HYDROGEOCHEMICAL AND ISOTOPIC INVESTIGATIONS ON PHREATIC AQUIFERS OF URBAN AND PERI-URBAN CLUSTERS OF KOZHIKODE DISTRICT, KERALA, SOUTHERN INDIA

Thesis submitted to the
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in partial fulfilment of the requirements for the degree of

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By
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CERTIFICATE

This is to certify that the thesis titled **"HYDROGEOCHEMICAL AND ISOTOPIC INVESTIGATIONS ON PHREATIC AQUIFERS OF URBAN AND PERI-URBAN CLUSTERS OF KOZHIKODE DISTRICT, KERALA, SOUTHERN INDIA"** submitted to the Cochin University of Science and Technology for the award of Ph.D. degree is a bonafide record of research carried out by **Mrs. Jesiya N P (Register No. 4273)** under my supervision. This thesis has not been formed part of any dissertation submitted for the award of any degree, diploma, associateship, or any other title or recognition from any University/Institution. It is further certified that 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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DECLARATION

I hereby declare that the work presented in the thesis entitled "**HYDROGEOCHEMICAL AND ISOTOPIC INVESTIGATIONS ON PHREATIC AQUIFERS OF URBAN AND PERI-URBAN CLUSTERS OF KOZHIKODE DISTRICT, KERALA, SOUTHERN INDIA**" has been carried out by me under the supervision of Dr. Girish Gopinath, Senior Scientist, Geomatics Division, Centre for Water Resources Development and Management, and further declare that this has not been submitted earlier in part or in whole to any University or Institute for the award of any degree or diploma.

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Dedicated to My Beloved Parents

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PREFACE

Groundwater, being the largest freshwater resource to humankind, plays a vital role in sustenance and development of a society. The global dependency on water resources for various purposes like domestic, industrial and irrigational needs is rapidly increasing. The situation is likely to worsen further as demand for freshwater will increase in the future with increase in population. As groundwater forms an important component of the total water supply on earth, the aquifers are often under stress, resulting in lowering of the water table, reduction in well yield, well interference due to close spacing of wells, drying up of springs and wells, severe water quality deterioration and so on. The dynamics of groundwater resources is sensitive to recharge processes from aquifers, hence groundwater problems (qualitative and quantitative) are generally found to be more pronounced in urban environment along with variability in spatio-temporal precipitation patterns and intensification of extreme climate events. The overall objective of the study is hydrogeochemical and isotopic characterization of phreatic aquifers in two different urbanized environments viz. urban and peri-urban zones of Kozhikode District, Kerala.

Evaluation of spatio-temporal variation of hydrogeochemical characteristics and inherent hydrogeochemical process of groundwater in phreatic aquifers of the urban and peri-urban clusters of the study area pointed out a distinct spatial variations exist between the groundwater of urban and peri-urban zones. Inter-ionic relationships and multivariate statistical analysis of hydrogeochemical parameters revealed that both urban and peri-urban phreatic aquifer geochemistry was controlled by silicate weathering and ion-exchange processes. The water quality of groundwater in majority of the wells in the urban and peri-urban regions were are within the permissible limits of BIS (2012) and WHO (2011) drinking water standards. A few wells in the urban alluvial phreatic aquifer showed influence of anthropogenic contamination indicated by the elevated concentration of nitrate and faecal contamination.

The origin and recharge mechanism of groundwater in the study area were determined using stable isotope techniques. The analysis of the stable isotope ratios of hydrogen and oxygen of the different water bodies and of rainfall in the region showed that the southwest monsoon and northeast monsoon rains contributed significantly to the aquifer recharge. Point recharge estimation of rainwater contribution to the groundwater was done using isotope mass balance method and it was found that monsoon rains contributed 35% in the urban alluvial aquifers, up to 39% in the urban laterite aquifer and 42% in the peri-urban laterite aquifer.

Spatio-temporal variation of groundwater quality aspects and Groundwater Quality Index was derived using Geographic Information System (GIS) based Multi Criteria Decision Making (MCDM) technique. Through this technique, the study area could be divided into four groundwater suitability zones for drinking purpose. Of the total urban area, 24%, 42%, 34% were categorized as highly suitable, suitable and moderate to poor groundwater suitable zone respectively, whereas 84%, 11% and 5% of the peri-urban zone were covered under highly suitable, suitable and moderate to poor groundwater suitable zones respectively. Hydrogeologic characteristics of phreatic aquifers, the high population density residing in the coastal plain, improper groundwater use pattern and influence of surface water resources like the Kallayi River and Cannoli canal may together imparted the moderate to poor quality status of the study area.

Geospatial analysis endowed an efficient platform for linking different environments (urban and rural continuum), different hydrogeological and environmental factors. Groundwater vulnerability and groundwater potential analysis carried out using customized GIS based Fuzzy-Analytic Hierarchy Process (FAHP) technique and the spatial data thus obtained act as an essential dimensions for monitoring and planning the changing urban and peri-urban spatial environment. The analysis pointed out that majority of the highly potential groundwater zones of the urban cluster were vulnerable to contamination due to intense anthropogenic activities. Validation analysis of groundwater vulnerability and groundwater potential zones revealed that remote sensing and GIS based approach is a powerful decision making tool for sustainable water management in urban and peri-urban environment..

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CHAPTER 1

INTRODUCTION

1.1. General introduction

Groundwater (GW) system employs a dynamic role in nature due to its ability to interact with the ambient environment, relative stability, and well-organized spatial distribution of its flow (Toth, 1999). United Nations reported that more than 2 billion people worldwide depend on GW for their various needs such as for agriculture, irrigation, industrial, domestic, etc (United Nations, 2015). As groundwater forms an essential component of the total water supply the situation have been likely to worsen by drivers of change, such as global population, urbanisation, agricultural intensification or climate change, that can be directly or indirectly attributed to human activity (Hutchins et al. 2018; Proskuryakova et al. 2018; Wen et al. 2019). The impacts of these drivers of change were more pronounced in an urban environment resulting in lowering of the water table, drying up of springs and wells at many places, adverse changes in water chemistry, etc (Foster et al. 1999; Howard and Gelo, 2002; Kløve et al. 2014; Boughariou et al. 2018; Le Brocque et al. 2018). An activity often referred as overdraft, over-development, or groundwater mining very often in the groundwater system of the urban zone where the use of groundwater has been significantly exceeding natural rates of aquifer replenishment (Foster, 2001; Howard and Gelo, 2002; Al-Kharabsheh and Ta'any, 2003). While intensive use of groundwater can generate considerable social and economic benefits, particularly in the short term, it will lower the regional potentiometric surface, thereby reducing well yields, increasing pumping costs, etc. (Bao and Fang, 2012). Reduced groundwater head can also persuade poor quality water to enter deeper parts of the aquifer from rivers and polluted shallow aquifer systems, more seriously leads to land subsidence, Inflow of saline water from deeper geological formations or the sea (Larson et al. 2001; Buapeng et al. 2006; Ebrahimi et al. 2016; Katsanou and Karapanagioti, 2017, Kakar et al. 2019). Release of contaminants to the subsurface where it has the potential to degrade groundwater quality and further limiting its utility.

India covers more than 30% of the global irrigated land and as per country-wise groundwater utilization list (Margat and VanderGun, 2013) and over the world; India consumes the largest volume of global groundwater resource (Goldin, 2016). In most of the States in India, withdrawal of groundwater for both agricultural and industrial use has been more than what can be recharged (Jat et al. 2009 a). Rise in population, urbanization, change in anthropogenic water use, erratic behaviour of the annual and seasonal distribution of precipitation and temperature witnessed by the country leading to radical changes in groundwater recharge and modifying the existing mechanisms (Alley, 2001; Misra, 2011; Bhanja et al. 2017). Modified the landscapes carried out the major changes in the hydrological cycle such as large scale removal of natural vegetation, drainage patterns, decrease in the natural depressions which store surface water, decrease in the rainfall absorbing capacity of soil, expansion of impervious areas (roads, concrete footpaths, rooftops and driveways), etc. (Jat et al. 2009 a; Panda et al. 2007). Urban impermeabilization leads not only to reduced infiltration rate but also increase direct runoff volumes, which frequently produces floods like those that frequently occurs in parts of the country (Misra, 2011; Gautam et al. 2017; Singh et al. 2019; Jesiya and Gopinath, 2019 b). Qualitatively, groundwater is considered as a safer source in comparison with surface water and groundwater in the operational zone of open dug wells were found potable since ages (Saha and Sahu, 2015, Saha et al. 2018). But due to various anthropogenic reasons, slowly this zone became contaminated with faecal collies, nitrates, etc (Ramesh and Elango, 2012; CGWB, 2014; Kumar et al. 2016 a; Rajmohan and Amarasinghe, 2016; Srinivas et al. 2017). In India, major geogenic contaminants occurred in groundwater are fluoride and arsenic and these have been a major health concern and possessing confronts for safe water supply (Jadhav et al. 2015; Chakraborti et al. 2016; Kumar et al. 2016 a; Thakur and Mondal, 2017; Podgorski et al. 2018).

Kerala, the region encompasses with heavy rainfall and abundant surface water resources, the availability of water resources, especially groundwater is not uniform throughout (Shaji, 2011). The state has been experiencing drastic changes in landuse patterns and agricultural practices in the state were brings out conversion of a considerable area of paddy cultivation, mixed crops, scrubland and evergreen forest into built-up areas, highly water intensive commercial crops, rubber plantations, etc (Chattopadhyay, 2005; Sheeja et al. 2011). The high density of population and urban settlements in coastal zones of Kerala including the current study area has been reaching such an alarming proportion (Jesiya and Gopinath, 2015). These changes were enhancing high demand for freshwater resources both in urbanized and outer zones of an urban continuum.

Presently, along with this drastic change in landuse pattern, the state practising exploitation of groundwater from unconfined aquifers through dug wells to uncontrolled exploitation of groundwater resources with the advent of technology, high-speed rigs and quality deterioration of surface water (Shaji, 2011, CGWB, 2012). Groundwater abstraction structures like wells have increased to five million in Kerala in accordance with urban expansion and area for shallow water table decreased for the past three decades clearly depicting an increasing depth trend (Nair et al. 2016). George, (2016) studied that the construction boom in Kerala severely affected the replenishable capacity of groundwater as it is one of the major ingredients in the construction of buildings. Recently, the quality of groundwater resources of the state particularly groundwater in phreatic aquifers has been getting deteriorated by various effluents and anthropogenic activities (Shaji, 2011; Damodaran and Balakrishnan, 2018). Incidences of high fluoride, nitrate, and salinity have been reporting from Chittur block of Palghat districts significantly in tandem with the increase in groundwater abstraction (Shaji et al. 2018). Bacterial contamination is being reported from all districts in dug wells and studies have shown that faecal contamination is present in 95% of drinking water wells (CWRDM, 2011; Megha et al. 2015; Sreekala et al. 2018).

Over the world, there is a growing need for greater responsiveness and protection of groundwater due to its key role in supporting a range of economic, social and environmental values and its significance in the hydrological cycle (Foster and Chilton, 2003). Proper planning and sustainable management of groundwater development are impossible without adequate knowledge and understanding of factors that influence its occurrence, distribution and processes that govern its hydrogeochemical characterization. In most applications, complementary environmental isotope analyses together with hydrochemical measurements are recommended to facilitate a comprehensive and thorough interpretation of groundwater resource characteristics (Hamutoko et al. 2017; Hassen et al. 2018).

The major objective of the present study is to identify the spatial and temporal changes of hydrogeochemical characteristics with a special emphasize on water quality, inherent hydrogeochemical process and recharge mechanism involved in the phreatic aquifers of two differently urbanised environments. These approaches perceptibly help to emphasize the hydrodynamics of the groundwater and to constitute an efficient tool to conceptualize the functioning of the aquifer system. Integration of geospatial, multivariate and multi-criteria decision-making techniques (MCDM) along with hydrogeochemical and isotopic characterizations have been fostering an efficient approach to generate a water resource database for overall development on a sustainable basis, which can lend a hand to planners and decision makers for the sustainable groundwater management.

1.2. Review of Literature

Groundwater-Challenges and constraints:

Water has two fundamental functions namely being a prerequisite for life on earth as well as being an economic resource or commodity for further developments (du Plessis, 2019). These two roles are often in conflict all around the world mainly due to continued competition between different water usages, human livelihoods as well as the environment. Global climatic change, increasing population, expanding irrigated agriculture areas and economic development are drivers for an ever-increasing demand for water worldwide (Hoanh et al. 2015). The continued competition between water usages has consequently led to the exploitation of water through different human activities which have been increasing the risk and placed great pressure specifically on aquatic ecosystems and the life which they support (Pimentel et al. 2012; Holden, 2018; du Plessis, 2019).

Groundwater resources have been playing an important role in sustaining water needs of both urban and rural communities of worldwide (Gleeson et al. 2016; Lopez-Maldonado et al. 2017) and it is being increasingly utilized to serve a growing worldwide demand for freshwater (Rugel et al. 2016). Groundwater also provides a valuable base flow, supplying water to rivers, lakes, and wetlands, thus serving as an essential resource for maintaining various ecosystems that depend on it (Bernadez et al. 1993; Lee et al. 2018). Within a system, the dynamics of hydrological processes are governed partially by the spatio-temporal characteristics of input and output hydrogeological and landuse conditions (Singh and Fiorentino, 2013). Therefore, Human-induced conversion and modifications in geographical components lead the changes in the interactions on hydrological cycle quantitatively and qualitatively (Graniel et al. 1999; Kumar, 2013).

Over 2 billion people (35% of the world population) suffer from severe water stress (Wada et al. 2010; Alcamo et al. 2017). Lee et al. (2018) stated that the groundwater withdrawal amount in Asia accounts for the majority (72%) of global usage value caused by intensive agricultural activities and explosive population growth over the region including Bangladesh, China, India, Iran, and Pakistan (Shah, 2005; Gleeson et al. 2012; FAO, 2016). In developing countries, groundwater scarcity and pollution unreasonably influence the poor because they are frequently not able to keep up with sinking groundwater levels or to find alternative sources when their groundwater resource becomes polluted (Naz et al. 2016; Lopez-Maldonado et al. 2017). FAO (2016) stated that intensive groundwater withdrawal have been exceeding natural replenishment in numerous arid and semi-arid areas of the World. From the south western United States, Mexico, northern China to India, local groundwater users and governments at all levels realize that the once so abundant and economic groundwater resource is getting scarcer, increasingly polluted and thereby affecting options for social and economic growth and development (Kemper, 2004).

Groundwater in urban areas is a particular concern especially in drinking/domestic purpose (Gleeson et al. 2016). Over 50% the world's population now lives in urban areas, a figure that is expected to approach 60% by 2030 and 70% by 2050 (Howard and Gerber 2018). Intensive urbanization thereby rising living standards, industrial growth, increasing the demand for water and this demand has put enormous stress on the limited water resources (Foster, 2001; Kulabako, et al. 2007). Rugel et al. (2016) stated that intensive groundwater extraction has been shown to reduce stream baseflows (Onodera et al. 2008), resulting in increased water temperatures, lowered dissolved oxygen (Stromberg et al. 1996), diminished assimilative capacity, reduced habitat complexity, negative impacts on stream (Sophocleous, 2002), riparian and upland biota (Richardson et al. 2007; Chiu, et al. 2017), etc. Furthermore, an rapid expansion of small, unplanned urban centres and peri-urban settlement have been leading an increase in number of buildings, roads, and other settlements which make the land surface impermeable to the infiltration of precipitation, diminishing the natural recharge of the aquifer (Hirata et al. 2006; Wiles and Sharp 2008; Del Campo et al. 2014). These activities causes the failure of the soil and vadose zone, anthropogenic contamination generation, sources and attenuation of these contaminants to groundwater, etc (Lapworth et al. 2017; Shaad and Burlando, 2018). The phenomenon is severe in cities located over water table aquifers but is also present in urban areas that overlie semi-confined and confined aquifers (Escolero et al. 2000; Foster et al. 2001; Chen, 2003; Onodera et al. 2008; Mohamed and Hassane, 2016; Nogueira et al. 2019).

