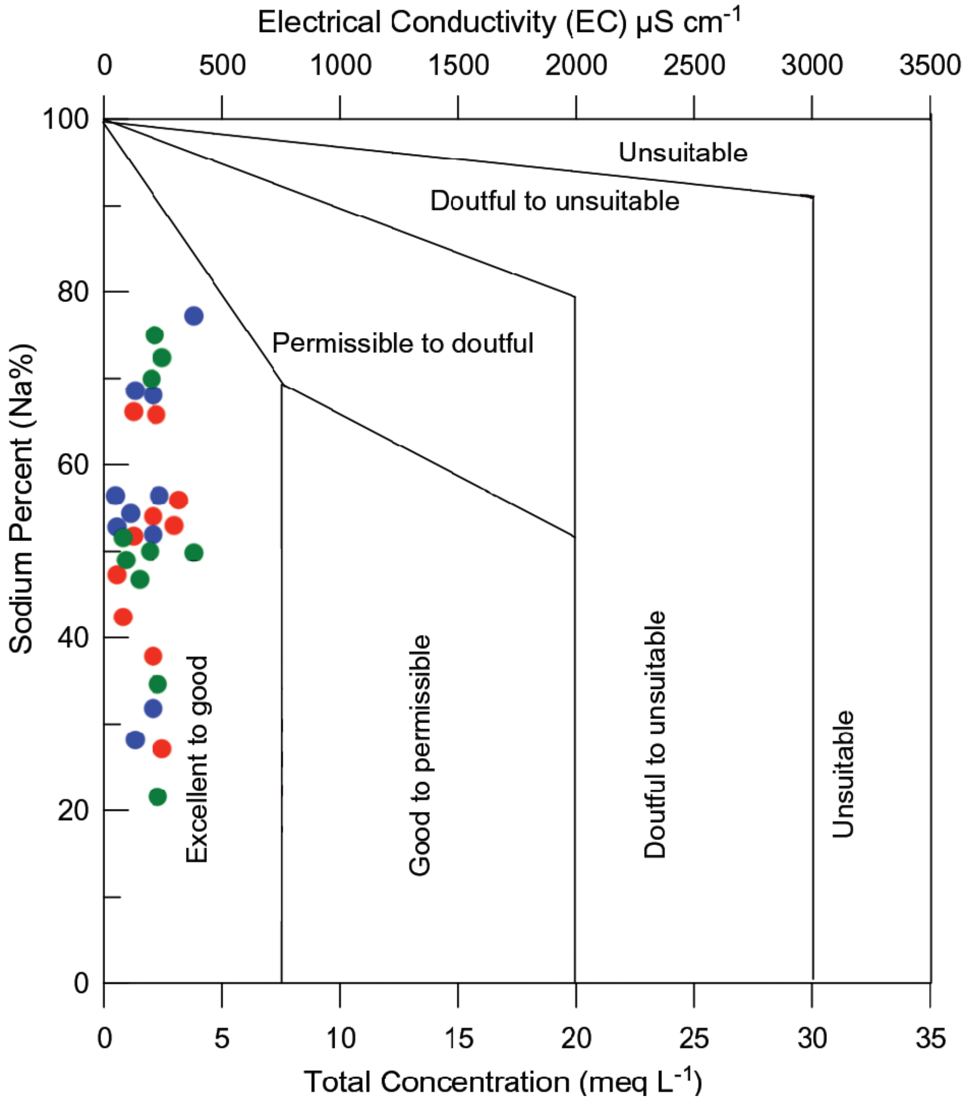


Fig. 6.11 Quality of highland well water samples as per Wilcox (1955). Refer Fig. 6.6 for colour codes of samples.

Majority of samples in the study area are suitable for irrigation as per Kelly Index. KI in the present study varies from 0.4 to 2.09 in lowland samples, 0.46 to 0.98 in midland and 0.48 to 0.97 in highland samples. The sample SW4 of lowland during monsoon and post-monsoon seasons has an increased concentration of sodium as per Kelly's ratio. This may be due to saline water intrusion in the area. The permeability Index (PI) worked out for the samples indicate that the well waters of the study area are suitable for irrigation. The soil permeability is affected by the long term use of irrigation water as it is influenced by Na^{+}, Ca^{2+}, Mg^{2+} and HCO_3^{-} content of the soil. PI has been evolved to measure the soil permeability for assessing the suitability of water for irrigation purposes. The PI is classified under class I (>75%), class II (25–75%) and class III (< 25%). Class I and class II waters are categorized as good for irrigation. Class III waters are unsuitable with 25% of maximum permeability. About 33% of lowland, 67% of midland and 87% of highland samples come under class I category whereas the rest of the samples fall in category class II. None of the samples fall in class III, from which it can be inferred that all the well water in the studied area can be used for irrigation. The PI value is yet another method for testing Irrigation Water Suitability. As per this method, all the samples of the area are suitable for irrigation.

Generally, Ca^{2+} and Mg^{2+} maintain a state of equilibrium in groundwater. More Mg^{2+} present in water affects the soil quality, converting it to alkaline which in turn decreases crop yield (Szabolcs and Darab, 1964). Magnesium Hazard (MH) values >50 are considered harmful and unsuitable for irrigation purposes. About 85% of samples are found to be fit for irrigation as per MH value. The sample SW1, SW5, SW6 and SW12 of monsoon season and SW14 of pre-monsoon and SW15 of post-monsoon seasons are found to be unfit for irrigation as per MH value. From this it is clear that with the exception of a few samples of the study area, all the other samples are suitable for irrigation for a wide variety of crops.

6.4 Spring water potential

Most of the springs in the study area are perennial and are highly productive throughout the year. In this study, free falling types of springs alone are considered for discharge computations. Free falling type springs (Water is emerging through an orifice above ground level) are segregated in two specific areas in the Ithikkara and Kallada river basins. 1) springs located in the highlands close to lineaments, and 2) springs emerging from sandstone-carbonaceous clay interface of the Neogene outcrops exposed in the coastal cliffs and other escarpments. Out of the total 13 free falling type of springs, 5 are located in highland and 8 in coastal lowland which are generally emerging from the base of the escarpments. The estimated total annual water yield of these springs computed from seasonal discharge measurements amount to 256.25 million litres per year (mlpy). Out of this, 59% of the total discharge (151.40 mlpy) is contributed by lowland springs and remaining 41% (104.83 mlply) by highland springs. The water discharge potential of individual springs are given in Table 6.6**.** Among the highland springs, SP18 located at Pathekkar is the most productive with an estimated annual discharge of 104.83 mlpy. The lowest discharge (9.53 mlpy) is noticed for the spring at Kulathupuzha Ambedkar Colony (SP12). In the lowland, Ozhukupara spring (SP4) recorded the maximum water discharge (43.4 mlpy) and Ammarathu Mukku spring (SP5) registered the minimum discharge (10.36 mlpy). The average spring water discharge of pre-monsoon, monsoon and post-monsoon seasons are 6.7, 9.6 and 10 mlpy for the highland and 5.5, 6.6 and 7.3 mlpy for the lowland. The variations in the discharge characteristics are dependant greatly on rainfall in the area with the lowest discharge in pre-monsoon and highest in monsoon and post-monsoon seasons. This clearly indicates the rain-fed / rain-influenced nature of the springs of the study area. Therefore, any change in climate/rainfall pattern in the area will have a direct effect on the fate of these springs. Like the case of upland springs, the coastal springs also exhibit higher discharge of water during monsoon and post-monsoon seasons. People living in the vicinity of the springs use spring waters for domestic purpose, especially during summer months.

Table 6.6 Spring water discharge measured in mlpy during pre-monsoon (PRM), monsoon (MON) and post-monsoon (POM) seasons.

Physiography	Spring code	Water Discharge (mlpy)			Annual discharge (mlpy)
		PRM	MON	POM	
LOWLAND	SP1	5.50	6.05	7.77	19.32
	SP2	3.80	4.32	5.20	13.32
	SP3	3.50	4.13	4.83	12.46
	SP4	11.80	15.20	16.40	43.4
	SP5	3.10	3.80	3.46	10.36
	SP6	2.33	4.83	4.95	12.11
	SP7	5.20	7.26	7.86	20.32
	SP9	5.20	7.43	7.48	20.11
	Total	**40.43**	**53.02**	**57.95**	**151.4**
HIGHLAND	SP12	2.60	3.46	3.47	9.53
	SP15	6.90	8.30	8.10	23.3
	SP16	6.90	13.83	13.93	34.66
	SP18	10.40	12.97	13.97	37.34
	Total	**26.8**	**38.56**	**39.47**	**104.83**
Grand Total		**67.23**	**91.58**	**97.42**	**256.23**

mlpy: million litre per year.

6.5 Water table in wells – A seasonal analysis

Groundwater level indicates the elevation of atmospheric pressure of the aquifer. Any phenomenon that produces a change in pressure on groundwater will cause a variation in groundwater level. Rain fall plays a major role in fluctuation of water level. Both South West and North East monsoons are active in the study area; however, the former influence more than the latter. Water level fluctuations in observation wells in different periods indicate the net change in the groundwater regime in response to the recharge and discharge components. Groundwater occurs under phreatic conditions in the weathered mantle of crystalline rocks and in the shallow zones of sedimentary formation. Water level data of 29 wells from different locations of of Ithikkara and Kallada river basins are subjected to analysis for the period 2010 to 2015 (Data Source: CGWB, Kerala region). Fig 6.12 shows the spatial distributions of wells subjected to water level study. These wells were monitored four times a year during January, April, August and November. The water levels during April reflect pre-monsoon and those of August reflects the post-monsoon conditions. Shallow water level is recorded in the western coastal region and it is deeper in thick laterites. Fig 6.13 illustrates the spatial variation of groundwater levels in pre-monsoon and post-monsoon for the period 2010-2015. Groundwater level data indicates that, the depth to water level in the observation wells in the study area varies from 0.88- 25.5 meter below ground level (m.bgl). Isolated pockets of shallow water level less than 2 m bgl have been observed in 4% of wells, and 2 – 5 m.bgl is noticed in 20 % of wells. In majority of wells (65%) water level varies between 5 to10 m.bgl. 10% wells are showing water level in the depth range of 10- 20 m and the remaining 1% are showing in the range of 20-25 m.bgl. The water level trend of groundwater for the period 2010- 2015 in pre-monsoon and post-monsoon seasons are given in Tables 6.7 and 6.8. Out of the total monitored wells 55% wells are showing a rising trend and 45% a falling trend in