Groundwater resource - An Indian perspective:

The natural groundwater availability and recharge in India are extremely heterogeneous because of diversity in hydrogeologic set-up and climatic conditions (Mukherjee et al. 2015; Bhanja, 2016; Bhanja et al. 2017). The aquifer system in India is widely varying from the Great Himalayan ranges in North to coastal alluvium in the south. However the consolidated rock formations in the region were unfavourable to groundwater, Bhabars and Terais at the foothills of the lofty mountain chain act as a potential groundwater recharge zone for the aquifer systems downhill (Chatterjee and Purohit, 2009). The most productive and extensive multiple aquifer systems have been occurring in the Indo-Gangetic (IG) alluvium is underlain by thick unconsolidated deposits of Quaternary age holding some of the most potential aquifer systems in the world (Mukherjee et al. 2015; MacDonald et al. 2016). However, the most populous IG basin has been prevalent in Intense irrigational activities, followed by domestic demands on groundwater (CGWB, 2012; CGWB, 2014).

Kumar et al. 2005 reported that increasing agricultural demand for a rising population has resulted in a four-fold increase in production of crops (50–204 million tons) in between 1950 to 2000, severely stressing groundwater resources.

Around two-fifths of India's agricultural output is contributed from areas irrigated by groundwater. Therefore, the contribution from groundwater to India's Gross Domestic Product (GDP) has been estimated as about 9% (Mall et al. 2006; Saha et al. 2018). Large parts of the north Indian shallow alluvial aquifers are anoxic and are enriched with elevated As concentrations it is believed to have further intensified due to extensive groundwater abstraction (Mukherjee et al. 2008; Saha et al. 2010; Mukherjee et al. 2011; Bhattacharya et al. 2014). Rapid depletion in groundwater storage has been observed in the intense agricultural regions in the Indian Sub-Continent (CGWB, 2017). Seawater intrusion resulting in aquifer salinization has been observed in many of the coastal aquifers adjoining the Bay of Bengal and Arabian Sea (Srinivas et al. 2017). Highly brackish groundwater is also prevalent in the inland aquifers of several states (CGWB, 2015). Moreover, the distribution of usable, potable groundwater in the Indian subcontinent is not uniform and there is a growing concern about the availability of safe water in many areas due to presence of natural contaminants such as dissolved arsenic (As) and fluoride (F), and high salinity, etc.

The declining groundwater resource of India, supporting almost one-fifth of the global population and also the largest groundwater user (higher than the sum of the total groundwater abstraction of the United States and China, the second and third countries), has been of great concern in recent years (Bhanja et al. 2016). Groundwater has been the mainstay for meeting nearly 90% of rural drinking need, 62% of irrigation need and more than 50% of urban water demands of the country are met up from aquifers (Saha et al. 2018). Adimalla et al. (2018) stated that over-exploitation of groundwater had become one of the severe problems in many countries, including India. The annual extraction of groundwater in India is the highest in the world, which even supersedes that of the USA and China put together (National Groundwater Association, 2016). Viewed in the international perspective of '<1,700 m/person/year' as water stressed and '<1,000 m/person/year' as water scarce, India is water stressed today and is likely to be water scarce by 2050 (Gupta and Deshpande, 2004).

Groundwater of Kerala- Quantitative and qualitative issues:

The region of Kerala flanked by the Western Ghats and Lakshadweep has a distinctive hydrological cycle dominated by high monsoonal rainfall. Though the State is blessed with plenty of water resources and rainfall, the availability of water resources, especially groundwater is not uniform throughout (Shaji, 2011). Kerala terrain has been varied in its hydrogeological and geomorphological characteristics and hence the groundwater potentials differ from place to place (Nazimuddin, 1993; Gopinath, 2003; Gopinath and Seralathan, 2004; Dinesh Kumar et al. 2007; Jacks and Thambi, 2018; Swetha et al. 2017). Physiographically, the state can be divided into three zones namely the Coastal plains, the midlands and the high land (Water atlas of Kerala, 1995). A major portion of the State is underlain by the crystalline rocks of Archaean age. Sedimentary formations of Eocene to Recent overlie these crystalline rocks along the coastal belt.

Groundwater irrigation has less importance only in Kerala and about 40%-60% of areas with low to moderately stage of groundwater development except in 10%-20% semi-critical blocks (CGWB, 2012). At the meantime, Kerala experiencing considerable change in landuse pattern and agricultural practice of the state for the recent decades (Chattopadhyay, et al 2005; Kumar, 2006). The groundwater developments were expanded from construction of wells in repository zones of groundwater such as valleys to uncontrolled groundwater exploitation due to the growing dependence on groundwater, quality deterioration of surface water and advantage of technology, etc. (Shaji et al. 2011). Like other region, Kerala also having groundwater development and its environmental implications like overexploitation (Shaji et al. 2018), decline of water levels (Hameed et al. 2015; Joseph et al. 2016), seawater ingress, quality deterioration, (Laluraj and Gopinath, 2006; Manjusree et al. 2009; Rejith et al. 2009; Gopal et al. 2017, Jesiya and Gopinath, 2019), waterlogging, climate change, etc. lack of proper solid waste management system causes major threats to groundwater environment of Kerala. Anilkumar et al. 2015 were studied on the ground water quality near the municipal solid waste dumping sites and reported that concentration of nitrate in ground water were reached at alarming state (Nitrate >45 mg/L) due to contaminant leachate. Coastal aquifers are important and subject to considerable stress as the population density in coastal areas is usually high (Jacks and Thambi, 2017). Various studies reported that saline water intrusion into groundwater (Manjusree et al. 2009; Umadevi et al. 2010; Prasanth et al. 2012; Kumar et al. 2015; Gopalan and Chikkamadaiah, 2015; Achari et al. 2017; Damodaran and Balakrishnan, 2018). Coastal aquifers underwent over-exploitation leads to a decline in GW level furthermore causing saline intrusion and the associated increase in concentrations of total dissolved solids (TDS) can eventually render freshwater resources unusable (Sherif and Hamza, 2001).

Over usage of fertilizers and pesticides in agricultural regions, human and animal wastage and unplanned drainage systems are some of the essential causes resulting in overall groundwater degradation and depletion. Jesiya and Gopinath, (2019 a & b) pointed out that open, unlined drains and the pollution dumping sites in the recharge areas act as a source of pollution to the groundwater. The unlined sewage channels are more hazardous in polluting the groundwater due to its perennial nature, but not much attention is paid to evaluate their impact on the groundwater quality.

Successful management of coastal groundwater resources depends largely on the accurate assessment and prediction of aquifer behaviour and the saline water–freshwater interface both under the natural and the anthropogenic conditions (Damodaran and Balakrishnan, 2018). These statistics ought to be kept constantly before our policymakers to change their perceptions of water as an abundant rather than a scarce resource and change the manner in which the protection of water resources implemented.

Hydrogeochemical characteristics of groundwater:

The behaviour of groundwater in the Indian sub-continent is highly complicated due to the occurrence of diversified geological formations with considerable lithological and chronological variations, complex tectonic framework, climatological dissimilarities and various hydro-chemical conditions (Rawal et al. 2016). Interaction and flow occur simultaneously at all scales of space and time, although at correspondingly varying rates and intensities (Toth,1999) namely Chemical interaction such as dissolution, hydrolysis, hydration, ion-exchange oxidation-reduction processes; Physical interaction and Kinetic interaction with the transport processes of water, aqueous and nonaqueous matter, and heat. The interactions on hydrological cycle were being modified quantitatively and qualitatively in most of the water resources as a result of the developmental activities such as landuse change, irrigation, construction of dams and reservoirs, etc. (Pagano and Sorooshian, 2002; Kumar et al. 2005; Sharma, 2017). It is essential that the conservation of surplus monsoon runoff that flows into the sea is conserved and recharged to augment groundwater resources.

Integrated approaches of various hydrogeochemical and isotopic indicators with a thorough knowledge of the regional and local geological conditions proved as more suitable techniques to deal with issues related to the complex groundwater system. (Mulder et al.

1990; Zhu et al. 2007; Jha et al. 2007, Yoshikoshi et al. 2009). Also, the increasing worldwide pressure under conditions of global anthropogenic and climatic change often triggers an integrated multi-disciplinary approach to address the scientific issues involving water resources. Concerns for long-term human and environmental health make it important to understand how geological conditions control flow dynamics in coastal aquifers and how water and chemical fluxes change in the freshwater-saltwater interface (Han et al. 2011). To successfully describe groundwater flow, transport, and geochemical interactions under variable density conditions about real-world problems, detailed and accurate characterization of the subsurface is required (Post, 2005; Han et al. 2011).

Due to the heterogeneities and discontinuities in fractured rocks, the flow and transport processes of groundwater are complex in comparison to those in porous media. Distinguishing groundwater flow, sustainability of groundwater, transport of pollutants, siting of successful boreholes and wells, geothermal resources, etc. were also significant challenges in complex subsurface structures (Farsang et al. 2017; Comte et al. 2018). Various studies on integration of isotopic and hydrochemical indicators are applied to investigate the origins of groundwater salinity, delineating flow systems and groundwater salinization processes, examine migration of the fresh–saltwater interface and understand the mixing relationships between saline water bodies and surrounding freshwater in many coastal aquifers (Reilly and Goodman,1985; Kim et al. 2006; Marimuthu et al. 2005; Kim et al. 2009; Schiavo et al. 2009, Han et al. 2011; Srinivasamoorthy et al. 2011). The relationships and spatio-temporal variations of natural and anthropogenic factors which are influencing the aquifer systems, as well as the limits and hierarchy of their interactions between the components can be statistically demonstrated (Kitanidis, 1997; Dragon, 2006; Kolsi et al. 2013; El Alfy, 2017; Machiwal and Jha, 2015; Bradai et al. 2016; Vrzel et al. 2018). Vrazel et al. 2018 stated that understanding of relative contributions of these sources to groundwater is essential for the prediction of potential impacts of pollutants on water supplies, development of management practices to preserve water quality, and diversity of remediation plans for sites that already polluted.

Demarcating the character of the groundwater in various space was proved to be an important technique in solving different geochemical problems (Chebotarev, 1955; Back and Hanshaw, 1965; Hem 1970; Srinivasamoorthy et al. 2011). In recent years some researchers have focussed on groundwater quality studies for various usages in India have been increased. (Somasundaram et al. 1993; Jat et al. 2009 a & b; Arumugam and Elangovan, 2009; Khan et al. 2011; Marghade and Malpe, 2015; Gautam et al. 2017; Adimalla and Venkatayogi 2018; Adimalla et al. 2018). Multi-disciplinary scientific tools such as geochemical and isotopic tracers have been helping in addressing (Faybishenko et al. 2000; Scanlon et al. 2002; de Vries and Simmers, 2002) the problems associated with the fractured rock aquifers.

The hydrogeochemical processes and hydrogeochemistry of the groundwater vary spatially and temporally, depending on the geology and chemical characteristics of the aquifer. Lakshmanan et al. (2003) stated that hydrogeochemistry of Lower Palar River basin, India contributed by the carbonate weathering and dissolution, silicate weathering and ion-exchange processes. Calculation of mineral saturation index and thermodynamic equilibrium studies (Garrels and Christ, 1965) to decipher the possible reactant and product minerals (Srinivasamoorthy et al. 2011). Deutsch and Siegel, (1997) stated that mineral equilibrium calculations for groundwater are useful in predicting the thermodynamic control on the composition of groundwater and the approximate degree to which the groundwater has equilibrated with the various carbonate mineral phases such as Calcite, Dolomite, and Magnesite (Deutsch and Siegel, 1997). Saturation index approach, it is possible to predict the reactive mineralogy of the subsurface from groundwater data without collecting the samples of the solid phase and analyzing the mineralogy (Deutsch and Siegel, 1997; Martinez and Bocanegra, 2002). Babiker et al. (2007) studied that the chemistry of groundwater is not only related to the lithology of the area and the residence time the water is in contact with rock material, but also reflects inputs from the atmosphere, from soil and weathering as well as from pollutant sources such as mining, land clearance, saline intrusion, industrial and domestic wastes. Excessive irrigation activities also resulted in groundwater pollution in India (Pawar and Shaikh, 1995; Sujatha and Reddy, 2003). Multivariate statistical methods such as factor and cluster analysis have been used to draw meaningful information from large volumes of environmental data, and these techniques have often been used in exploratory data analysis as tools to classify samples and identify major pollution sources (Panagopoulos et al. 2016; Reghunath et al. 2002; Srivastava et al. 2012; Ghahremanzadeh et al. 2018). Kumar et al. 2016 b, stated that the fresh shallow and deep groundwater chemistry controlled by both natural conditions of rock-water interaction and anthropogenic effects. Various hydrochemical analyses including graphical representation such as piper, Gibb’s plots, bivariate diagrams of ions, cross plots of ionic ratios, etc reveals the inherent geochemical process of the GW (Piper, 1944; Guggenmos et al. 2011). The above said hydrochemical features enable to classify and find out the dominant groups whereas a correlation to find out the similarities in water types classes (Zaporozec, 1972; Mahloch, 1974). Groundwater quality evaluation through various standard chemical analyses further applied for classification, correlation analysis, etc. Krishna et al. (2009) studies on assessments of heavy metal pollution in water using multivariate statistical techniques in an industrial area, Medak District, Andhra Pradesh, India indicated the necessity and usefulness of multivariate statistical techniques for evaluation and interpretation of the data. The study provides better information about the water quality and designs for some remedial techniques to prevent the pollution caused by hazardous toxic elements in the future. Raiber et al. (2012) attempted 3D visualization of the results of the multivariate statistical analyses and distribution of groundwater nitrate concentrations in the context of aquifer lithology and thus enabled the link between groundwater chemistry and the lithology of host aquifers. Such endeavours can be applied to various hydrogeological settings to synthesize geological, hydrogeological and hydrochemical data and present them in a format readily understood by a wide range of stakeholders. Thus enables more efficient communication of the results of scientific studies to the wider community.

Groundwater contains minerals carried in solution, the type and concentration of which depends upon several factors like soluble products of rock weathering and decomposition in addition to external polluting agencies and changes in space and time. As a result of chemical and biochemical interaction between groundwater and contaminants from urban, industrial and agricultural activities along with geological materials through which it flows, it contains a wide variety of dissolved inorganic chemical constituents in various concentrations (Dehnavi et al. 2011). Prasanth et al. (2012) tried to evaluate the groundwater quality and its suitability for drinking and agricultural use in the coastal stretch of Alappuzha District, Kerala, India. The groundwater quality controlled by several factors, including climate, soil characteristics, the manner of circulation of groundwater through the rock types, area topography, etc. (Reghunath et al. 2002). Water quality gets modified in the course of movement of water through the hydrological cycle and the operation of the following processes such as evaporation, transpiration selective uptake by vegetation, oxidation/reduction, cation exchange, dissociation of minerals, precipitation of secondary minerals, mixing of waters, leaching of fertilizers and manure, pollution, and biological process (Appelo and Postma, 1993). Factors influencing the salinization process and quality of GW area are naturally occurring salts in the parent aquifer material, surface water importation, lateral flows from an adjacent saline aquifer, saltwater intrusion, and lack of sufficient drainage. Apart from these factors, the interaction between the groundwater and river water and the mixing and non-mixing of different types of groundwater may also play important roles in determining the groundwater quality (Reghunath et al. 2002).

Hydrogeochemical Studies using various classification, correlation studies of ions conducted by in various regions of the world by Houatmiya et al. (2016); Adimalla and Venkatayogi, 2017; Li et al 2016; He and Wu, 2018, identified that the rock-water interactions and geogenic sources are the main controlling factors of hydrogeochemistry.