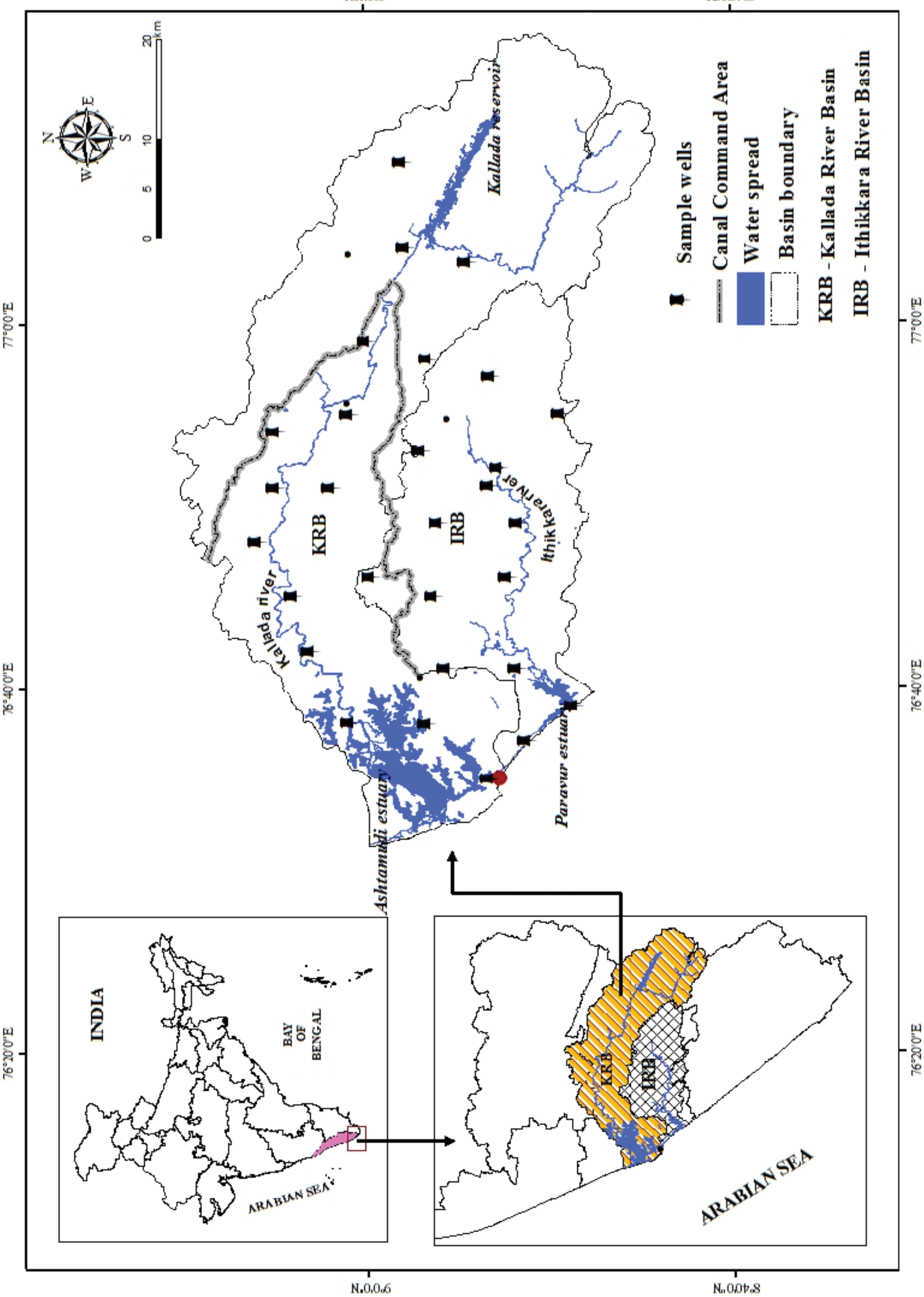


Fig. 6.12 Spatial distribution of wells from which groundwater levels were recorded.

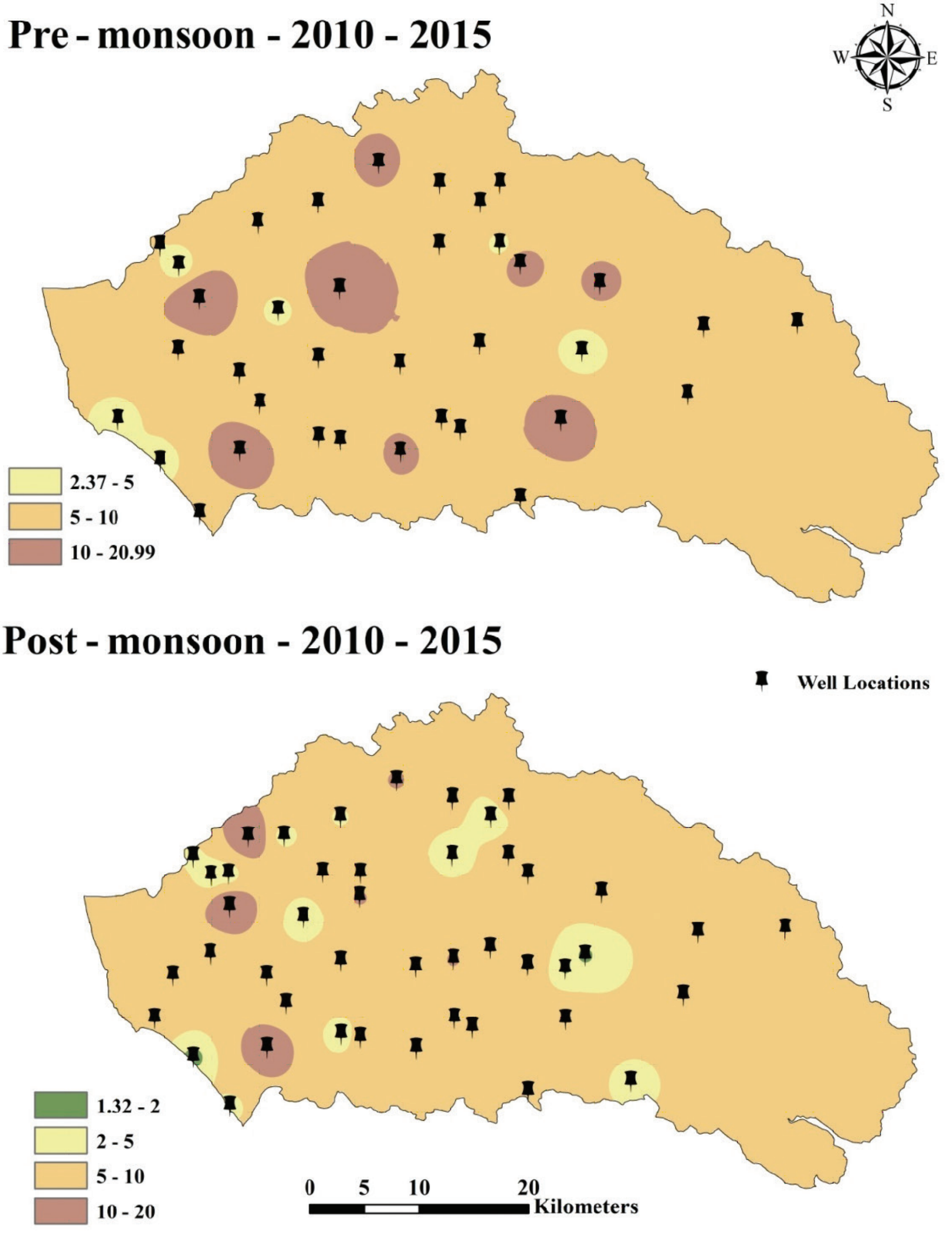


Fig. 6.13 Spatial distribution of groundwater levels during the period 2010 - 2015.

Table 6.7 Water level trend of groundwater (rise and fall) between the period 2010 – 2015 during pre-monsoon season

Sl. No	Block Name	Well Location	No.of Observations	Rise (m/year)	Fall (m/year)
1	Anchal	Channapetta	6		0.183
2		Ayur		0.011	
3		Kulathupuzha			0.153
4		Ailara			0.131
5		Thadicaud		0.584	
6		Thenmala		0.098	
7		Aryankavu			0.145
8		Edamon			0.104
9	Chadayamangalam	Kadakkal	6	0.452	
10		Akkal		0.492	
11		Oyur		0.032	
12		Chadayamangalam		0.613	
13		Ummanoor		0.683	
14	Chittumala	Perinad	6		0.122
15		Kadapuzha		0.583	
16		Kumbalam		0.748	
17	Ithikkara	Ithikkara	6	0.007	
18	Mukhathala	Nalila	6	0.040	
19	Kottarakara	Kottarakara	6	0.689	
20		Kutavettur			0.105
21	Kollam	Kollam	6	0.524	
22	Pathanapuram	Avaneeswaram	6		0.871
23		Pathanapuram			0.688
24		Punnala		0.002	
25		Kunnada			0.666
26	Punalur	Punalur	6		0.966
27	Sasthamkotta	Sasthamkotta	6	0.002	
28	Vettikavala	Pavithreswaram	6		0.37
29		Kulakada	6		0.738

Source: CGWB, Thiruvananthapuram

Table 6.8 Water level trend of groundwater (rise and fall) between the period 2010 – 2015 during post-monsoon season

Sl. No	Block Name	Well Location	No.of Observations	Rise (m/year)	Fall (m/year)
1	Anchal	Channapetta	6		0.068
2		Ayur			0.010
3		Kulathupuzha			0.160
4		Ailara			0.142
5		Thadicaud		0.001	
6		Thenmala			0.900
7		Aryankavu			0.012
8		Edamon			0.236
9	Chadayamangalam	Kadakkal	6		0.218
10		Akkal		0.6	
11		Chadayamangalam			0.270
12		Ummanoor		0.345	
13	Chittumala	Perinad	6		0.798
14		Kadapuzha			0.103
15		Kumbalam			0.025
16	Ithikkara	Ithikkara	6	0.001	
17	Mukhathala	Nalila	6		0.174
18	Kottarakara	Kottarakara	6	0.06	
19		Kutavettur			0.775
20	Kollam	Kollam	6	0.083	
21	Pathanapuram	Avaneeswaram	6		0.242
22		Pathanapuram			0.910
23		Punnala		0.349	
24		Kunnada		0.155	
25	Punalur	Punalur	6		0.198
26	Sasthamkotta	Sasthamkotta	6		0.179
27	Vettikavala	Pavithreswaram	6	0.001	
28		Kulakada	6	0.001	

Source: CGWB, Thiruvananthapuram

water level during pre-monsoon (2010-2015) period. However during post monsoon 35% wells have a rise in water level and 65% show a falling trend. The few stations located in Central part and western part of study area shows a falling trend in NE and SW monsoons. Stations located in the vicinity of Kallada Irrigation project command area shows a rising trend. It is noted that Kumbalam in Chittumala block (19 – 25 m.bgl) of the study area is shows a depleting trend. Dynamic groundwater resource estimation study by CGWB (2011) categorises Chittumala block in semi-critical unit (GEC, 2009).