Studies were proved the capability to distinguish the role of geological and hydrogeological factors on groundwater chemistry (Cloutier et al. 2008). Schot and Van der Wal, 1992 applied principal components and clusters analysis to hydrochemical data to show the regional impact of human activities on groundwater composition. In the study of Farnham et al. (2003), the application of multivariate statistical analysis to trace element chemistry of groundwater helped identify rock-water interaction processes and groundwater redox conditions. When the hydrogeochemical interpretation combined with the knowledge of the geological and hydrogeological setting, multivariate statistical methods can also help understand groundwater flow in complex aquifer systems (Farnham et al. 2000; Stetzenbach et al. 2001). The incidence of fluoride, salinity, arsenic, nitrate, etc and Pollution of groundwater due to industrial effluents and municipal waste in water bodies are the major concern related to groundwater quality in many cities and industrial clusters in India (Kumar and Shah, 2006). Kumar et al. (2016 b) studied the seasonal variation of water quality factors and its overall mineralization processes and found out that salinity as the primary problem followed by nitrate contamination and suggested special attention. The conceptual geochemical model depicted that water table fluctuation resulting from heavy pumping/withdrawal and recharge in association with the variation in DO, $HCO_{3,}$ and Fe regulates the water–mineral equilibrium. Also, the study suggested that in the subsurface environment, complex interactions are simultaneously functioning, and hence, significant seasonal variations are likely to be very influential due to monsoonal recharge and subsequent changes in the saturation states of the water.

Hydrochemical investigation on coastal aquifers focused on to evaluate the saline intrusion process (Srinivasamoorthy et al. 2013). The degradation of groundwater quality in a coastal region due to natural processes such as saline water intrusion, wind-driven sea spray and marine aerosols, and interaction of groundwater with aquifer matrix high evaporation and low and erratic rainfall (Rajmohan et al. 2009; Srinivasamoorthy et al. 2011) in a coastal environment leads the sea water intrusion leading poor water quality of coastal aquifers. Studies of Laluraj et al. (2005) on shallow aquifers in the coastal zones of Cochin and Rao, (2006) on Guntur regions of Andhra Pradesh were indicated the poor water quality due to saline intrusion.

Isotopic systematics:

Environmental isotopes (e.g., $\delta^{18}O$, $\delta^{2}H$, $\delta^{3}H$) widely applied in groundwater studies for better understanding of groundwater origin, infiltration areas, groundwater dynamics, and its vulnerability to pollution (Aggarwal et al. 2012, Gat, 1996, Lachniet and Patterson, 2002). Stable isotopes of oxygen and hydrogen are particularly useful as tracers of hydrological processes in aquifers since their signatures or compositions are not affected by rock-water interactions at the usual low groundwater temperatures and provide insight and support into comprehensive water resources assessment and management (IAEA-TECDOC-1507, 2006; Salifu et al. 2017). Isotopic composition in conjunction with geochemical properties has also been used to understand climatic signatures in the groundwater and to understand climatic controls on observed geochemical properties of groundwater (Navada and Rao, 1991; Navada et al. 1993; Sukhija et al. 1998, 2006).

Groundwater vulnerability to pollution depends on groundwater mean residence time and a relative contribution of river water versus local precipitation to groundwater. Recent researchers intense on environmental isotopes of oxygen and hydrogen ($\delta^{18}O$ and $\delta^{2}H$), tritium ($\delta\ ^{3}H$) and concentrations of nitrate (NO_3^-) were used to investigate hydrological pathways, mean residence time and interactions between surface water and groundwater (Ala-Aho et al. 2015; Martinez et al. 2015; Rautio and Korkka-Niemi, 2015; Rugel et al. 2016; Petitta et al. 2017). Kebede et al. 2017 conducted a comprehensive analysis of the state of surface-water/groundwater interaction from the headwater to the Nile Delta region using piezometric and isotopic ($\delta^{2}H$,$\delta^{18}O$) techniques revealed that the Nile changes from a gaining stream in the headwater regions to mostly a losing stream in the arid lowlands of Sudan and Egypt.

The studies on recharge processes and mechanism of groundwater flow in fractured hard rocks, where homogeneities and discontinuities have a dominant role, vital to address the problem of a realistic assessment of groundwater potential and its sustainability. Sukhija et al.2006 were pointed out wide variations in chloride, $\delta^{18}O$ and ^{14}C concentrations of groundwater observed in space and time could only reflect the heterogeneous hydrogeological setting and recharge processes of groundwater in the studied fractured rock aquifers in granites in the fractured granites of Hyderabad, India.

Studies on the dynamics of surface water of the northern Indian Ocean are important as they significantly affect monsoon systematics and consequently the water availability over India. A complex interplay of several factors/processes which include river influx and ocean currents, direct precipitation and evaporation govern these dynamics.

Natural or anthropogenic perturbations in any of these controlling factors/processes can have far-reaching and non-linear consequences to meteorology, atmospheric chemistry and heat budget of the region. Study of tracers such as oxygen and hydrogen isotopic ratios (δ^{18}O and δ D) that essentially track the water molecules and salinity are best suited for studying the involved dynamical processes. Surface water mixing in the Bay of Bengal (BOB) inferred from the spatio-temporal distribution of d O and salinity (Achyuthan et al. 2013).

Choice of an environmental stable isotope approach to study the influent and effluent conditions based on the fact that the river water originating in the Himalayas depleted in deuterium and oxygen-18 contents compared to the groundwater recharged from rainfall in the plains. This distinct difference in the stable isotope levels helps in identifying the contribution of one to the other. This isotope approach was used by other investigators under different climatic and geological settings to confirm river recharge to groundwater and to identify the relative contribution of different components of runoff (Navada and Rao, 1991). Long-term average groundwater recharge, which is equivalent to renewable groundwater resources, is the major limiting factor for the sustainable use of groundwater. Compared to surface water resources, groundwater resources are more protected from pollution, and their use is less restricted by seasonal and inter-annual flow variations. Using ($\delta^{18}O$ *or* $\delta^{2}H$) isotopes isotope-balance approaches (Jeelani et al. 2010; Coplen, 2011; Jeelani et al. 2013; Sacks et al. 2014; Ala-Aho et al. 2015; Jeelani et al. 2015) have been used in numerous hydrological studies to quantify groundwater inflow to lakes (Krabbenhoft et al. 1990 a, b; Schuster et al. 2003; Saleem and Jeelani, 2017).

Geospatial approach for groundwater management:

The data acquired from the current hydrogeological studies can be analyzed and combined by taking advantage of databases properties, and particularly of geographic information system (GIS) databases (Gogu et al. 2001; Johnson 2009; Chenini et al. 2015;

Bombino et al. 2016). A GIS is a powerful computer-based tool for integrating and analyzing data obtained from a wide range of sources (Zaporozec 2002; Hagon and Green, 2017). GIS is now widely used to create digital geographic databases, to manipulate and prepare data as input for various model parameters, and to display model output (DeVantier and Feldman, 1993; Burrough et al. 2015). Urban development will not be halted for water considerations, hence, there is an urgent need to guide urban planners on how to manage urban development with minimal damage to groundwater resources (Carmon and Shamir, 2010). Multi-criteria decision making (MCDM) is primarily concerned with how to combine information from several criteria to form a single index of evaluation (Heywood et al. 1995). GIS is a best technique suited for handling a wide range of criteria data at multi-spatial, multi-temporal and multi-scale from different sources for a time-efficient and cost-effective analysis (Ahmed et al. 2016; Tutić et al. 2018). Therefore, there is a growing interest in incorporating GIS capability with MCDM processes. Spatial MCDM has also become one of the most useful methods for landuse and environmental planning, as well as water and agricultural management (Chen et al. 2010).

Geographical information system provides the potential for handling complex spatial data and its integrated approaches lend a hand to deal with various groundwater resource investigations such as site suitability, groundwater quality & vulnerability assessment and groundwater modeling for movement, solute transport & leaching (Rao and Jugran 2003; Jha and Chowdary, 2007; Dinesh Kumar et al. 2007; Murthy and Mamo 2009; Chowdhury et al. 2010; Jha et al. 2010; Machiwal et al. 2011; Prasanth et al. 2012; Neshat et al. 2014; Kumar et al. 2014; Machiwal et al. 2018). Water-sensitive urban development means consideration of the expected impacts on the quantity and quality of water in the sources in the area developed and/or the water used in this area. Such planning covers two domains: one deals with the effects of urban development on the hydrological cycle and the water sources; while the other deals with the engineering aspects of water supply and use (Carmon et al. 1997). The current thesis deals with the former domain. Multi-Criteria Decision Making (MCDM) techniques serve as a promising method for the optimization of groundwater resources and its management by adding structure, audibility, transparency, and rigour to the decision (Dunning et al. 2000; Flug et al. 2000; Machiwal et al. 2011; Joubert et al. 2003). Analytic Hierarchy Process (AHP) and its extension, the Analytic Network Process (ANP) is a family of approaches that enables pairwise comparisons of criteria which determines how much more important one is that the other and converting the pair-wise comparisons to weights according to the relative importance of criteria (Jesiya and Gopinath, 2019 a). With the availability of user-friendly and commercially supported software packages, AHP/ANP has found wide recognition and application among water researchers (Huang et al. 2011, Kavurmaci and Ustun, 2016). According to Ishizaka and Lusti (2006), AHP and ANP can function even with incomplete or inconsistent inputs, by using matrix algebra (involving either Eigen value-based or similar calculation methods) to produce weights, overall scores, and measures of consistency.

The traditional AHP is works with crisp judgments and is accompanied by uncertainty and therefore not enough to reflect the human thinking style effectively (Kahraman et al., 2003). The fuzzy AHP technique which is an advanced analytical method developed from the traditional AHP proposed by Van Laarhoven and Pedrycz, (1983) facilitated to overcome this problem and to have a more confident decision. It can view as Fuzzy inference systems enable to work in the presence of a wide number of variables, as they produce aggregated index, are able to handle linguistic attribute and treat draft information without losing the important part of the concepts (Aryafar et al., 2013; Şener and Şener, 2015; Mohamed and Elmahdy, 2017; Jesiya and Gopinath, 2019 b).

Geospatial techniques provide a powerful package for integrating and analyzing data obtained from a wide range of sources (Zaporozec, 2002). Jat et al. (2009 a) illustrated an integrated approach for the assessment of potential impacts of urbanization of Ajmer city, India regarding groundwater quality and recharge. Because of the advancement of the techniques, researchers could able to evaluate the potential problems on water quality in the zone and generated a water resource database for the sustainable database of the city.

Literatures discussed above to ensure the need for detail geospatial studies particularly on phreatic aquifer systems which are easily prone to contamination by various natural and anthropogenic factors. These shallow aquifers are prone to contamination by seepage from septic systems, effluent untreated sewage systems and possibly manure and fertilizers spreading in agriculture land as well. The vulnerability map is the subdivision of the area into several hydro-geological units with different levels of vulnerability which shows the distribution of highly vulnerable areas, in which pollution is very common because contaminants can reach the groundwater within a very short time. Recognition of groundwater vulnerability to pollution will help in protecting groundwater sources and managing groundwater quality conflicts. Groundwater monitoring and mathematical modelling are costly in regional scale vulnerability assessment therefore subjective modelling are needed to assess the potential of groundwater contamination by nonpoint sources over large geological areas involving a variety of hydrogeological settings. Many approaches have been developed for assessing groundwater vulnerability and can be grouped into three major categories (Tesoriero et al. 1998; Babiker et al. 2005) such as overly and index methods, process-based simulation models, and statistical methods. Overlay index methods of the factors controlling the movement of pollutants (e.g., net recharge and depth to groundwater table) can evaluate over a large area, which makes them suitable for regional-scale assessment (Thapinta and Hudak, 2003). Overlay index methods applied in various studies are the DRASTIC model (Aller et al. 1987), the GOD (Foster, 1987), The AVI rating system (Stempvoort et al. 1993), the SINTACS method (Civita, 1994), the German method (Von Hoyer and So¨fner 1998), the EPIK (Doerfliger and Zwahlen 1997), and the Irish perspective (Daly et al. 2002). A process-based approach which use simulation models to capture the physical, chemical, and biological reactions that occur from the surface through the groundwater regime by modeling to estimate the extent of contaminant plume and its transport but resourceful results depend on intensive fieldwork and collection of primary and secondary data. As it generally requires a large amount of primary and secondary data to apply the mathematical models for creating the principal tool, such methods seem more complex and difficult to use on a regional scale.

Statistical methods use data on the known areal contaminant distribution and describe the contamination potential for a specified geographical region using the available data in the regions of interest (National Research Council, 1993). Statistical methods use statistics to determine associations between spatial variables and actual occurrence of pollutants in the groundwater. Regression analysis, linear modelling, principle component analysis, fuzzy models, hierarchical analytical process, kriging are some of the statistical methods to expresses vulnerability regarding the probability of contamination (National Research Council, 1993). Intrinsic aquifer vulnerability can be assessed using overlay and index methods and statistical methods. However process-based simulation models are popular for assessing specific vulnerability (Bazimenyera and Zhonghua, 2008). Process-based methods and statistical methods are not commonly used for vulnerability assessment because they constrained by data shortage, computational difficulty, and the expertise required for implementing them.

The DRASTIC system is the widest method used to evaluate intrinsic vulnerability for a wide range of potential contaminants (Stigter et al. 2006; Al-Abadi et al. 2017). It is an overlay and index model designed to produce vulnerability scores by combining several thematic maps. It was originally developed in the USA under a cooperative agreement between the National Water Well Association (NWWA) and the US Environmental Protection Agency (EPA) for detail hydrogeological evaluation of pollution potential. The word DRASTIC is an acronym for most important factors within the hydrogeological settings which control groundwater pollution. The hydrogeological setting is a composite description of all major geologic and hydrogeological factors which affect the groundwater movement into, through, and out of the area. To correlate the urban factors and groundwater status (Al Adamat et al. 2003; Muhammad et al. 2015) has also tried to develop a risk map by integrating the DRASTIC map with the landuse map. It is done to assess the potential risk of groundwater to pollution in the study area. The intrinsic vulnerability is the natural susceptibility to contamination based on the physical characteristics of the environment while specific vulnerability defined as accounting for the transport properties of a particular contaminant or group of contaminants through the subsurface (Liggett and Talwar, 2009). Al Abadi et al. (2017) and Brindha and Elango, 2015, attempted to differentiate these two using normal DRASTIC and pesticide DRASTIC assessment. The difference between the two versions of DRASTIC is in the assignment of relative weights for the seven DRASTIC factors. The studies were supported that multidisciplinary approaches proved as an effective tool for local authorities who are responsible for managing groundwater resources (Rahman, 2008, Kabera and Zhaohui, 2008, Ghosh et al. 2015; Mirlas et al. 2015).

1.3. Environmental settings

Urban and selected peri-urban clusters of the Kozhikode district located in the south-west coast of India has been selected for the study and has an areal extent of 524 km^2 with 36 km seashore and lies between North latitudes 11º 7’23.11’’ and 11º 28’35.67’’ and East longitudes 75 º 42’0.87’’ and 75 º 57’ 47.49’’ (Figure 1.1). The urban cluster having an areal extent of 212 km^2 is a second order urban zone with a population density of 3746 person/km^2 (Census 2011). As per the State Urbanisation Report - Kerala, 2012, analysis of population, basic infrastructure, built up nature and administrative set up revealed the scope of further densification of the population density and physical development in and around the urban cluster. Thus areas with high-density physical development and with more than two closely located higher order (up to 5th order) urban centres are delineated into an urban cluster of the study area (Jesiya and Gopinath, 2019 a). The urban cluster of the study area shows high potential for development contributing to the economic development of the entire northern region of the State. According to Census, 2011 the population density of the urban cluster is 3746 persons per km^2 and is greater than the State average.

Even though the region is drained by four rivers (namely Chaliyar River, Kadalundi, Kallayi and Korapuzha - Figure 1.1), polluted surface water, high demand on groundwater resources, saltwater intrusion, quality deterioration and coastal erosion are some of the problems faced by the coastal groundwater system (Plate 1.1 a & b). The Cannoli canal is a part of National Waterway (NW-3) system that passes through the urban cluster and the area between the coastline and as per a report on Master Plan for Kozhikode Urban Area – 2035 (2012), canal is known to be the most active zone of the city.

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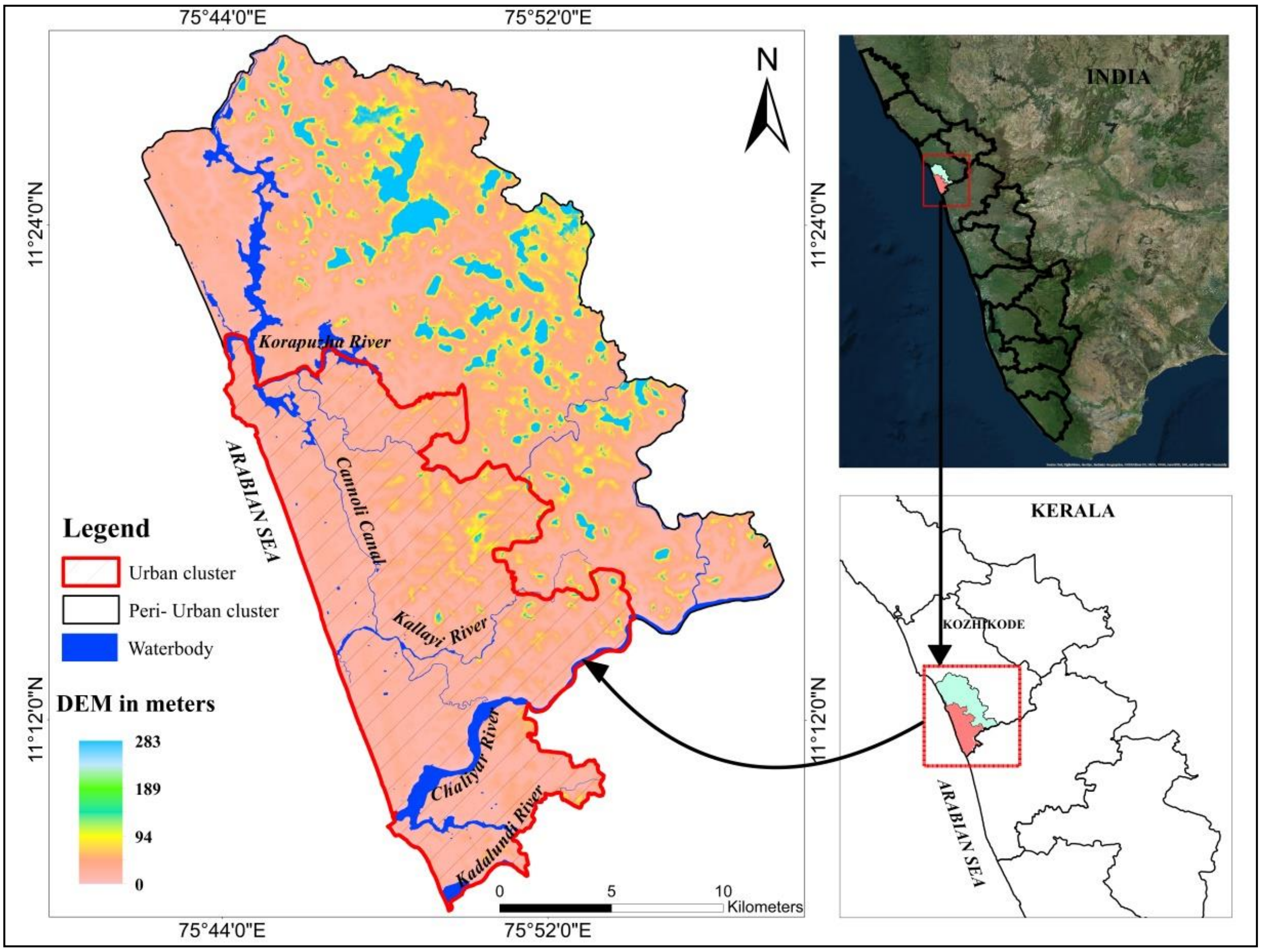

Figure 1.1. Basemap of the study area (urban & peri-urban cluster) with Digital Elevation Model

The peri-urban zone of the study area was covered an area of 312 km^2. Domestic water demand (in MCM/year) on urban and peri-urban area were prepared in accordance with census of India (1991-2011) report and environmental analysis report for Kerala Rural Water Supply and Sanitation (KRWSS) Project (2000) (Figure 1.2). The trend shown in figure 1.2 had been indicating that there is chances of merging some of peri-urban centres to urban in the near future.

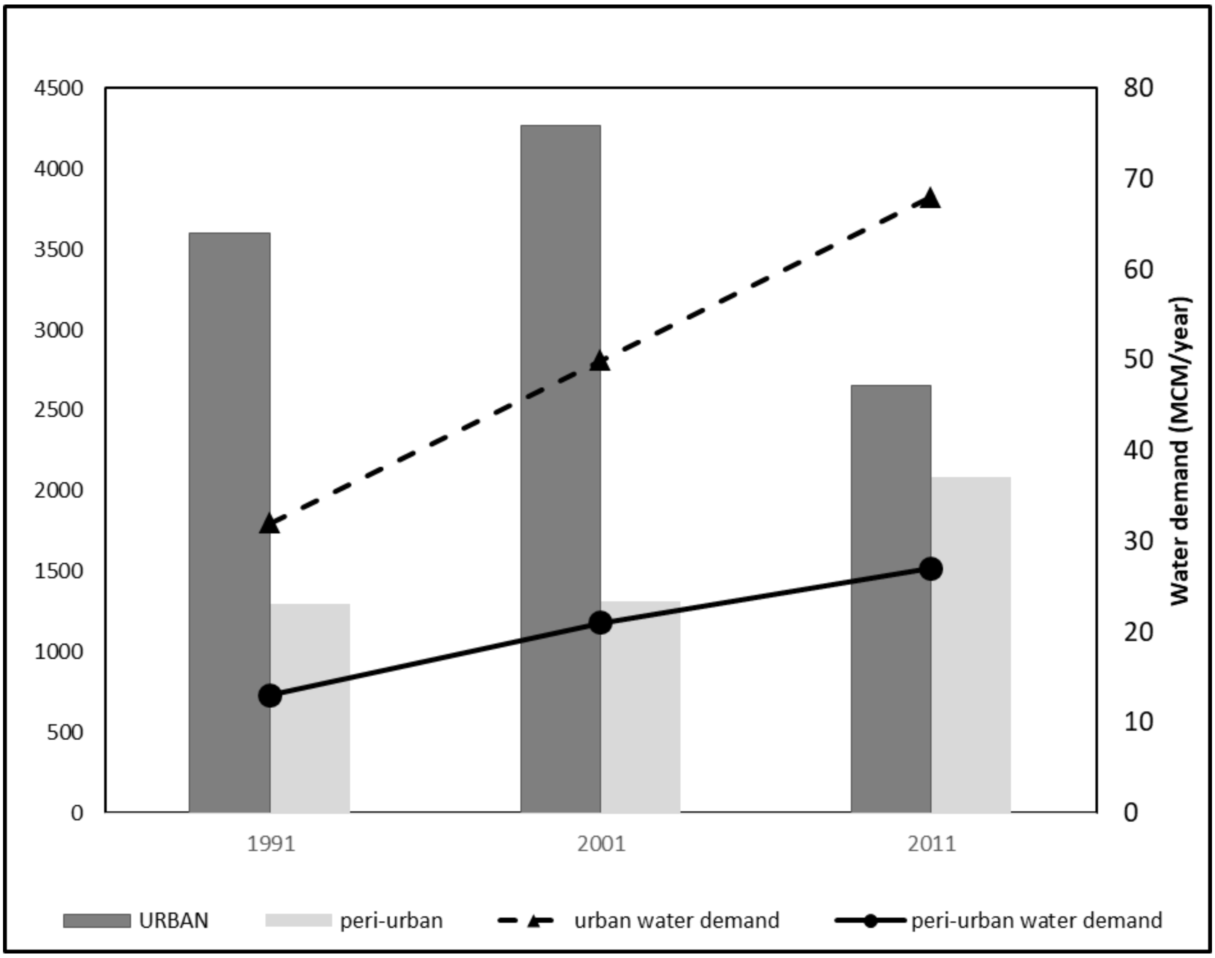

Figure 1.2. Decadal Population density along with domestic water demand in MCM/year for urban and peri-urban zone.

Plate 1.1 a & b. Polluted waterbodies in the study area

1.3.1. Regional geology

The study area is situated on the southern part of the peninsular shield having gently sloping terrain, from the Wayanad plateau to the east to the coastal plain in the west. It constitutes rolling midland and coastal terrain (Figure 1.3).

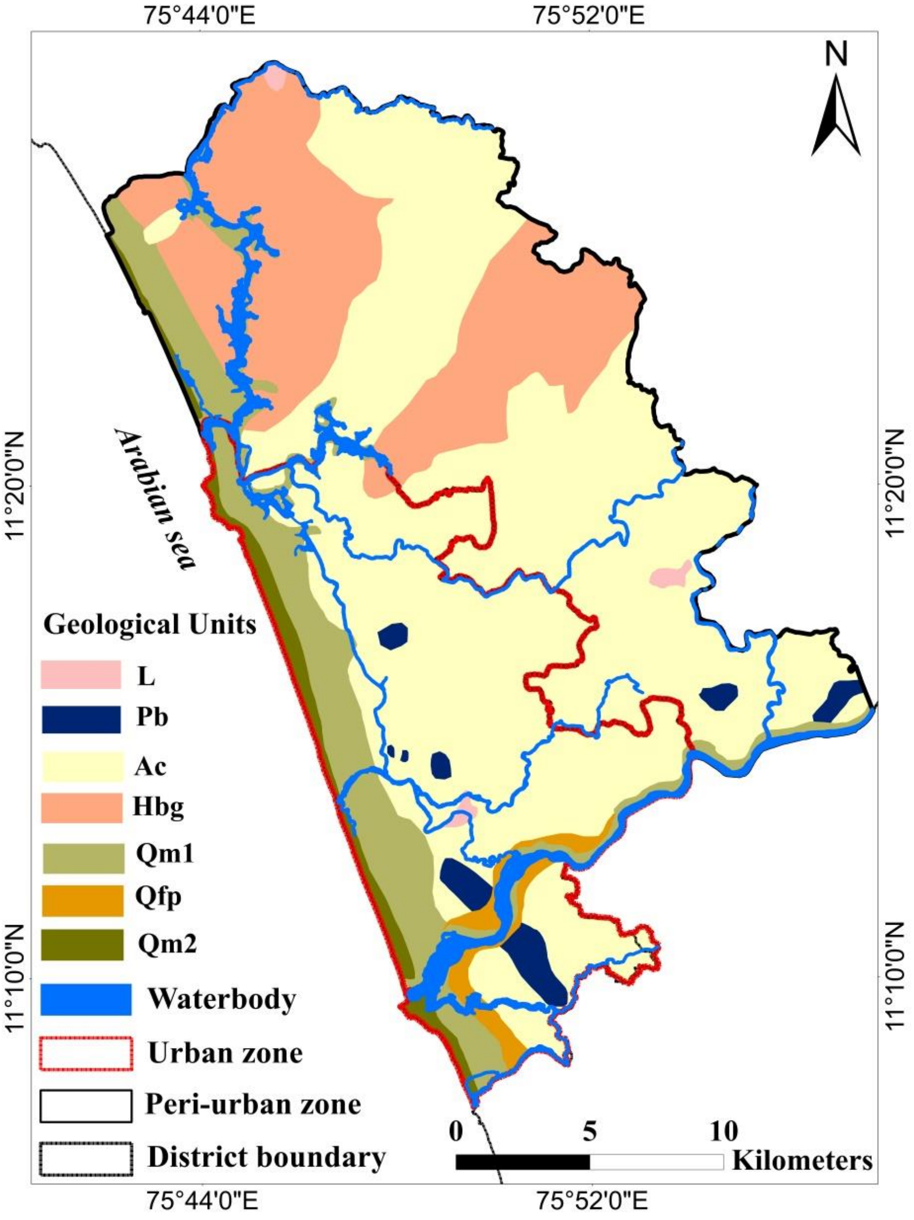

Figure 1.3. Geology map of the urban and peri-urban clusters of the study area (L-Laterite, Pb-Pebble bed, Ac-Charnockite, Hbg-Hornblende-biotite Gneiss, Qm1-Guruvayur formation, Qm2-Kadappuram formation(Marine), Qfp-Periyar formation (Fluvial))

The area can be divided into three geological belts viz. a linear NW-SE trending gneissic belt -along the middle extending from north to south, a Charnockite belt occupying large areas in the south, and a narrow coastal belt. The coastal plain is very narrow, 5-10 km wide, gently sloping with a maximum height of about 10m in the east. It comprises depositional landforms of marine, fluvial and fluvio-marine origin. There is a well-developed beach all along the coast with sea cliffs and rocky beaches near Quilandy, Elathur and Kappad.

Plate 1.2. Thick Laterite formation on the eastern part of the study area

The midland region is quite wide with elevations ranging from 30–300 mother region has undulating topography with numerous ridges, moderately sloping spurs, intervening valleys, flat and domal hills and broad valley floors, all alternating with laterite capped hummocks and narrow alluvial strips (Plate 1.2). The narrow coastal belt, with alluvial deposits, is a high potential aquifer with the depth of groundwater ranging from 0.3 to 3 m below ground level(mbgl) and yield of 50 lps. The midland region with thick laterite cover and the depth of water level varies from 5 m below ground level. The area occupies five different types of soil texture such as imperfectly drained-clay, moderately well drained-clay, moderately well drained-sandy, well-drained-clay, and well-drained gravelly clay. The majority of the study area is dominated by the well-drained-gravelly clay (Geological Survey of India, 2005).

1.3.2. Landuse/ landcover statistics

The standard image processing techniques were applied for the analysis of imageries- ResourceSat-1 & ResourceSat-2 (IRS-P6) LISS III (23.5m) satellites for the year 2005, 2010 and 2015 using ERDAS Imagine v.2014. The analysis was enabled to ascertain the probable landuse classes and have been refined based on ground truth data and detailed field reconnaissance. Overall accuracy for landuse/landcover classification has been found to be more than 90% and Kappa statistics was 0.89 for all the classified images.