6.6 Delineation of groundwater potential zones using GIS

Delineation of groundwater potential zones using Remote Sensing and GIS tools are being used widely all over the world. In recent years, extensive use of satellite data along with conventional maps (thematic) and rectified ground truth data, has made it easier to establish base line information of groundwater potential zones (Magesh *et al.,* 2012). Remote Sensing not only provides a wide-range scale of space-time distribution of observations, but saves time and money to a greater extend (Yeh *et al.,* 2009). In addition it is widely used to characterize the earth surface (such as lineaments, drainage patterns and lithology) and also to examine the groundwater recharge zones (Sener *et al.,* 2005). Applications of remote sensing and GIS for exploration of groundwater potential zones are carried out by a number of researchers around the world, and it was found that the involved factors in determining the groundwater potential zones were different, and hence the results vary accordingly. Teeuw (1995) relied only on the lineaments for groundwater exploration and others merged different factors apart from lineaments like drainage density, geomorphology, geology, slope, land-use, rainfall intensity and soil texture (Sander *et al.,* 1996; Das, 2000; Sener *et al.,* 2005; Ganapuram *et al.,* 2008). The derived results are found to be satisfactory based on field survey and it varies from region to region because of varied geo-environmental conditions. Exploitation of groundwater resources has increased in the past decades, leading to over-consumption of groundwater, which eventually caused a series of geo-environmental problems such as decreased groundwater levels, water level depletion, and pollution and deterioration of water quality, etc.

6.6.1 Thematic layers used

i) Geomorphology: Geomorphology has a dominant role in the movement and storage of groundwater in the study area (Thomas *et al.,* 2009). The relief, slope, depth of weathering, type of weathered material, thickness of alluvium, nature of the deposited material and the overall assemblage of different landforms are the result of the long term denudation by fluvial process. The area lies on the western slope of the Western Ghats, has been subjected to weathering and erosion, resulted in peneplanation. General geomorphological milieu of the area, having elevation between 30- 200, is generally classed as lower plateau which is capped by residual laterite. These laterite act as a major formation that absorbs and transmits water to the open wells in the area. Therefore a higher rank has been assigned to this unit of course next to the valleys which is the obvious location of groundwater source in a crystalline undulated terrain like that of Kerala. The erosional and depositional landforms identified in the study area were structural hills, linear ridges, pediplains and floodplains (Refer: Fig 2.2, Chapter II). Active flood plain has higher groundwater level, and hence it is the best landform for high groundwater potential, thus given higher weightage.

ii) Slope: Topography relates to the local and regional relief and gives an idea about the general direction of groundwater flow and its influence on groundwater recharge (Gupta and Srivastava, 2010). Slope plays significant role in infiltration vs. runoff. Infiltration is inversely related to slope, i.e. more gentle the slope, infiltration would be more and runoff would be less. Digital Elevation Model derived from SRTM data with 30 m resolution (Fig. 6.14) is used for preparing the slope map of the region. Slope map is categorized into 5 classes (in degrees), i.e., 0 - 5.35, 5.35 -10.94, 10.94 - 18.05, 18.05 - 27.14, 27.14 - 67.43 (Refer: Fig. 2.1, Chapter II). Classes having less value are assigned higher rank due to almost flat terrain while classes having maximum value are categorized in lower rank due to relatively high run-off.

iii) Lithology: One of the most important requirements for groundwater occurrence and flow is that the geological horizon must be porous and permeable, so that it may store and permit easy movement of water. The lithology map (Fig. 2.3, Chapter II) of the study area was prepared by digitizing following GSI (2005). Geologically area forms part of Pre Cambrian Crystalline rocks composed of mainly charnokite and khondalite, which are undergone weathering to form at the surface by laterite at varying depths and also a part of the area is occupied by by the metamorphic variant viz., migmatite complex, Valley and low lying areas are covered by fluvial materials like colluvium and alluvium composed of sand, silt and clays of proportion. Generally hard rocks are unable to hold or transmit water due to the absence of porosity unless otherwise traversed by intersecting features like fractures, joints or fault planes. the groundwater is occurring under water table condition in the pore spaces of the weathered material viz., laterite. Therefore extent of laterite and its thickness is considered as one of the factors controlling groundwater under unconfined condition in a tropical crystalline terrain. Therefore the lithological unit, laterite has been assigned a higher rank next to valley fill material which is composed of sandstone and clay.

iv) Soil: Soil (Refer: Fig 2.4, Chapter II). of the study area includes four main

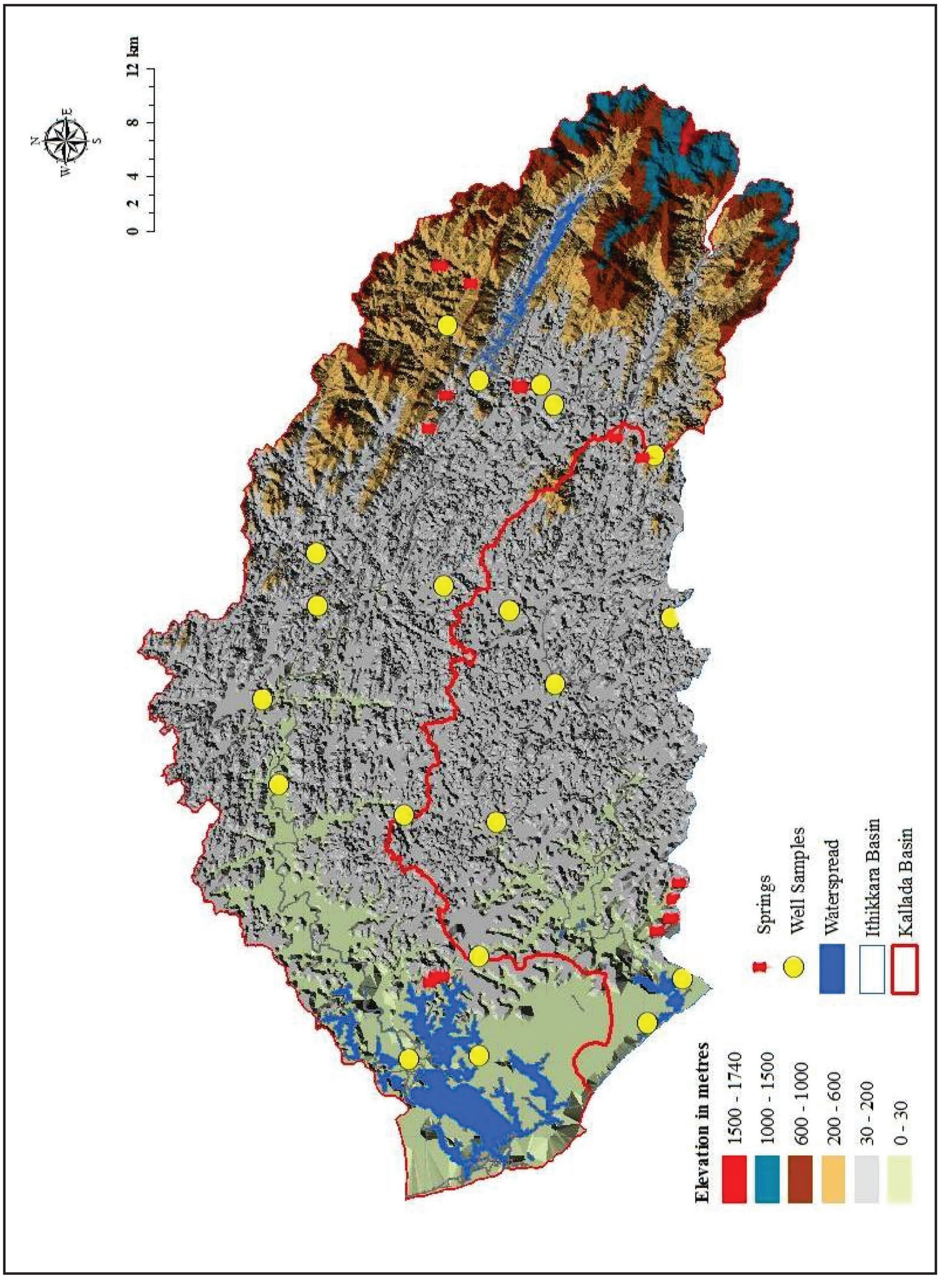


Fig. 6.14 Digital Elevation Model (DEM) of the study area.

categories namely gravelly clay, loam and clay. Weight of soil has been assigned on the basis of their infiltration rate. Gravelly clay has high infiltration rate, hence given higher priority, while clayey soil has least infiltration rate hence assigned low priority.

v) Drainage Density: A drainage map (Refer: Fig. 2.5, Chapter II) of the area gives information about the permeability of rocks in addition to indicating the yield of the basin (Wisler and Brater, 1959). The drainage map was prepared by digitizing the Survey of India toposheets at 1:50000 scale. Drainage density is an inverse function of permeability, and therefore it is an important input parameter for assessment of groundwater zone. The drainage density of the watershed is calculated as: Dd = L/A; where, Dd is the drainage density of watershed, L is the total length of drainage channel in watershed (km) and A is the total area of watershed (km^2). The less permeable a rock is, the less the infiltration of rainfall. This gives origin to a well-developed and fine drainage system. In the present study, since the drainage density can indirectly indicate the groundwater potential of an area due to its relation to surface run-off and permeability, it was considered as one of the indicators of groundwater occurrence. High drainage density values are favourable for runoff, and hence indicates low groundwater potential zone. High drainage density is an unfavourable site for groundwater existence, moderate drainage density has moderate groundwater potential and less/no drainage density is high groundwater potential zone (Todd and Mays, 2005). Low network of drainage course indicates presence of highly resistant and permeable rock while high drainage course indicates highly weak and impermeable rocks (Karanth, 1989). For groundwater prospecting, higher rank was assigned to low drainage density zones and a lower rank was assigned to high drainage density zones. The drainage density of entire study area varies from 3.44 km/km^2 to 14.39 km/km^2 (Refer: Fig. 2.6, Chapter II).

vi) Land use/Land cover: The Land use/Land cover mapof the area (Refer: Fig. 2.8, Chapter II) provides important indications of the extent of groundwater requirement and utilization. The synoptic viewing through remote sensing has provided the multi-spectral data, which has been utilized for classifying LULC. Land use map was prepared from the LISS III satellite image and was classified according to supervised classification method. After geo-referencing and atmospheric correction, the images were classified using a Maximum Likelihood Classification (MLC) algorithm in a per-pixel classification approach. The major land use/land cover classes such as dense forest, open forest, plantation, mixed vegetation, open scrub and dense scrub were identified in the study area. From the point of view of land use, crop land with vegetation is an excellent site for groundwater exploration (Todd and Mays, 2005). The area with water bodies is good for groundwater recharge and fallow land is poor for it (Chowdary *et al*., 2008). Basin area covered by forest, crop land and water bodies are favourable for groundwater potential zones.

vii) Lineament density: Lineaments are defined as naturally occurring linear or curvilinear features. Lineaments were delineated from principal component analysis of IRS and Landsat images along with the shaded relief maps generated from SRTM DEM with different sun azimuths and sun elevations using ERDAS 9.1. Lineaments play an important role in groundwater recharge in hard rock terrains. The groundwater potential is high near high density lineament zones and vice versa (Srivastava and Bhattacharya, 2006; Rashid *et al*., 2012). In hard rock terrains, lineaments represent areas and zones of faulting and fracturing resulting in increased secondary porosity and permeability and are good indicators of groundwater potential (Kumar *et al*., 2007). Lineament density is the total length of all the lineaments present in the basin/watershed divided by the area of basin/watershed. Lineament density map was prepared by dividing the study area into 1 km/1km grids and the lineament density values then obtained were interpolated by inverse distance weighted (IDW) interpolation method. The Lineament density (Refer: Fig. 2.7, Chapter II) of the study area varies from 0.26 to 4.10.

viii) Topographic Wetness Index: The topographic wetness index (TWI) was used commonly to quantify topographic control on hydrological processes and reflects the potential groundwater exfiltration caused by the effects of topography, thus higher TWI value represented higher groundwater potential value. The index is a function of both the slope and the upstream contributing area per unit width orthogonal to the flow direction. Its definition is as follows:

$$TWI = \ln(\alpha)/\tan\beta$$

Where ‘α’ denotes the local upslope area draining through a certain point per unit contour length β Denotes slope angle A higher TWI indicates a gentler slope and larger slope area. TWI (Fig. 6.15) of the study area ranges from 2.52 to 21.73.

ix) Rainfall Distribution: The rainfall distribution map is prepared using the data obtained from the CWRDM and data collected from secondary sources (Fig. 6.16). Rainfall distribution along with the slope/gradient of the terrain directly affects the infiltration rate of water; hence increases the groundwater potential of an area.

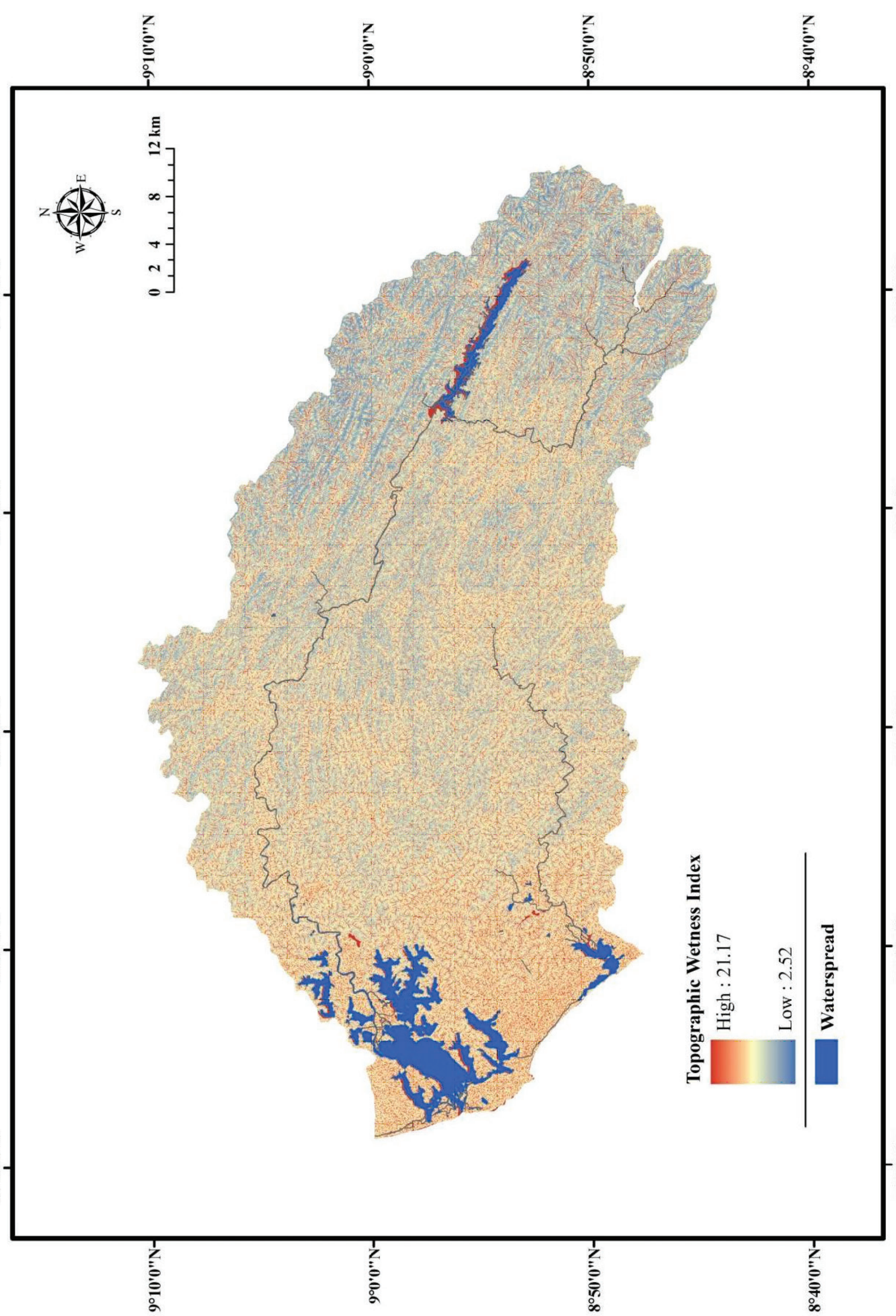


Fig. 6.15 Map showing Topographic Wetness Index (TWI) of the study area.

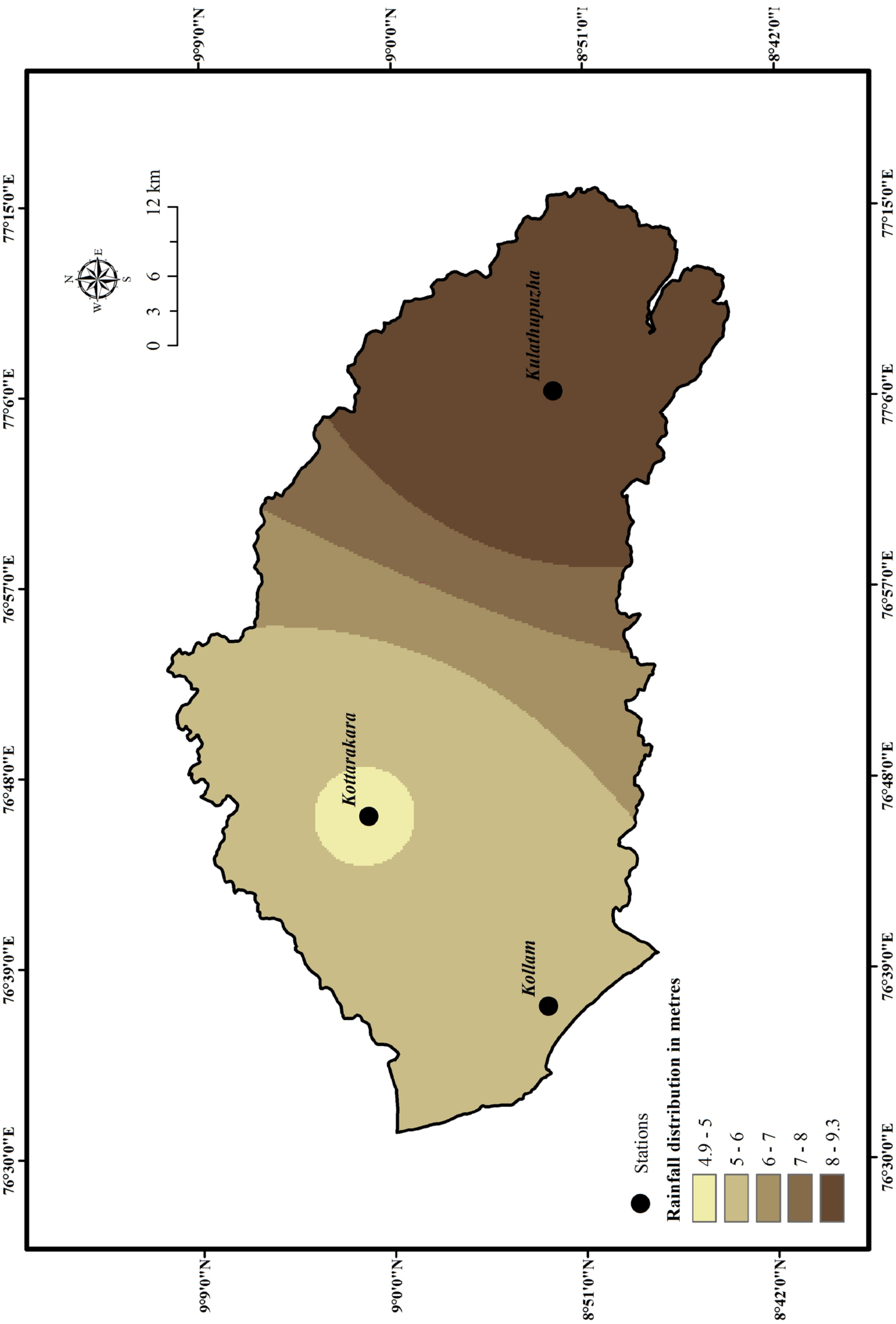


Fig. 6.16 Rainfall distribution of the of the study area.