Table 1.1. Statistics of landuse/landcover classes of the study area for years (2005, 2010 and 2015)

Landuse/landcover classes	Area (km^2)		
	2005	2010	2015
Waterbody	23.5	19.4	19.3
Vegetation	456.4	385.8	330.9
Builtup area	39.6	89.5	140.3
Others	5.5	30.2	34.5

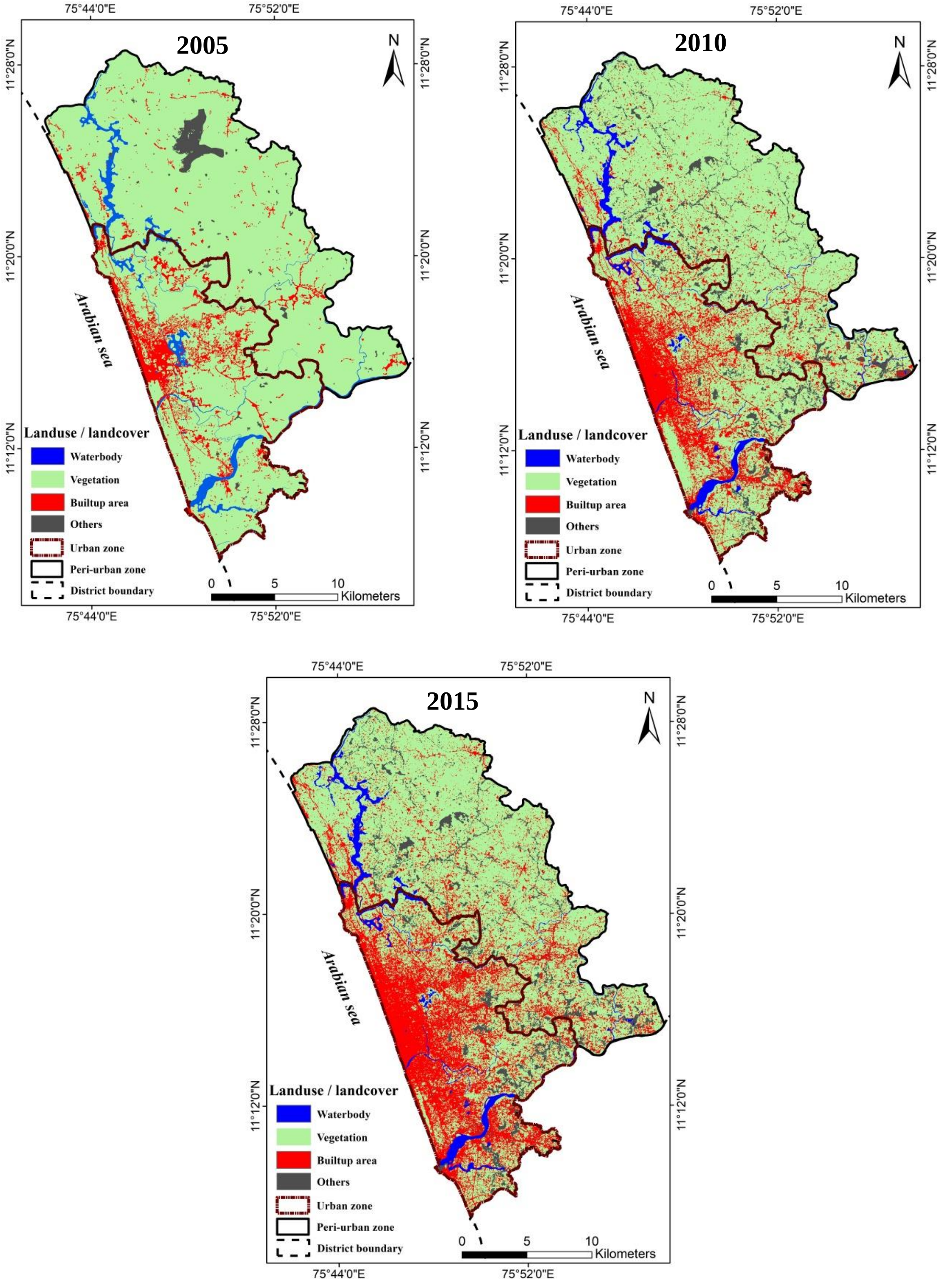

Figure 1.4. Landuse/ landcover map of urban and peri-urban clusters of the study area for years 2005, 2010 and 2015

Landuse/ landcover classes of the study area (Figure 1.4 a, b &c) with a special emphasize on three major classes such as waterbody, vegetation and Built up area depicted the gradual growth of built-up zone/impervious area such as houses, commercial buildings, industries, roads, etc. and decline in vegetation and water bodies. This implies that the land is being used for urbanization at a gradual rate. Statistics of landuse classes for three years was shown in Table 1.1.

1.3.3. Rainfall and other meteorological parameters

The urban and peri-urban clusters are in a humid tropical region with an average annual rainfall of about 3400mm. The climate of the area is divided into four seasons – summer, South West Tropical Monsoon period, North East Tropical Monsoon period and winter. Two monsoon seasons experienced by the study area are South-West and North-East monsoons. The southwest monsoon enters the coast in June and lasts till September and is the main cause of rainfall. About 20% to 25% of the annual rainfall is recorded in the month of November and December due to the northeast monsoon. Average annual rainfall pattern of the study area shown in figure 1.5 and the SW and NE monsoons mainly contribute with 82.77 % of the rainfall in the area. The month of June experiences maximum rainfall. The months of July, August and October also receive heavy rainfall. The minimum and maximum temperatures are around 23.5^{o}C and 34^{o}C. The temperature reaches its peak in the month of April and attains minimum in January. The relative humidity ranges from 74 to 92 % during morning hours and from 64 to 89% in evening hours.

The monsoon months record high humidity. The wind speed ranges from 8.1 to 12.6 km/h. The maximum wind speed is during April and minimum in November. The annual Potential Evapotranspiration (PET) is 1505.7 mm. The monthly PET ranges from 92.9 to 170.2 mm. The PET is less than the rainfall during May to November and hence the possibility of recharge to groundwater regime is more during these months (CGWB, 2013).

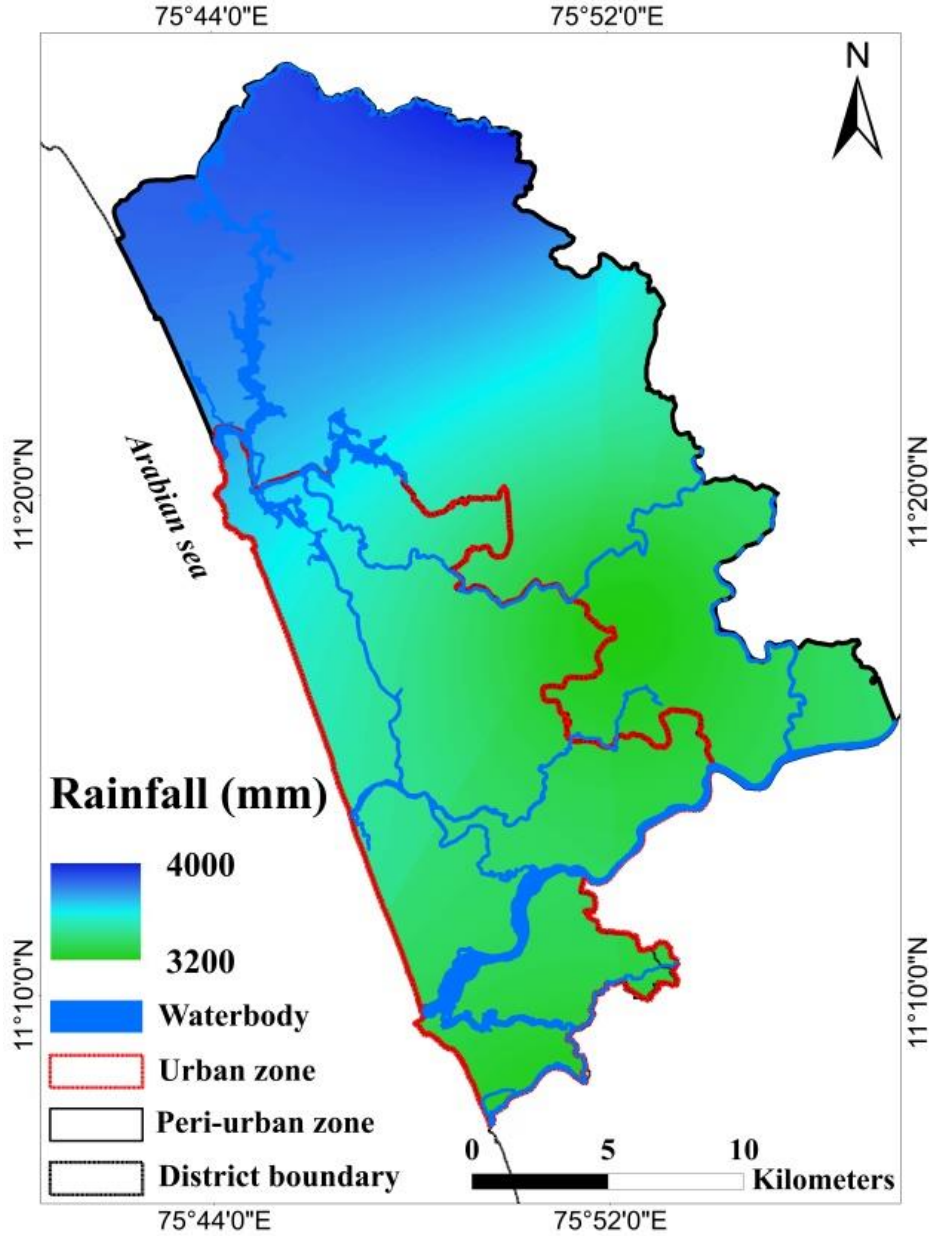

Figure 1.5. Rainfall pattern of the study area

1.4. Relevance of the study

Migration from rural to urban continuum has been causing significant menaces to urban aquifer system includes unscientific exploitation of aquifers, impermeabilization of aquifer recharge area, decline in groundwater level, pollutant attenuation from various point and non-point sources, etc. A root-level understanding of the processes that have been occurring in the flow regime enables to trace out the confronts of groundwater. Therefore, the study area selected for the work includes not only the urban zone but also the peri-urban zone which has the tendencies to reach the urban level impressions. While considering the urban growth pattern of the study area, there is an unscientific development visible in the fringe zone. Peri-urban zone is under pressure for further urban growth, but lack of infrastructure and developmental control inhibits the same. These unscientific development leads to conversion of agricultural lands, filling up of water bodies, low-lying marshy areas, and wetlands for urban needs (Figure 1.4).

Major environmental issues occurring in phreatic aquifers of urban and peri-urban zones of the study area are decline in water level, water scarcity, salinity ingress in coastal aquifers and water quality deterioration, etc. (CGWB,2013). Salaj et al. (2018 a) reported that groundwater sources found in various parts of the coastal stretch of Kozhikode are deteriorating in quality due to seawater intrusion and this event is mainly occurring in erosional coastal zones and densely populated urban areas through seepage movement and due to diffusion of seawater. Sources of major water pollutant in groundwater aquifers of Kozhikode may occur from failing septic systems, manure and fertilizer applications, mining, or anthropogenic activities (Harikumar and Chandran, 2013). Localised water pollution is prevalent in urban clusters in the study area. Unscientific *well* construction and maintenance, close proximity of latrines to well, septic tank effluents, infiltration of dissolved animal faecal matter have enhanced the risk of bacteria and other harmful microorganisms getting into shallow groundwater of the study area (Jesiya and Gopinath, 2019 a). Megha et al. (2015) studied groundwater contamination in rural village of Kozhikode and pointed out that present distances between wells and latrines coupled with the level of hygiene of the wells in the study are insufficient to prevent groundwater contamination. CGWB, (2013) was reported incidence of localized pollution from many areas in the Kozhikode district, especially due to effluent and sewage discharges from factories and hotels. Njelianparamba, a major solid waste dumping site situated in the study area where an average of 200 tonnes of waste per day is dumped in 18 hectares. Due to lack of proper solid waste treatment facility in this dump yard, leachates were discharged into water bodies and contaminated the shallow groundwater regime (Chonattu et al. 2016; Jaseela et al. 2016; Salaj et al. 2018 b).

Working Conditions of the primary canals, natural and human-made secondary drainages are in poor status to carry peak flows and there are missing links in existing drainage networks seen in the study area (Jesiya and Gopinath et al. 2019 a). It is mainly because of low coverage and lack of scientifically-designed drainage system (Amrut-Kozhikode-2017). Silts and waste materials were filled in most of the ponds and tanks (Plate 1.1 a & b) and due to this siltation ponds are not recharging to groundwater system (CGWB, 2013). The scenarios include direct discharge of wastewater directly into the ground/soil, leakages from improper drainage system were enhanced the groundwater contamination. An integrated approach of hydrogeochemical, isotopic and geospatial investigation on urban and peri-urban phreatic groundwater regime by considering existing environmental issues are requisite for identifying how groundwater behaves with the dynamics of urban development.

1.5. Objectives

The objectives of the study are as follows,

1. To evaluate the spatio-temporal variation of hydrochemical characteristics and inherent hydrogeochemical process of groundwater in phreatic aquifers of the urban and peri-urban clusters of Kozhikode district, Kerala, India.
2. To understand the characteristics and functioning of the groundwater system, identification of recharge mechanism and estimation of contribution of rain water to groundwater using environmental stable isotopes.

3. To demarcate the drinking water suitability zones of groundwater in two differently urbanized environments using GIS (Geographic Information System) based ANP (Analytical Network Process) technique.
4. To determine the aquifer vulnerable zones using customised Fuzzy- AHP (Analytical Hierarchy Process) DRASTIC-L model and delineate groundwater potential zones to set up a scientific GIS database of the urban-peri urban environment.

CHAPTER 2

MATERIALS AND METHODS

The materials and methodology section include four major subsections such as primary data collection (field reconnaissance and data collection), processing of water samples, secondary data gathering and finally integration of acquired information in the geospatial platform. The details of the materials and methodology and adopted for the study is as follows.

2.1. Primary data collection

2.1.1. Field investigations

Detailed field investigations were undergone in the study area and ensured that the groundwater sampling sites selected for the study were a true representation of the problem that tried to address in the study.

2.1.1.1. Identification and description of sampling sites

Based on the degree of urbanization, the study area boundary fixed to 525 km^2 and further divided into two zones ie, urban and peri-urban clusters (State Urbanization Report, 2012). Field visits were carried out to know the geological and environmental features of the area. During the initial field visit, SOI toposheet (1:50,000) and Google map of the study area were served as the basemap and location identifier. The sampling sites (Well points) located in various landuse classes and Landuse pattern (Figure 1.4) of the study area were identified using SOI Toposheet and google map which was ground-truthed in the field (figure 2.1). The sampling periods fixed as two cycles each having a pre-monsoon (March-April) and post-monsoon (November – December) sampling. Well locations were identified and demarcated using Garmin GPS unit.

2.1.1.2. Groundwater level measurements

A detailed well inventory of 85 observation wells (dug wells) i.e, 35 numbers from urban and 50 numbers from peri-urban (Figure 2.1), had done in pre and post-monsoon period of the years 2014 and 2015. Well inventories were demarcated using Garmin GPS unit. A detail well inventory questionnaire was prepared and the information relevant for the hydrogeological scenario of the study area were investigated. Physical dimensions of the wells, hydrogeological parameters such as depth to water level and total depth of well, type of well and well lining, nature of well (perennial/ seasonal) were inventoried as per the requirement.

2.2. Sampling and analytical techniques

2.2.1. Groundwater sampling for hydrochemical analyses

All geochemical decisions are based on the assumption that correct, reasonably accurate and reliable data availability. Sampling is one of the most basic and important aspects of water quality management. Sampling campaigns for geochemical and isotopic analyses were performed in pre and post-monsoon seasons as per standard methods illustrated in APHA (2012). Groundwater samples had been collected from 85 dug wells at a depth of 1.5 m to 13 m in the urban and peri-urban clusters of Kozhikode district during pre-monsoon and post-monsoon along with a maximum representation covering the entire study area (Figure 2.1; Plate 2.1 a & b). In situ, measurements of pH, electrical conductivity (EC) and TDS were performed using the portable multi analyzer kit.