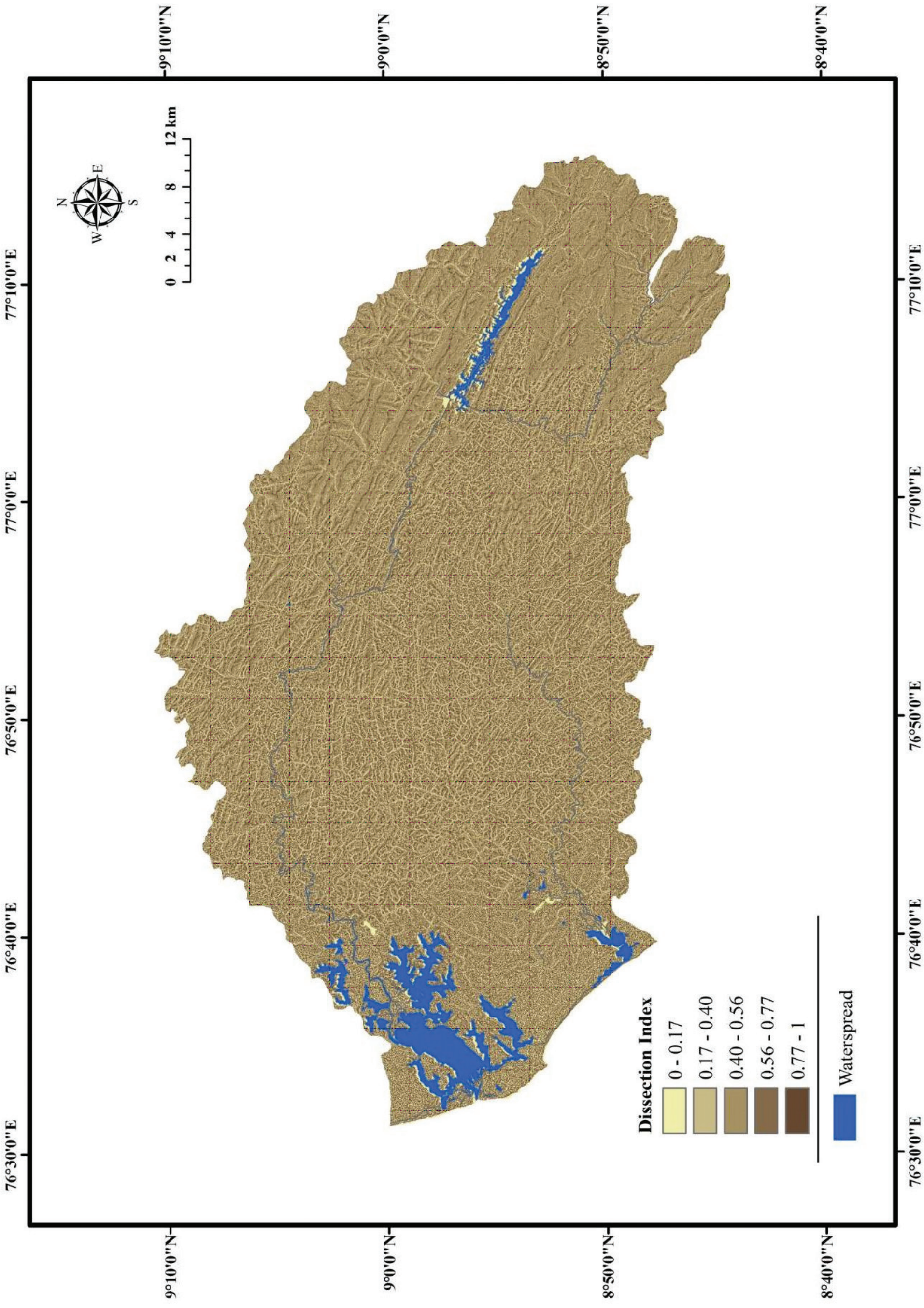


Fig. 6.17 Map showing dissection index of the study area.

x) Dissection Index: Dissection Index (DI) is a parameter referring to the degree of dissection or vertical erosion, and the stage of landforms development in any given watershed (Singh and Dubey, 1994); (Fig. 6.17). DI is the ratio between the total relief (relative relief) and absolute relief of the basin which always varies between zero (complete absence of dissection and hence the dominance of flat topography) and 1 for infrequent cases such as vertical cliff topography at the sea shore, or vertical escarpment of hill-slope. The lower value of DI will have high influence on the groundwater potential of an area.

xi) Roughness: In an area of undulated terrain like that of Kerala, the degree of undulation can be expressed in terms of roughness. More the roughness means the area is more undulated and vice versa. Generally undulated topography is characteristic of a mountainous region where weathering and erosion processes continuously modify the landscape into a smooth and plane surface in long run. If there is considerably thick weathered zone, such area can be treated as groundwater potential zone to a limited extent than a highly rugged terrain where normally only a thin layer of weathered zone exist and therefore no scope for groundwater occurrence. Roughness is synonymous to relief ratio. The roughness (Fig. 6.18) of the study area ranges from 0 to 7.79. The groundwater potential will be high in low roughness area.

xii) Curvature: Curvature is quantitative expression of the nature of surface profile. It can be concave upward or convex upward profiles. Gentle slopes usually attain concave upward profile in platform. In the convex profile water tend to decelerate and in the concave upward profile water tends to accumulate which is true for groundwater also. The curvature (Fig. 6.19) of the study area ranges between -13.68 to 14.08.

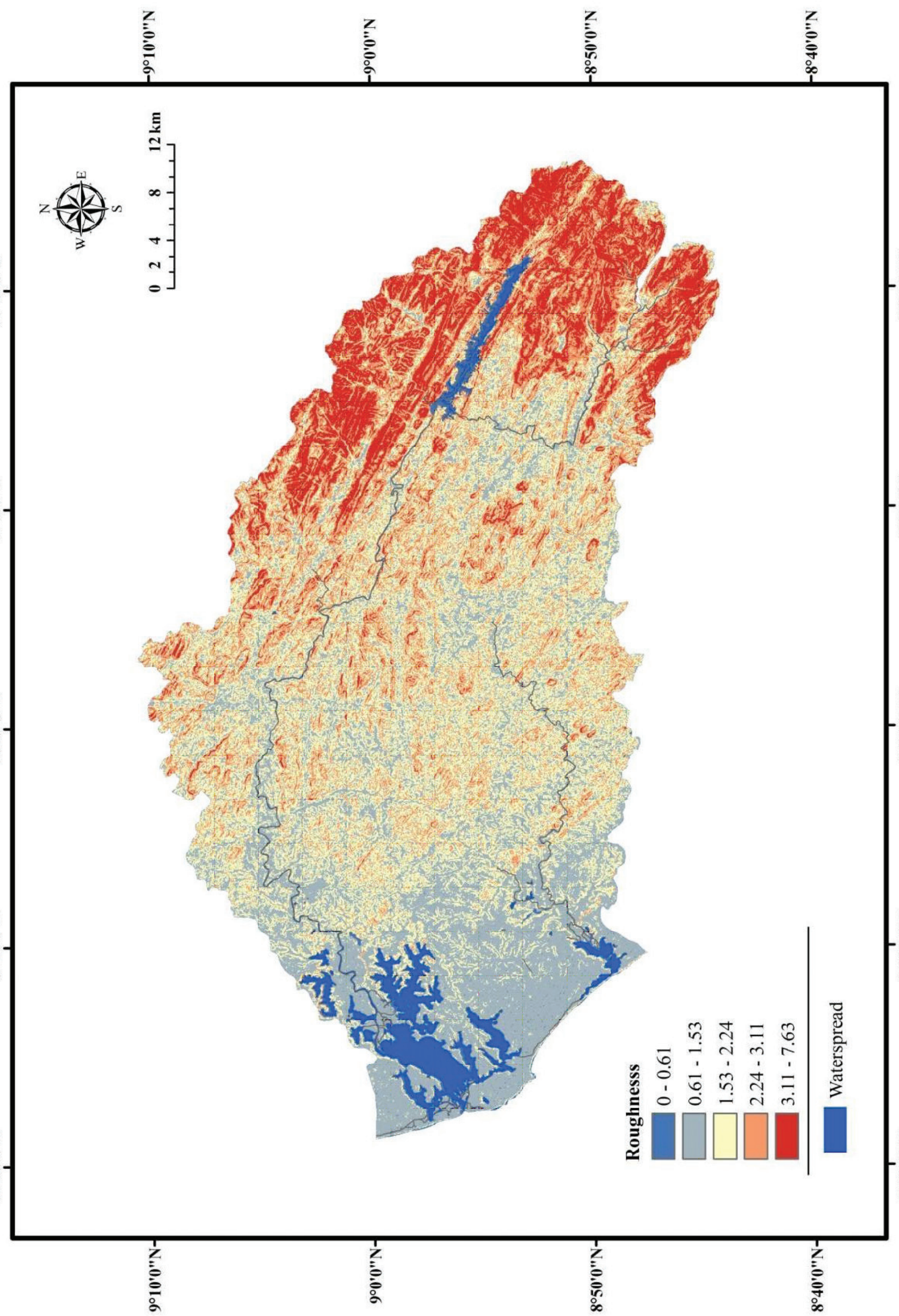


Fig. 6.18 Map showing roughness of the study area.

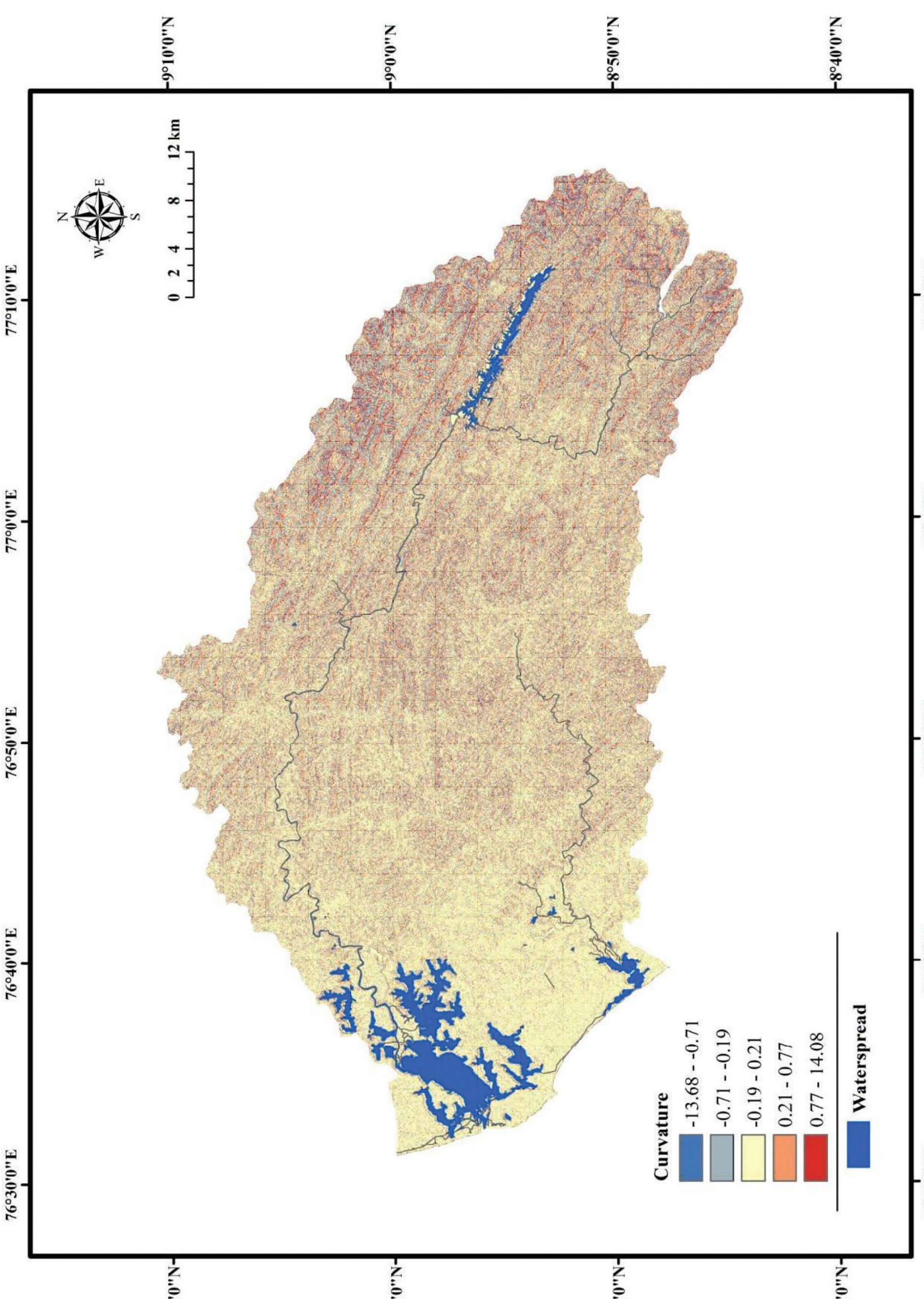


Fig. 6.19 Map showing curvature of the study area.

xiii) Depth to Water Level: Depth to water level (Refer: Fig. 6.21, Section 6.5) of dug wells in the study area for the pre-monsoon period (2010 - 2015) is being interpolated using IDW method.

xiv) Topographic Position Index: Topographic Position Index (TPI) is a topographic position classification identifying upper, middle and lower parts of the landscape. Topographic Position Index (TPI) compares the elevation of each cell in a DEM to the mean elevation of a specified neighbourhood around that cell. Mean elevation is subtracted from the elevation value at center.

$$TPI_i = M_0 - \sum\nolimits_{n-1} M_n / n$$

where M_0 = elevation of the model point under evaluation, Mn = elevation of grid, n = the total number of surrounding points employed in the evaluation. (Guisan *et al*., 1999; Weiss, 2001; Jenness, 2006). High TPI values would be found near the tops of hills while low TPI values would be found in valley bottoms (Fig. 6.20). TPI values near zero would be found on either flat ground or somewhere in mid slope. High ranking was given to area with low TPI values for its chances of groundwater potentiality.

6.6.2 Groundwater potential zones in the study area

The groundwater potential zones were obtained by integrating all the thematic maps in a linear combination model using the spatial analyst tool in ArcGIS 10.2.2 software. A Weighted Index Overlay Analysis (WIOA) method was adopted and the ranking value (Table 6.9) is assigned for each class of individual thematic maps according to the influence of the different parameters on groundwater potentiality. WIOA is a simple and straight forward method for a combined analysis of multiclass maps. WIOA method takes into consideration the relative importance of the parameters

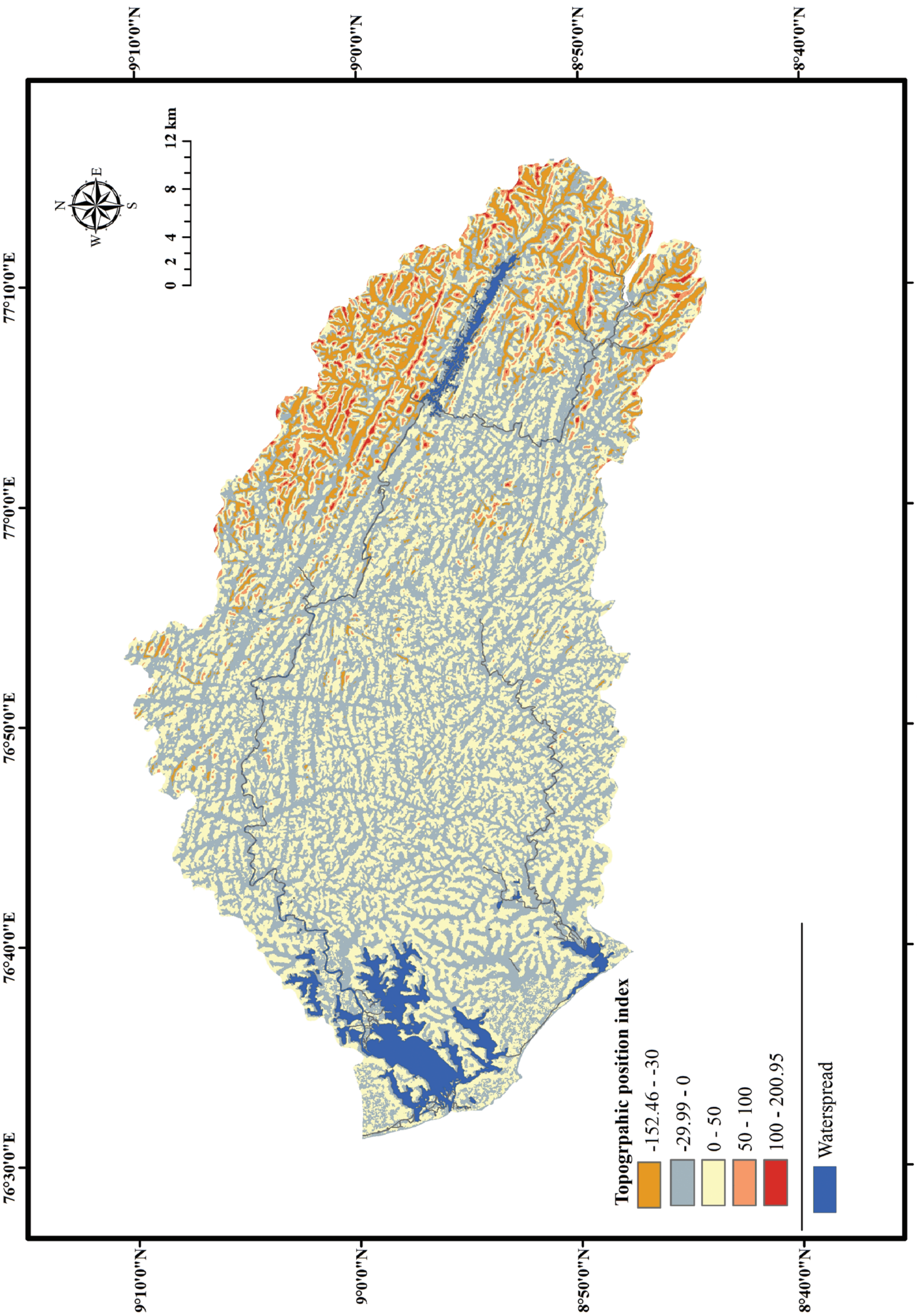


Fig. 6.20 Map showing topographic position index of the study area.

and the classes belonging to each parameter.

Table 6.9 Weight assigned to different factors of thematic layers

Factor	Class	Weight	Factor	Class	Weight
Slope (in degrees)	0 – 5.35	10	Lineament Density	0 – 0.26	2
	5.35 – 10.94	8		0.26 – 0.69	4
	10.94 – 18.05	6		0.69 – 1.24	6
	18.05 – 27.14	4		1.24 – 1.98	8
	27.14 – 67.43	2		1.98 – 4.10	10
Geomorphology	Valley Denudational Hills	6	Rainfall distribution (in metres)	5 – 5.7	2
	Young Coastal Plain	10		5.7 – 6.6	4
	Lower Plateau (Lateritic)	7		6.6 – 7.5	6
	Valley	9		7.5 – 8.3	8
	Denudational Hills	3		8.3 – 9.2	10
	Old Coastal Plain	10	Land use	Forest	2
	Terraces	7		Plantation	4
	Canal	10		Built up	6
Geology	Coastal sand and alluvium	7		Barren Land	8
	Sandstone and clay	8		Agriculture Land	1
	Khondalite group of rocks	1		Mixed Vegetation	7
	Charnokite group of rocks	1	Soil	Clay	2
	Laterite	5		Gravely Clay	4
	Migmatite group of rocks	1		Loam	6
Drainage Density (km/km^2)	0 - 3.44	10		Gravely Loam	8
	3.44 - 5.20	8			
	5.20 – 6.83	6			
	6.83 – 8.76	4			
	8.76 – 14.47	2			

Contd...