Plate 2.1 (a &b) . Groundwater sampling from shallow aquifers / Open well

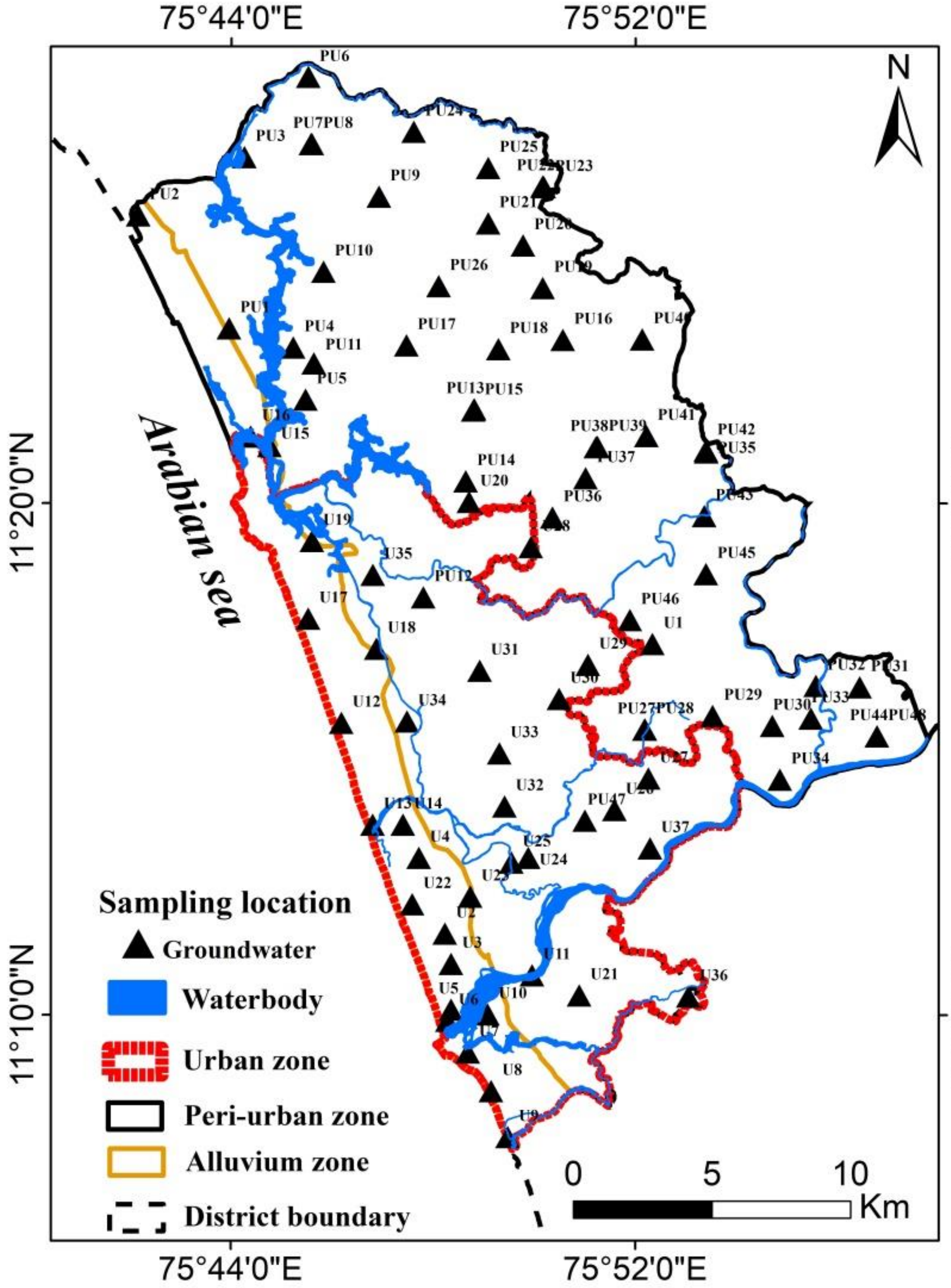

Figure 2.1. Sampling location map of the study area for hydrochemical study

2.2.2. Groundwater sampling for stable isotope analyses

Groundwater samples (42 Nos.) from urban and peri-urban phreatic aquifer were collected both in pre and post-monsoon seasons of the year 2014 and 2015 and stored in High Density Polyethylene bottle of 60 ml (HDPE) capacity. Sampling was done after the confirmation that the dug wells were not stagnant and was being used daily.

Therefore 42 number of groundwater samples which are more suitable for stable isotope studies, were selected from the total 85 number of observation wells. The samples were collected from the bottommost layer using the Standard Water Sampler (Ruttner 2L). After opened the sampler lowered into the water by rope and upon reaching the bottommost depth the messenger mechanism was released and closes the lids of the sampling tube. HDPE bottles were closed tightly after sample collection in order to avoid isotope exchange with air moisture. Temperature for each water samples was measured by dipping a built-in thermometer in the sampler. A discharge cock at the lower lid opened and collected the sample to the specified bottles. River water samples (5 Nos) from both mid land and low land streams were collected in the same manner.

2.2.3. Rainwater sampling for stable isotope analyses

Two rainwater sampling unit for rainwater collection established at the selected urban (low land) and peri-urban (mid land) zones of the study area. A photograph of rainwater collection unit was shown in plate 2.2.

2.2.4. Groundwater sampling for bacteriological analyses

Groundwater samples (42 nos) which are selected from the total 85 no of observation wells were collected and transferred to 100ml sterile bottles. Collected groundwater samples were stored in an ice-cold condition and subjected to bacteriological analysis immediately.

Plate 2.2. Rainwater collection established for isotope sampling

2.2.5. Hydrochemical analyses

The groundwater samples were analyzed at the Central Water Quality laboratory, CWRDM for the physical, chemical and biological characteristics of water samples following the standard procedures recommended by American Public Health Association (APHA), 2012. Groundwater samples were collected in pre-cleaned plastic polyethylene bottles for major elements after the stabilization of pH, and electrical conductivity. Prior to sample collection, the plastic bottles were rinsed two to three times with the respective groundwater sample. Cations and anions were determined following the standard procedures recommended by American Public Health Association (APHA, 2012), standard methods for examination of water and waste water. The procedure for these analyses is stated below.

The alkalinity of water can be determined by titrating the water sample with Sulphuric acid of known values of pH, volume and concentrations. Titration with Ethylene Diamine Tetra Acetic acid (EDTA) solution using Eriochrome Black-T (EBT) as an indicator is used for the measurement of Hardness in water. Since the action of the indicator and the formation of the metal EDTA complex is governed by pH. Hence the pH of the solution is kept nearly constant by adding a basic buffer NH_4OH- NH_4Cl Buffer solution (pH~ 9-10).

The quantity of calcium in the water will be determined by titrating water sample with a standard EDTA of known volume and concentration. Based on the stoichiometry of the reactions and the number of moles of EDTA required to reach the endpoint, the concentration of calcium content in water is calculated. 1 mL of NaOH is used as a buffer. An indicator, Murexide (ammonium purpurate) which combines only with calcium is used. The indicator imparts a pink colour to the solution while there are calcium ions that have not complexed with EDTA.

Magnesium hardness is obtained by checking the difference between Calcium hardness and Total Hardness. Argentometric titration is used for the estimation of chloride in water. Both sodium and potassium were analyzed using the Systronics flame photometer 128. Prepare a blank and sodium calibration standard, in any of the applicable ranges, 0-100, mg Na/L.

The turbidimetric method of measuring sulphates is based upon the fact that barium sulphates tend to precipitate in a colloidal form of uniform size and that this tendency is enhanced in presence of sodium chloride, hydrochloric acid and glycerol. The absorbance of the barium sulphates formed is measured by a spectrophotometer at 420 nm and the sulphates ion concentration is determined by comparison of the reading with a standard curve. Standard solutions for the above analysis were prepared from the respective salts of Analytical Reagent grade. The concentration of dissolved ions was expressed in milligrams per litre (mg/l) and the analytical precision for the observations were measured through charge balance error (in %) calculation (Lewis, 1981) by converting the ion concentrations into equivalents per million (meq/l) and each was found within the factor of reliability (+ 5%).

Scatterplots, cross plots, piper diagram, box plots and thematic maps were used as tools for addressing and characterizing the inherent hydrogeological processes in the aquifer system. Graphical plots and Piper diagram were used to analyse and represent the statistical distribution of hydrochemical facies.

Multivariate statistical analysis was used to illustrate the origin of solutes in groundwater and enable to classify the groundwater samples in accordance with its inherent geochemical processes. It enables to distinguish the major driven factors whether it is natural/anthropogenic controlling the groundwater chemistry. Multivariate statistical analysis such as factor analysis, Mann-Whitney-U test and Agglomerative Heirarchial Cluster analysis (AHC) were performed in XLSTAT software. Factor analysis was performed using varimax rotation method. The varimax rotation makes the interpretation easier by maximizing the variance of the squared factors loadings by column. Sampling adequacy checked with the Kaiser-Meyer-Olkin(KMO) test. Eigenvalues and Eigenvectors were derived through the Varimax rotation process and factors with eigonvalue > 1 were selected for further factor processing. The number of variables were minimized to factor loadings such as high, medium and lower loading and thus initiated the interpretations (Davis and Sampson, 1986). Agglomerative Hierarchical Cluster analysis (AHC) an exploratory data mining technique were performed to assemble the observed data into clusters in such a way that groundwater belonging to the same class are more similar to one another than water from other clusters.

The analysis run with Ward's method and (Belkhiri and Narany, 2015) Euclidean Distance as a measure of similarity. Center/reduce option were chosen to avoid the influence of scale effect on clustering.

2.2.6. Bacteriological analyses

The bacteriological investigation was done in terms of Most Probable Number (MPN) of Total coliform and faecal coliforms (APHA). The bacterial measurement included total coliform count (TCC), faecal coliform count (FCC) and *E. coli* and as per standard method for water analysis. Total coliform, faecal coliform counts were appraised and documented in Most Probable Number units per 100 ml (MPN/100ml). The method used in bacteriological analysis is MTD Technique (Multiple Tube Dilution Technique). As per Bureau of Indian Standards (BIS), 2012 drinking specifications, E.coli and faecal coliform bacteria should not be detectable in 100 ml of sample.

2.2.7. Stable isotopic analyses

Stable oxygen ($\delta^{18}O$) and hydrogen (δ D) isotopes were measured after the equilibration with a fixed amount of purified tank CO_2 and Pure H_2 gases respectively. Thus, equilibrated CO_2 (Epstein & Mayeda, 1953) and H_2 (Horita,1988; Brand,1996) gases analyzed in Isotope Ratio Mass Spectrometer (IRMS) at the Physical Research Laboratory (PRL) to obtain the $^{18}O/^{16}O$ and D/H ratios.

Expressing the stable isotope data is as natural abundance which is reported as delta values, δ in units of per mil (mil = 1000) written as ‰. It is a relative measurement made against a laboratory's own reference material, also known as working standard which is calibrated against an international standard. The delta values are calculated from measured isotope ratios as,

$$\delta\ (‰) = \frac{Rsample - Rstandard}{Rstandard}\ X\ 100$$

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

Thus for ^{2}H,

$$\delta\ (‰) = \frac{Rsample - Rstandard}{Rstandard}\ X\ 100$$

$$\delta^{2}H = \frac{[(^{2}H/H)_{sample} - (^{2}H/H)_{standard}]}{(^{2}H/H)_{standard}}\ X\ 1000$$

Generally, δ units are quoted relative to an internationally recognized standard which is arbitrarily set to 0‰. For ^{18}O and ^{2}H, this is Vienna Standard Mean Ocean Water (V-SMOW). The International Atomic Energy Agency (IAEA, Vienna, Austria) and the National Institute of Standards and Technology (Washington, DC, USA) supply the above standards.The analytical precision of isotopic measurements was ±0.1% for $\delta_{18}O$ and ±1% for δD.

2.3. Secondary data collection

Details of secondary data sets required for the baseline study were illustrated in Table 2.1 and other data sources required for groundwater vulnerability assessment (DRASTIC-L) and groundwater potential zone assessment were given in Table 2.3 and Table 2.5.

2.3.1. Data sources

Details of the data sources used in the study were given in Table 2.1. All GIS data used in this study are classified as topographic data, collateral data and thematic data. The topographic and thematic data are classified as spatial data whereas the collateral data as attribute data.

2.4. Geospatial analyses

Geospatial analyses employed in the study includes (i) satellite data processing using image-processing techniques (eg: landuse/landcover map, geomorphology) (i) generation of topographic maps showing physical characteristics of the study area (eg: base map, road network, drainage, physiography, etc) (iii) generation of thematic maps (eg: geology, soil) (iv) geostatistical analysis (v) overlay analysis (vi) digital spatial database generation using ArcGIS 10.5.1 platform etc. Details of various geospatial methods used in the study given in 2.4.1, 2.4.2 and 2.4.3. sections of chapter 2.

Table 2.1. Data sources used for baseline investigations

Data Type	Features	Source of acquisition	purpose
Topographic Data Base map	Rivers/water bodies, major roads, railways.	Toposheets of Survey of India.	To delineate the administrative boundary of various administrative units and also to identify various types of water bodies, different categories and grades of roads and railways.
Collateral data Demographic data	Population density	Bureau of Economics and Statistics Division	To identify the distribution, density, growth of population for different locations and for different periods.

2.4.1. Geostatistical analysis

Spatial distributions of the water quality parameters (Table 2.2) were established with the support of various analysis tools in ArcGIS Environment. Geostatistical vizard endowed a user-friendly platform for the interpolation of field observations (point features). Exploratory Data Analysis (EDA) were done using Geostatistical Wizard in ArcGIS v.10.5.1 to check the distribution of point features (Aquifer location). Normal Q-Q plots for all parameters were performed to analyse the asymmetry on its spatial distribution. After the analysis, spatial interpolations of physico-chemical and bacteriological parameters were performed to prepare the spatial data using Inverse Distance Weighted (IDW) technique of Geostatistical Analyst tool in ArcGIS 10.5.1.

2.4.2. Groundwater suitability analysis

The groundwater suitability analysis for urban and peri-urban clusters was carried out through an integrated application of Geographic Information System (GIS) and Multi Criteria Decision Making (MCDM) technique. The analysis involves three steps, viz establishment of Groundwater Quality Index (GWQI) parameters, deriving normalized weights using ANP and preparation of Groundwater Suitability Map. The methodology employed for groundwater suitability analysis was given in the flow chart (Figure 2.2). Range of Water quality parameters for quality ratings and ANP analyses were determined based on Bureau of Indian Standards (BIS 2012) and World Health Organization (World Health Organization 2011) for drinking water (Table 2.2). ANP model building for met the goal of Groundwater Quality Index (GWQI) estimation was established through commercially available Super Decisions v.3 software. The SuperDecisions is the software that implements AHP and ANP and was developed by the team of the creator of the method, Thomas Saaty (www.superdecisions.com). Normalized weights derived after pairwise comparisons of each groundwater quality parameter within and between parameters and its were input to each raster data of the factors using reclassification method and all these factors were integrated with weighted sum overlay analysis in the spatial analyst tool of Arc GIS 10.5.1. The resultant raster data with GWQI values (raster values) of the urban and peri-urban clusters were divided into four classes such as highly suitable, suitable, moderately suitable and unsuitable zone according to the drinking water suitability. A detailed discussion on GWQI estimation and suitability assessments were given in chapter 5.

Table 2.2 Drinking water specification with respect to Bureau of Indian Standards (BIS 2012) and World Health Organization (WHO 2011)

Parameter	**BIS Standards (2012)**	**WHO Standards(2011)**	**Water Quality status**
Physical Parameter			
pH	6.5-8.5	6.5-8.5	Acceptable Limit (AL) as per BIS
	No Relaxation		Permissible limit in the absence of alternate source (PL) **as per BIS**
Electrical conductivity (µS/cm)	-	1500	PL
TDS (mg/L)	500	500	AL
	2000		PL
Chemical Parameter			
Sodium (mg/L)	-	200	PL
Potassium (mg/L)	-	12	PL
Calcium (mg/L)	75	75	AL
	200		PL
Magnesium (mg/L)	30	50	
	100		
Chloride (mg/L)	250	250	AL
	1000		PL
Sulphate (mg/L)	200	250	AL
	400		PL
Total Alkalinity (as CaCO3), mg/L	200	500	AL
	600		PL
Total Hardness (as CaCO3), mg/L	200	-	AL
	600		PL

Biological Parameter			
Bacteriological quality	Detectable		Must not be detectable in any 100 ml sample. In the case of large supplies, where sufficient
	Non-Detectable		

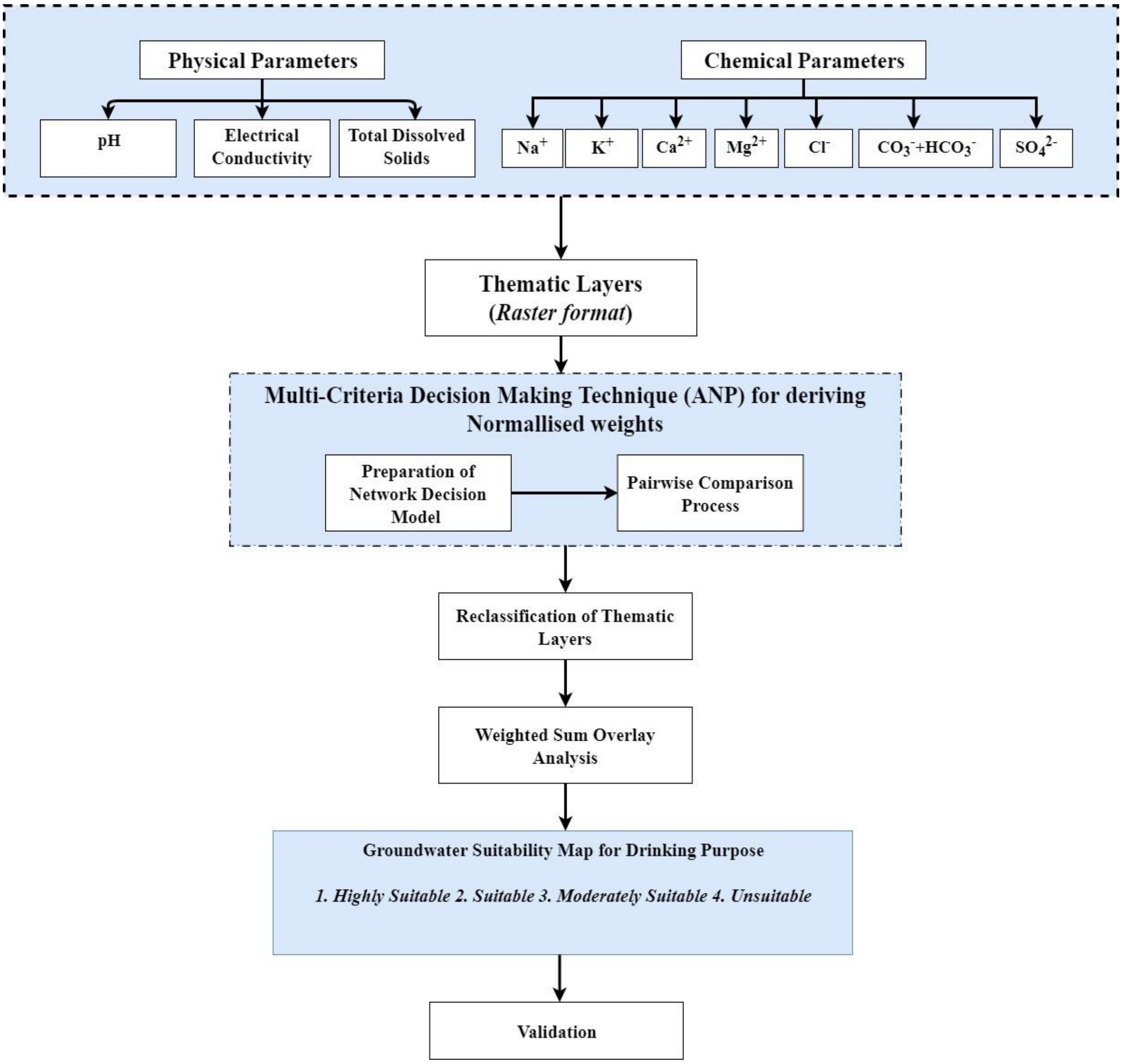

Figure 2.2. Flow chart showing methodology for groundwater suitability zonation using hydrochemical parameters

2.4.3. DRASTIC-L vulnerability analysis

The word "DRASTIC" is an acronym abbreviated for all the geological and hydrological factors which control the groundwater flow into through and out of an area (Sener and Sener, 2015). These are **D**epth to water table (D), net **R**echarge (R), **A**quifer media (A), **S**oil media (S), **T**opography (T), **I**mpact of vadose zone (I) and hydraulic **C**onductivity (C). The study area threatened with various impacts from the urbanization and therefore the existing DRASTIC model was not enough to explain those impacts in vulnerability assessment. Hence land use/landcover (**L**) of the study area was introduced as an additional parameter in the groundwater vulnerability analysis. Computation of aquifer vulnerability scores for the urban and peri-urban environment was performed using a FAHP (Fuzzy-Analytical Heirarchial Process)-GIS based DRASTIC-L vulnerability Index method. The method involves three steps, viz preparation of geo-database of DRASTIC-L parameters, the relative ranking of these features through numerical ranking method-Fuzzy Analytical Hierarchical method (FAHP) and spatial and non-spatial integration through ArcGIS v.10.5.1. A flow chart shown in figure 2.3 illustrated the methodology for FAHP-DRASTIC-L method.

2.4.3.1. Preparation of geo-database of DRASTIC-L parameters

Data sources of DRASTIC-L parameters which were used for aquifer vulnerability assessment in urban and peri-urban clusters of the study area given in Table 2.3. Geographical Information system endowed a platform for converting spatial and non-spatial data sets in various formats from various sources into a geo-referenced digital format. A series of geo-processing functions such as digitization, geostatistical analysis, etc performed in GIS environment. Geology, hydrogeology, Soil permeability thematic data were derived using a series of geo-processing functions on the corresponding data sources. Point features such as well depth, rainfall layer and hydraulic conductivity were interpolated using inverse distance weighted (IDW) algorithm in GIS. Landuse/landcover data were obtained from the supervised classification of IRS P6, LISS III (23.5m Spatial resolution) satellite data. Slope (in %) analysis was performed with SRTM DEM (30 m) data by means of spatial analyst tool of ArcGIS 10.5.1.

Table 2.3. Data sources for the preparation of DRASTIC-L model parameters

Data Type	**Source**	**Data format**	**Scale**
Groundwater level	Field Investigation	Vector	-
Water level fluctuation	Field Investigation	Vector	-
Slope	SRTM DEM	Raster	30 m
Soil Permeability	Department of soil survey and soil conservation, Kerala	Vector	1: 50000
Rainfall	Indian Meterological Department (IMD)	Raster	-
Geology & Hydrogeology	Geological Survey of India, Hyderabad	Vector	1:250000
Litholog data	Central Groundwater Board, Thiruvananthapuram	Vector	-
Soil texture	National bureau of Soil Science(NBSS), India	Vector	1: 50000
Hydraulic conductivity data	Central Groundwater Board, Thiruvananthapuram INDIA-WRIS- http://www.india-wris.nrsc.gov.in/	Raster	-
Landuse/landcover	Satellite Data (IRS-P6 , LISS III) (National Remote Sensing Centre) *Path/Raw- 99/66*	Raster	24m

2.4.3.2. Deriving numerical index using Fuzzy-AHP method

The hierarchy model network for eight hydrogeological parameters to evaluate groundwater vulnerability and, namely depth to water (D), net recharge (R), aquifer media (A), soil media (S), topography (T), impact of vadose zone (I) , conductivity of aquifer (C) and landuse class (L) were created using FuzzyAHP v 3.1. The FuzzyAHP is a web application that makes it possible to evaluate alternatives by classical AHP method or its version suitable for the fuzzy environment. Besides solving classical (fuzzy) MCDM (multiple-criteria decision-making) problems, it can be also used for group decision-making and decision-making under risk (http://fuzzymcdm.upol.cz/fuzzyahp/CriteriaList).

Each DRASTIC-L parameters assigned a subjective ranking of 1-9 based on expert's opinion and from relevant scientific outcomes. Ranking 1 assigned for components with least contaminant potential and 9 assigned for highest contaminant potential. These judgments/scores further undergone Fuzzy-AHP (Analytical Hierarchical Process) for determining a composite normalized index value. Apart from AHP, in FAHP method pairwise comparison of criteria and sub-criteria elements were expressed with Triangular Fuzzy Numbers (TFNs). TFNs enable to avoid vagueness, imprecision and uncertainty of the linguistic scale.

The linguistic scale of importance assigned for pairwise comparisons of one attribute over another in the Fuzzy AHP method (Table 2.4). The numbers 1/2, 3/2, 1, 5/2, 2, 7/2, 3, 7/2, 4 and 9/2 were used as fuzzy scaling ratios corresponding to the strength of potential for one element over another with interval values instead of crisp numbers. The criteria and sub-criteria with varying rate of potential to vulnerability (different scale of importance) assigned with abovesaid TFNs (Table.2.4) and transformed into a pairwise comparison matrix. The ratings associated with each factor were discussed in detail in chapter 5.

Table 2.4. Linquistic scale of importance for pairwise comparisons

Scale of importance	Traingular Fuzzy scale	Triangular fuzzy reciprocal scale
Just equal	(1,1,1)	(1,1,1)
Equally Important	(1/2, 1,3/2)	(2/3, 1, 2)
Weakly more important	(1, 3/2, 2)	(1/2, 2/3, 1)
Moderately more important	(3/2, 2, 5/2)	(2/5, 1/2, 2/3)
Strongly more important	(2, 5/2, 3)	(1/3, 2/5, 1/2)
Very strongly more important	(5/2, 3, 7/2)	(2/7,1/3, 2/5)

Pairwise matrix was established using prior knowledge of the goodness-of-fit and the pairwise comparison matrix evaluated for eight DRASTIC-L parameters and its sub–classes were discussed in chapter 6 (Tables 6.1, 6.2 b, 6.3 b, 6.4 b, 6.5 b, 6.6 b, 6.7 b, 6.8 b and 6.9). Finally, the defuzzification processes were carried out to obtain normalized criteria weights/composite values from fuzzy membership values. Normalized weights derived after FuzzyAHP were integrated into corresponding raster layers using reclassification analysis and carried out fuzzy overlay analysis in ArcGIS. The equation for calculating the GroundWater Vulnerability Index (GWVI) is as follows,

$$\mathbf{GWVI = DrDw + RrRw + ArAw + SrSw + TrTw + IrIw + CrCw + LrLw}$$

where Dr is the rating for the depth to water table and Dw is the weight assigned to the depth to water table. Rr and Rw are the rating and the weight for net aquifer recharge respectively. Ar is the rating assigned to aquifer media and Aw is the weight assigned for the same. Sr is the rating for the soil media and Sw the weight for the soil media. Tr and Tw are the rating and the weight assigned to topography. Ir is the rating assigned to impact of vadose zone and Iw is the weight assigned to impact of vadose zone. Cr is the rating for rates of hydraulic conductivity and Cw the weight given to hydraulic conductivity. Lr is the rating for rates of landuse classes and Lw is the weight given to landuse classes. Eight data layers prepared in ArcGIS and converted to raster format with a uniform grid size of 25m X 25 m.

2.4.3.3. Sensitivity analysis

Aquifer vulnerability assessment requires validation to reduce subjectivity in the selection of rating ranges and weight and to increase reliability (Leal and Castillo, 2003). Single parameter sensitivity analysis (Napolitano and Fabbri, 1996) was performed to evaluate the resultant groundwater vulnerability and potential maps. The sensitivity analysis was evaluated the impact of each of the parameters on the groundwater vulnerability index. The theoretical weight assigned in the model were compared with the effective weight of each parameter by the given formula (Napolitano and Fabbri, 1996):

$$\mathbf{W = [P_r * P_W] * 100/V}$$

Where W is the effective weight of each parameter, P_r is the rating value of each parameter, P_w is the weight of each parameter and V is the overall vulnerability index. Validation of groundwater vulnerability map was performed with groundwater suitability index map and further parameter sensitivity was checked with statistical student's t-test.

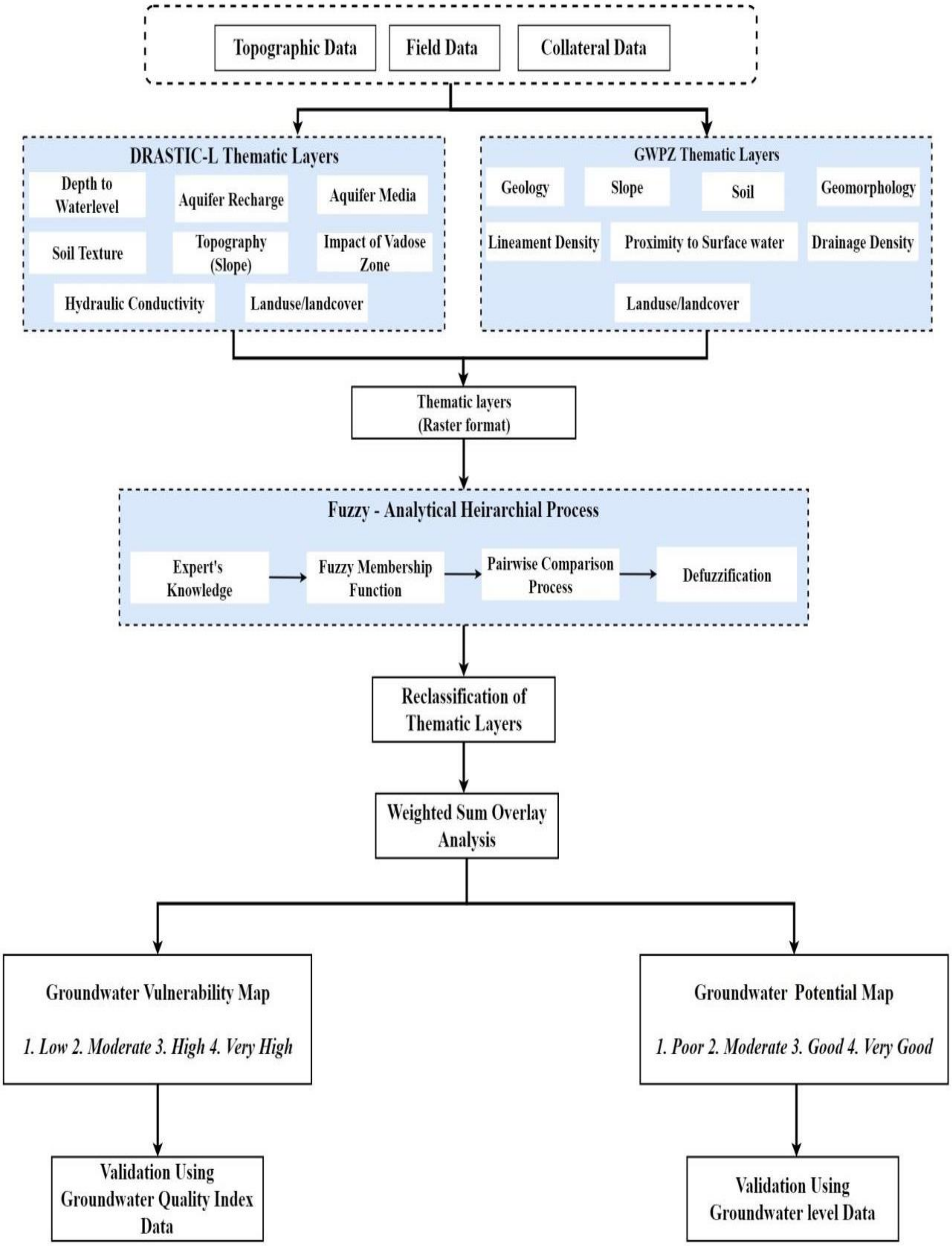

Figure 2.3. Flow chart showing GIS based FAHP methodology for groundwater vulnerability and potential analysis

2.4.4. Groundwater potential analysis

The factors influencing groundwater occurrence of a geographical area are Geology, geomorphological units, lineament and drainage density pattern, landuse/ landcover classes, soil types and slope factor. The groundwater potential zone (GWPZ) mapping were performed in the study using an integrated approach of remote sensing & GIS based fuzzy Analytical Heirarchial process (FAHP). The details of the data used in the study given in table 2.5 and a flow chart designed for GIS & remote sensing based FAHP method given in figure 2.3. The analysis was involved three steps, viz preparation of geo-database of factors influencing groundwater potential of an area, relative ranking of these features through numerical ranking method-Fuzzy Analytical Hierarchical method (FAHP) and spatial and non-spatial integration through ArcGIS 10.5.1(Figure 2.3).

2.4.4.1. Preparation of geo-database for groundwater potential assessment

Data sources of parameters used for potential assessment in urban and peri-urban clusters of the study area are given in Table 2.5. Geology, hydrogeology and soil texture thematic data were derived using a series of geo-processing functions such as georeferencing, digitization, etc. on the corresponding data sources (Table 2.5). Landuse / landcover classess of the study area was derived from IRS-LISS-III data. Drainage pattern was extracted from the 1:50,000 scale survey of India topographical maps and lineaments were delineated from thematic services of Bhuvan web portal. Further, line density analysis was carried out to prepare the lineament and drainage density data in km per square kilometre area. Slope (in %) analysis was performed with SRTM DEM (30 m) data by means of spatial analyst tool of ArcGIS 10.5.1. Finally proximity to surface water bodies was generated through buffer analysis using proximity tool of Analysis tools of Arc GIS 10.5.1.