Factor	Class	Weight	Factor	Class	Weight
Topographic Wetness Index	2.52 – 5.76	2	Dissection Index	0 – 0.17	10
	5.76 – 7.05	4		0.17 – 0.40	8
	7.05 – 8.83	6		0.40 – 0.56	6
	8.83 – 11.56	8		0.56 – 0.77	4
	11.56 – 21.17	10		0.77 - 1	2
Curvature	-13.68 - -0.71	2	Roughness	0 – 0.61	10
	-0.71 - -0.19	4		0.61 – 1.53	8
	-0.19 - 0.21	6		1.53 – 2.24	6
	0.21 – 0.77	8		2.24 – 3.11	4
	0.77 – 14.08	10		3.11 – 7.63	2
Depth to Water Level (in metres)	1.13 - 2	10	Topographic Position Index	-152.6 – 0	8
	2 - 5	8		0 – 50	6
	5 - 10	6		50 -100	4
	10 – 12.79	4		100 – 200.95	4

There is no standard scale for a simple weighted overlay method. For this purpose, criteria for the analysis are defined and each parameter is assigned importance. Determination of weightage of each class is most crucial in integrated analysis, as the output is largely depended on the appropriate weightage given to each thematic layer (Table 6.10). Relative importance leads to a better representation of the actual ground situation. The Figure 6.21 depicts the groundwater potential map prepared based on the present study.

The groundwater potential zone of the study area can be classified into three categories – low, moderate and high. About 37% of the study area (845.17 sq. km) falls in low category zone, 42% in moderate category zone (960.29 sq. km) and 21% of the area is in high category zone (460.73 sq. km). The groundwater potential zones delineated using the method is validated with data of springs and dug wells from field measurements and it was found that the overlay methods using GIS and Remote Sensing gives 95% accuracy.

Table 6.10 Contributing factors and rank in identifying groundwater potential zones

S. No	Contributing factor	Rank
1	Geomorphology	10
2	Landuse	9
3	Geology	8
4	Soil	5
5	Slope	6
6	Drainage density	4
7	Lineament density	7
8	Rainfall distribution	6
9	Topographic Wetness Index	6
10	Depth to water level	6
11	Curvature	4
12	Dissection Index	4
13	Roughness	3
14	Topographic Position Index	2

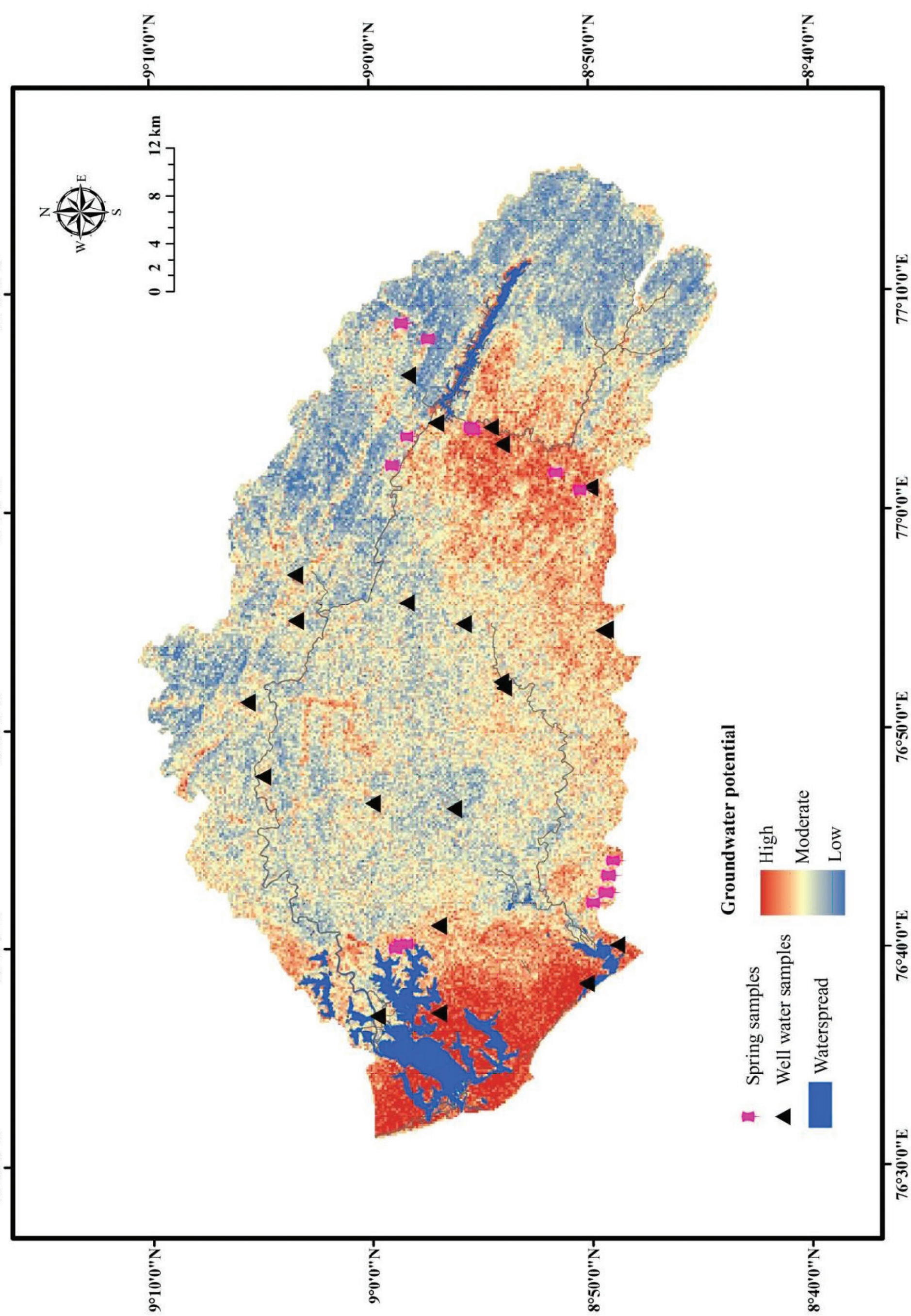


Fig. 6.21 Map showing groundwater potential zones of the study area.

Chapter - 7

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Water is a very vital natural resource for the sustenance of life on earth. The water-related issues are to be dealt with utmost priority in densely populated states of India like Kerala which receives six months surplus water from monsoon and the remaining months generally under water shortage. Man's influence on the quality of water is quite apparent and is now a major concern. The problem may worsen in future as the State is already in the grip of environmental issues. There is an imminent need to keep track the state of environment of the existing fresh water resources in addition to finding new and/or alternate sources for domestic and agricultural requirements. The present study has been undertaken with these views in mind. The study deals with the hydrochemical characterization and water quality assessment of spring and well water sources of two important river basins of Southern Western Ghats - the Ithikkara and the Kallada river basins draining Kollam district of Southern Kerala.

The study was under taken (1) to locate and map the natural springs in the study area, and (2) to assess their geo-environmental settings, water quality and drinking water potential, (3) to evaluate the hydrogeochemical processes of spring and well waters with special reference to silicate weathering, (4) to assess the causes for water quality changes, (5) to evaluate the water potential and delineate potential zones, and

(6) to suggest necessary remedial measures for improving the quality and quantity of spring and well water sources of the area. The fresh water sources of the rivers and its basin area play a key role in supporting the life, vegetation, trade and industry of many developmental centers in the study area including the Kollam Corporation – a fast growing development center in Southern Kerala.

The study area, Ithikkara and Kallada river basins, comprises a total area of 2359 sq.km which spreads mainly in the Southern Western Ghats and adjoining coastal lands. Physiographically, the entire area chosen for the present study falls within three broad physiographic units – the lowlands (< 8m above the mean sea level), midlands (8 – 75m amsl) and highlands (>75 m amsl). It is estimated that about 14.3% of the total area lies in the lowland coastalplains, 31.4% in the midland and the rest (54.3%) in the highlands. A considerable section of the people in the area depends on well and spring water sources for their fresh water requirements.

Geologically, the study area is composed of crystalline rocks of Archaean age which covers a greater part (>90%) of the region (especially in the highland and midland). Sedimentary deposits of Neogene to Recent ages occur in the lowlands. The important aquifer systems in the study area are: weathered, fissured and fractured crystalline formations, semi-consolidated Tertiary (Neogene) formations occurring along the coastalplain, laterite capping mainly in the midland and recent alluvium along the coast and valleys. A major portion of the study area is blanketed by lateritic soil. Brown hydromorphic soil, grayish onattukara soil, coastal/riverine alluvium and forest loam are also noticed in the area. The geomorphology of the basins includes coastalplain, floodplain, pediplain, denudational structural hills, piedmont zone, plateau, and residual hills. The land use of the study area shows a variety of classes that include built-up area, barren land, forest, plantation, agricultural field, mixed vegetation and water body.

A total of 18 physico-chemical parameters [Temperature, pH, Electrical conductivity (EC), Total dissolved solids (TDS), Dissolved oxygen (DO), Total hardness (TH), Sodium (Na^+), Potassium (K^+), Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Carbonate (CO_3^{2-}), Bicarbonate (HCO_3^-), Chloride (Cl^-), Sulphate (SO_4^{2-}), Nitrate (NO_3^-), Silicon dioxide (SiO_2), Iron (Fe^{2+}) and Fluoride (F^-)] , bacteriological parameters (Total Coliform and Faecal Coliform), and trace metals [Arsenic, Copper, Cadmium, Mercury, Lead, Nickel and Zinc] were analysed for spring and well water samples for three seasons – pre-monsoon, monsoon and post-monsoon in the year 2011- 2012.

The aquifers feeding the springs, chosen for the study, fall within both confined and unconfined categories. The springs in highland region emerge from unconfined type whereas the lowland springs emerge from confined type (ie, from Neogene formations). The springs that are seen in the highland region emerge to the ground surface mainly through weathered material – bed rock interface. Two broad varieties of springs occur, they are - 1) boiling type and 2) free falling type. In boiling type, water emerges through an orifice located below the water column of the spring pool, whereas in free falling type water emerges through an orifice located above general ground level.

The seasonal (pre-monsoon, monsoon and post-monsoon) analysis of physico-chemical parameters of the spring water samples reveals that except pH and bacteriological contents, all the other parameters satisfy the standards set by WHO (2011) and BIS (2012) for drinking water. Springs emerging from the extensively lateritised areas show high Fe^{2+} contents. Assessment of the dissolved heavy metasl shows that their contents in spring waters are well within the standard limits set by WHO and BIS. An overall evaluation of the bacteriological analysis in the highland

and lowland springs reveals that 88% of the water samples from lowland region during post-monsoon show incidence of bacterial contamination. The highland samples have high Total Coliform counts than lowland. The alkalis in spring waters of the study area occur mainly with chlorides than the other types of anions. Spring water samples of the coastal lowlands register high $Na^+$and Cl^- values compared with the highland counterparts. This may be attributed to the combined effects of anthropogenic and natural contributions (including marine aerosols in the coastal areas). In majority of the highland springs, concentration of alkaline earths (Ca^{2+}+Mg^{2+}) exceeds alkali metals (Na^++K^+). The process of silicate weathering contributes a major portion of dissolved solids to spring waters, especially in the highland. In 80% of the spring water samples in highlands, chloro-alkaline disequilibrium and prevalence of cation-anion exchange reaction are observed. The rest of the samples indicate base exchange reaction. About 67% of the samples show positive CAI values, indicating base exchange reaction in which alkaline earths (Ca^{2+} and Mg^{2+}) from the host rock or soil have been exchanged for Na^+ and K^+ in the water. Due to the combined effect of terrain gradients and lithological characteristics of the study area, the total solute content of the spring waters is significantly lower than those reported for the other springs in India. Two samples of lowland regions are saturated with respect to quartz, as the springs rise from highly permeable sandstone formation rich in quartz grains. There is an undersaturation of gypsum in lowland region which implies that soluble sulphate mineral phases are rare in the host aquifer and the application of fertilizer through irrigation return flow may be contributing bulk of the sulphates to the springs. The spring samples of highland region are found to be supersaturated with mineral phases like quartz, goethite and hematite. In lowland, the water bearing formation is mostly of friable sandstone whereas in highlands, rock weathering controls the Na, Ca, SiO_2, and HCO_3 contents in spring waters. A significant proportion of major dissolved contents of spring waters are derived from weathering of minerals in the host rocks. The thermodynamic stability diagram for the behavior of groundwater in the silicate system reveals that the chemistry of the spring waters favors kaolinzation and subsequent leaching of mobile elements like alkali and alkaline earth elements. Stability in the kaolinite field suggests that percolating water which is enriched in soil CO_2 reacts with silicate minerals (hydrolysis) in the host rocks, especially with the feldspars. The variation of Al *vs* pH, compared with gibbsite solubility diagram in lowland and highland region shows that the spring water samples are in close equilibrium with gibbsite.

An evaluation of the water quality parameters estimated in the present study reveals that the spring water of the study area can be used for drinking and other domestic purposes after pH correction and disinfection. Quality assessment for irrigation suitability based on RSC, SAR, and %Na values shows that the spring waters are good for irrigation. The results of the WQI values show that majority of the samples fall in Excellent to Good category. From the heavy metal pollution index measurements of spring waters, it is clear that the samples of the study area are not polluted with respect to these toxic metal contents. Regarding the spring water potential, most of the springs in the study area are perennial and highly productive throughout the year. The estimated total annual water yield of the springs computed from seasonal discharge measurements amount to 256.25 million litres per year (mlpy). There are variations in discharge characteristics in three seasons, which are dependant greatly on rainfall contributions of the area with the lowest discharge in pre-monsoon and the highest in monsoon and post-monsoon seasons. This clearly indicates the rain-fed nature of the springs in the study area. This points to the fact that, any change in climate/rainfall pattern in the area will have a direct effect on the fate of these springs in the study area.

The analysis of well water samples in the study area reveals that they are generally soft and moderately hard with varying pH (acidic to alkaline) values. The alkalinity values are comparatively high in lowland and highland whereas the values are substantially low in midland. Ca^{2+} and Mg^{2+} are the dominant cations in the groundwater sources which are followed by Na^{+} and K^{+}. The content of Fe^{2+} in the groundwater shows marked seasonal deviations. About 83% well water samples of pre-monsoon, 100% of monsoon and 67% of post-monsoon seasons of the midland region show bacterial contamination. Na^{+}/Cl^{-} ratio reflects the release of sodium to water mainly through silicate weathering. The dominance of Cl^{-} ion over Na^{+} is attributed to base exchange reactions taking place in the host rock. The dominant hydrochemical facies in the study region are $Ca^{2+}+Mg^{2+}$ / $Cl^{-}+SO_4^{2-}$, Na-Cl, Na-Ca-Mg-Cl-HCO_3 and mixed type. The saturation indices show that majority of samples are saturated with respect to the minerals quartz, goethite and hematite.

An overall evaluation reveals that the well water samples are chemically suitable for drinking and irrigation. In a few cases, pH correction is required before end use. Noticeable temporal variation is observed in the case of dissolved iron content. About 60% of pre-monsoon and 10% of post-monsoon samples exceed the limit (0.3 mg/L) prescribed by WHO (2011) and BIS (2012). Iron content during monsoon season is well within the prescribed limit. The WQI values computed for the well water samples prove that the samples fall within Excellent to Good category, except a few samples which are having high iron concentration. Various hydrochemical parameters determining the suitability for irrigation such as Percent Sodium (% Na), Sodium Absorption Ratio (SAR), Residual Sodium Carbonate (RSC), Kelly Index (KI), Permeability Index (PI) and Magnesium Hazard (MH) depict that water samples are suitable for irrigation.

In recent years, Remote sensing and GIS are widely used for groundwater resources assessment. In the present study, fourteen thematic layers (slope, soil, geology, geomorphology, rainfall distribution, land use, drainage density, lineament density, topographic wetness index, topographic position index, depth to water level, roughness, curvature and dissection index) have been used in GIS platform for delineating groundwater potential zones. Based on the study, the area has been categorized as high, moderate and low groundwater potential zones. A major part of the study area fall under moderate (42%) and high groundwater potential zones (21%). The remaining area (37%) falls under low groundwater potential zone. To test its validity, the locations of productive springs and wells in the study area have been geospatially overlaid on the groundwater potential zone map derived from GIS and Remote Sensing methods. It is found that 95% of the productive springs and wells fall in the moderate and high potential zones identified using the above methods.

The following are some of the suggestions / recommendations drawn from the study:

- The spring water sources in the study area should be used for drinking/ domestic purpose only after pH correction and proper disinfection.
- Detailed studies are to be initiated without much delay to identify / earmark the recharge areas of the springs.
- Once the recharge area is identified, specific action plans are to be prepared to protect these nature's gifts.
- Establish a monitoring system exclusively for the spring water sources for their better use/management.
- Develop a full proof distribution system for effective utilization of the spring waters of the area. In the present case, the distribution of water from springs

can be made by installing a collecting system, pumping system and distribution system. For each source, a cost effective tank made of Reinforced Cement Concrete (RCC) or rubble masonry or ferrocement concrete may be constructed to collect the water by gravity. The capacity of the tank is decided taking into account the yield of the spring, demand of water etc. The final distribution can be made utilizing gravity flow or pumping taking into account the location of the spring and the user outlets.

- Detailed studies are to be taken up to understand the extent of pollution from point and non-point sources to the groundwater regime.
- For ensuring the quality of water, effective and periodic maintenance and management of open dug wells are inevitable. Construct parapet wall and platform around the well. The premises of wells are to be kept hygienic and clean always.Measures are to be taken to stop the dumping of wastes into abandoned wells. Cover up the well to protect from litter falls and other solid contaminants using wire mesh or suitable nets.
- Bathrooms, septic tanks and cattle sheds are to be placed at a minimum distance of 15 metres or more from the well. The expert opinion of a hydrogeologist must be sought to ascertain the distance limit.
- Cultivators are to be encouraged to adopt modern irrigation techniques like drip irrigation to ensure optimal use of groundwater resource.
- A scientific management system co-ordinating all concerned Central and State agencies is to be formed for the sustainable development use of groundwater resources.
- Artificial recharge, rainwater harvesting etc., are to be popularised to minimise

the stress on groundwater resource.

- Strictly enforce the existing rules and regulations on water and water related environmental aspects.
- Create awareness among people at different levels to acquire 'Water Literacy' in order to ensure wise use and management of the pristine fresh water resources of the study area in particular and Kerala State in general.

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APPENDIX

PUBLICATIONS

***In peer reviewed journal*.**

1. Hema, C.N., Padmalal, D., Ammini, J., 2015. Hydrochemical assessment of tropical springs—a case study from SW India. Environmental Monitoring and Assessment 187, 48 : DOI 10.1007/s10661-014-4164-0.

In Abstract Volumes

1. Hema C.N and Vinod P G 2016. Spatial and temporal changes in the ground water resources of Ithikkara and Kallada River Basin, Kerala, SW India. (Abstract Volume) National Seminar on Groundwater Resources of Kerala: Trends, New Perspectives and Management Strategies organised by International and Inter University Centre for Natural Resource Management, Kerala University held on 4th and 5th of February 2016, pp 37.

2. Hema C.N, Padmalal D, Ammini Joseph and Vinod P G. 2016. Delineation of groundwater potential zones using GIS, Remote Sensing and AHP techniques -A case study from Southern Western Ghats. (Abstract Volume) National workshop on Western Ghats: Evolution and Environmental Issues conducted by National Centre for Earth Science Studies, Thiruvananthapuarm held on 1st and 2nd of January 2016, pp 27.

3. Hema C.N, Padmalal D, Ammini Joseph and Vinod P G. 2013. Water quality assessment of groundwater resources of two small catchment river basins, SW India. 'International Symposium on Role of Earth System Sciences and Human Prosperity' organised by Indian Society of Applied Geochemists held on 23rd, 24th and 25th of October 2013 at Hyderabad, pp 26.

4. Hema C.N 2013.Water quality assessment of the ground water resources of Ithikkara and Kallada river basins, Kollam District, Kerala. (Abstract Volume), Regional Seminar on Water Quality Assessment and Management of Kerala State conducted by NIH Belgaum, Kerala State Irrigation department (Hydrology) and Kerala State Groundwater Department held on 5th and 6th of February 2013 at Thiruvananthapuarm, pp 42.