Table 2.5. Data sources for the preparation of groundwater potential analysis

Data	Data type	Source of aquisition	Scale	Purpose
Geomorphology	Vector	Landuse Board, Govt of Kerala	1:50000	Landforms
Geology	vector	Geological survey of India, Hyderabad	1: 250000	Geological units/geological formation
Drainage	Raster	Toposheets of Survey of India	1:50000	Drainage density Proximity to surface water bodies
Lineament	Raster	Bhuvan	1:50000	Lineament density
DEM	Raster	SRTM	30m	Elevation data and Slope in %
Soil	Raster	National bureau of Soil Science (NBSS), India	1:50000	Soil Texture Soil permeability
Landuse/landcover	Raster	Satellite Data (IRS-P6 , LISS III) (National Remote Sensing Centre) *Path/Raw- 99/66*	24m	Landuse/landcover classes

2.4.4.2. Groundwater Potential Index (GWPI)

Groundwater potential index is a dimensionless quantification index was calculated using the ratings and weights values via fuzzy-AHP method for each of the controlling parameters. The equation used for generating groundwater potential score as Groundwater potential Index (GWPI) was given as follows,

$$\mathbf{GWPI = GrGw + GMrGMw + LDr\ LDw + DrDw + \quad TrTw + PrPw + SrSw}$$

where Gr is the rating for the geology of the study area, Gw is the weight assigned to the geological units and GMr and GMw the rating and the weight for geomorphology respectively. LDr is the rating assigned to lineament density and LDw is the weight assigned to lineament density. DDr is the rating for the drainage density and DDw is the weight assigned to drainage density and Sw and Sr the weight and rating for the soil texture respectively. Tr is the rating for topography (slope) and Tw is the weight assigned to topography. Seven data layers prepared in ArcGIS were converted to raster format with a uniform grid size of 25m X 25m resolution. Normalized weights were integrated into corresponding raster layers using reclassification analysis and carried out fuzzy overlay analysis in ArcGIS environment.

CHAPTER 3

HYDROGEOCHEMICAL CHARACTERISATION OF PHREATIC AQUIFERS IN URBAN AND PERI-URBAN CLUSTERS

Introduction

Groundwater geochemistry explores the processes controlling the chemical composition of groundwater and groundwater quality, which influences the use of this natural resources (Toth, 1979). The quality of groundwater may change during its exploration, or it may be affected by human activities and the impact of which is not always immediately evident (Goudie, 2018). Changes in groundwater chemistry caused by natural (geogenic) and anthropogenic process overlap will make the investigation of groundwater contamination more complicated particularly in cases of early phase groundwater contamination (Dragon, 2002, 2006). Monitoring and analysis of groundwater sources will provide information on characteristics of water and regular change in water quality. It will also enable to evaluate emerging water quality problems, understand the possibility of different pollutants, determine nature and extent of pollution control and treatment option for polluted water (Freeze and Witherspoon, 1967, Datta and Tyagi, 1996; Adimalla and Venkatayogi, 2018; Mostaza-Colado et al. 2018). Therefore, chapter 3 were attempted to establish a detailed evaluation of spatio-temporal variation of hydrogeochemical aspects , understanding of inherent hydrogeochemical processes in urban and peri-urban phreatic aquifers and creating a database which are useful for society as well as for the planning of water resources development of the region.

3.1. Spatio-temporal variations of hydrogeochemical parameters

Urban and peri-urban groundwater samples were collected and analysed for both pre-monsoon (March-April) and post-monsoon (November-December) seasons of years 2014 and 2015. Seasonal statistics of physico-chemical parameters were showed less significant variations in between two years (Table 3.1 a-d), therefore further spatio-temporal and statistical studies were carried out with hydrochemical data of groundwater from the year 2015 (Table 3.2 a-d).

3.1.1. Physico- chemical parameters

3.1.1.1 pH

pH value of urban alluvial phreatic aquifer ranged from 5.3 to 8.1 in pre-monsoon and that of post-monsoon season, value varied from 5 to 8.3 (Table 3.1 a). In urban lateritic aquifers pH value ranged from 4.6 to 7.3 in pre-monsoon and that of post-monsoon season, value varied from 4.5 to 7.1 (Table 3.1 b). pH value of peri-urban alluvial phreatic aquifer ranged from 5.2 to 5.8 in pre-monsoon and that of post-monsoon season, value varied from 5.6 to 8.4 (Table 3.1c). In peri-urban lateritic aquifers pH value ranged from 4.9 to 7.5 in pre-monsoon and that of post-monsoon season, value varied from 4.8 to 6.9 (Table 3.1 d).

Spatial distribution of pH value for both urban and peri-urban phreatic aquifers were showed that majority of the study area with a pH range of 5.5- 6.5 during both pre-monsoon (Figure 3.1 a) and post-monsoon seasons (Figure 3.1 b). In the entire study area, acidic behaviour (pH value < 5.5) of groundwater gets slightly changes to a neutral pH range from pre-monsoon to post-monsoon season. pH range of > 7.5 were observed in urban and peri-urban alluvial aquifers during post-monsoon confirmed the same. pH value of < 5.5 visible in north-west and south-east part of peri-urban zone during pre-monsoon were changed to a pH range of 6.5-7.5 and >7.5 in post-monsoon. The acceptable range of pH in water prescribed for drinking purpose by BIS 2012 and WHO (2011) is 6.5 to 8.5. Spatial distribution of pH shows that groundwater from the majority of the study area falls beyond the acceptable limit of BIS and WHO standards (6.5 to 8.5) during both seasons.

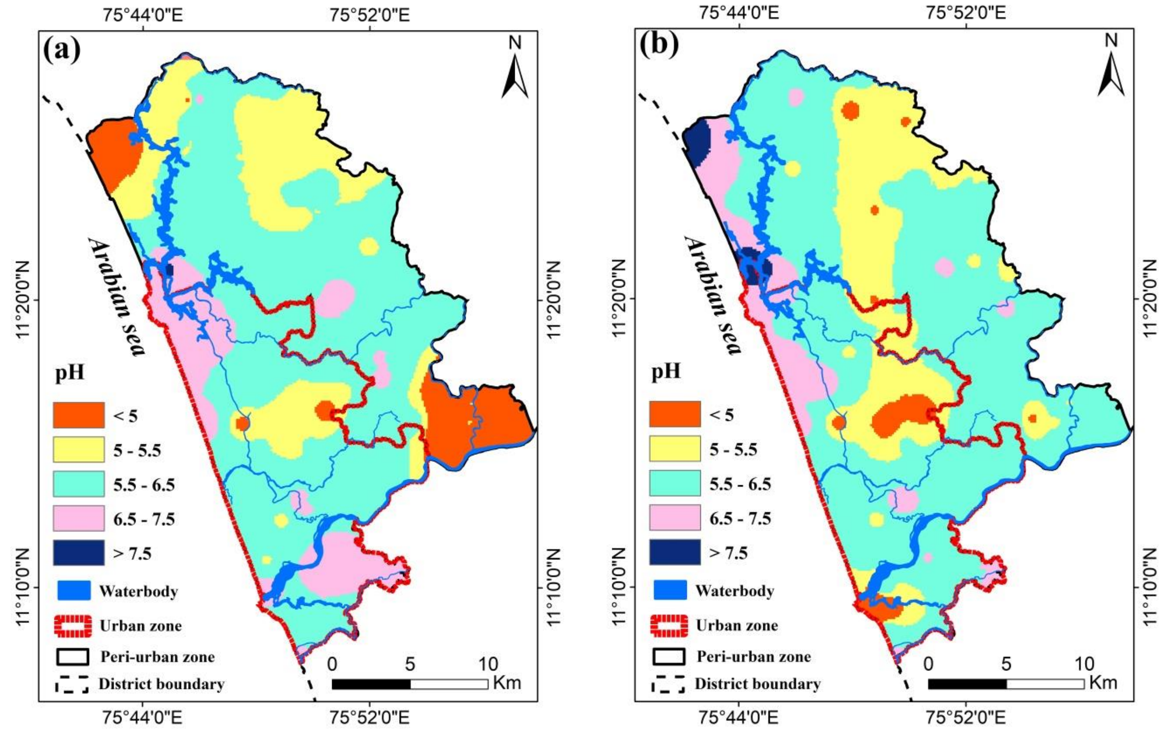

Figure 3.1. Spatial distribution of pH in the study area (a) Pre- monsoon (b) Post-monsoon

Slightly acidic (i.e pH 5.5 - 6.5) nature of groundwater caused by the addition of CO_2 through rainwater and dissolution of carbon dioxide and organic acids (fulvic and humic acids), which derived from the decay & subsequent leaching of plant materials ((Matthess and Pekdeger, 1981; Langmuir, 1997). Moreover, the acidic nature of the groundwater considerably visible in lateritic aquifer than alluvial may be related to the wide distribution of lateritic soil (CESS, 1997).

Table 3.1. (a). Seasonal statistics of physico-chemical parameters of groundwater in urban–alluvium phreatic aquifer

		pH	EC (µS/cm)	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	HCO_3^-+ CO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)
Pre-monsoon (2014)	**Average**	6.6	788.4	369.7	97.9	9.3	47.1	12.2	101.4	27.6	188.6
	Minimum	5.3	110.9	54.0	8.8	0.01	3.2	0.01	12.5	0.8	26.1
	Maximum	8.2	3810	2010	485	34	126	77.4	320.6	114	1344.2
Post-monsoon (2014)	**Average**	6.4	556.5	326.8	54.4	7.2	50.3	8.7	66.2	28.0	134.7
	Minimum	5	172.5	51.7	3.9	0.01	6.8	1.8	6.6	14.7	11.4
	Maximum	8.3	1251.0	1961.0	416.5	22.5	90.5	47.5	198.0	104.3	609.1
Pre-monsoon (2015)	**Average**	6.6	884.0	492.7	98.3	10.6	52.0	17.4	106.8	33.5	195.0
	Minimum	5.3	119.0	62.9	9.9	0.1	0.01	0.01	7.6	12.4	30.8
	Maximum	8.1	3580.0	2015.0	482.5	41.5	120.0	71.9	319.3	119.2	1349.6
Post-Monsoon (2015)	**Average**	6.4	524.6	364.8	68.5	8.1	44.3	9.9	76.7	28.0	130.1
	Minimum	5.0	150.0	62.0	6.6	1.4	15.1	2.0	4.0	2.6	17.8
	Maximum	8.3	1220.0	1980.0	402.3	35.6	85.6	53.5	204.0	106.1	601.5

Table 3.1. (b). Seasonal statistics of physico-chemical parameters of groundwater in urban – laterite phreatic aquifer

		pH	**EC (µS/cm)**	**TDS (mg/L)**	**Na^+ (mg/L)**	**K^+ (mg/L)**	**Ca^{2+} (mg/L)**	**Mg^{2+} (mg/L)**	**HCO_3^-+ CO_3^- (mg/L)**	**SO_4^{2-} (mg/L)**	**Cl^- (mg/L)**
Pre-monsoon (2014)	**Average**	6	251.4	159.3	23.9	4.4	23.4	9.6	36.5	20.3	43.4
	Minimum	4.6	46.6	30.1	6.1	3.3	4.4	16.5	6.6	0.01	20.5
	Maximum	7.3	1010	480	85.3	14.7	94.4	1	158.6	65.6	110.5
Post-monsoon (2014)	**Average**	**6.3**	**180.8**	**101.2**	**21.1**	**2.7**	**17.5**	**5**	**32.6**	**19.7**	**33.3**
	Minimum	**4.6**	**12.4**	**10.5**	**9.1**	**1**	**0.01**	**0.01**	**4.2**	**0.01**	**4**
	Maximum	**7.6**	**511**	**251.3**	**75.6**	**7**	**49.7**	**20**	**134.4**	**48.6**	**114.2**
Pre-monsoon (2015)	**Average**	5.9	245.2	130.4	20.5	3.1	21.5	5.5	35.5	15.8	35.6
	Minimum	4.6	44.9	24.1	5.6	0.6	4.8	0.01	8.4	0.01	18.6
	Maximum	7.3	832	440	82	12.3	81.6	24.3	141.8	61.4	106.4
Post-Monsoon (2015)	**Average**	**5.7**	**174.5**	**97.3**	**17.9**	**2.3**	**16.5**	**3**	**39.8**	**13.6**	**24**
	Minimum	**4.5**	**12.9**	**7.1**	**5.3**	**0.4**	**4.5**	**0.01**	**8**	**0.7**	**10.7**
	Maximum	**7.1**	**473**	**249**	**69.6**	**5.2**	**46.9**	**16.7**	**136**	**48.4**	**67.6**

Table 3.1. (c). Seasonal statistics of physico-chemical parameters of groundwater in peri-urban – alluvium phreatic aquifer

		pH	EC (µS/cm)	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	HCO_3^-+ CO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)
Pre-monsoon (2014)	**Average**	5.5	90.2	53.1	13.8	1.5	9.1	2.3	27.2	9.2	25.8
	Minimum	5.1	54.2	26.3	10.7	1.0	6.4	1.0	14.9	1.8	4.12
	Maximum	5.7	145.2	70.8	20.0	2.2	15.6	3.9	28.3	28.4	36.2
Post-monsoon (2014)	**Average**	6.6	296.5	126.8	14.4	5.2	30.3	8.7	61.2	18.0	24.7
	Minimum	5	62.5	51.7	7.9	0.01	6.8	1.8	12.6	1.7	11.4
	Maximum	8.3	751.0	361.0	23.5	12.5	50.5	17.5	168.0	36.3	39.1
Pre-monsoon (2015)	**Average**	5.5	89.1	47.1	10.9	1.8	8.6	0.6	16.0	8.7	20.1
	Minimum	5.2	51.7	27.2	6.5	1.0	4.8	0.01	12.6	1.3	7.7
	Maximum	5.8	139.0	73.4	15.3	3.4	11.1	1.9	21.0	33.3	34.7
Post-Monsoon (2015)	**Average**	6.4	262.1	138.1	12.5	2.0	22.3	5.3	61.6	15.1	20.6
	Minimum	5.6	59.5	31.6	8.3	0.6	9.0	1.8	20.0	1.7	10.7
	Maximum	8.4	772.0	407.0	17.5	4.2	37.7	11.9	132.0	28.9	32.0

Table 3.1. (d). Seasonal statistics of physico-chemical parameters of groundwater in peri-urban – laterite phreatic aquifer

		pH	**EC (µS/cm)**	**TDS (mg/L)**	**Na^+ (mg/L)**	**K^+ (mg/L)**	**Ca^{2+} (mg/L)**	**Mg^{2+} (mg/L)**	**HCO_3^- + CO_3^- (mg/L)**	**SO_4^{2-} (mg/L)**	**Cl^- (mg/L)**
Pre-monsoon (2014)	**Average**	5.8	117.8	74.5	10.5	2.0	18.0	3.5	35.1	8.8	27.0
	Minimum	4.9	29.1	28.5	1.7	0.01	4.8	1.0	8.5	0.8	5.1
	Maximum	7.5	297.0	224.0	32.3	7.7	56.0	10.7	160.6	37.6	60.3
Post-monsoon (2014)	**Average**	6.3	130.8	61.6	11.1	2.7	17.5	5.0	32.6	5.7	16.3
	Minimum	4.6	21.4	21.0	9.1	1.0	0.01	0.01	4.2	0.01	4.0
	Maximum	7.6	311.0	141.0	35.6	5.0	69.7	20.0	94.4	48.6	64.2
Pre-monsoon (2015)	**Average**	5.8	116.8	63.7	10.9	1.7	12.6	3.5	33.9	5.7	22.3
	Minimum	4.9	29.2	15.3	3.9	0.3	0.01	0.01	6.6	0.1	3.9
	Maximum	7.5	292.0	219.0	35.5	4.8	36.4	13.6	150.6	36.6	65.6
Post-Monsoon (2015)	**Average**	5.7	101.7	54.6	9.4	1.4	10.5	2.1	26.2	4.4	16.5
	Minimum	4.8	30.5	16.3	3.0	0.2	0.01	0.01	4.0	0.2	3.6
	Maximum	6.9	278.0	138.0	26.4	5.3	48.3	7.9	88.0	44.0	53.4

Table 3.2 (a). Physico-chemical parameters of groundwater in urban phreatic aquifer during pre-monsoon period (March-April 2015)

Sample code	pH	EC (µS/cm)	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	HCO_3^-+ CO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)
Alluvium										
U1	6.9	458	242	22.9	7.1	42.8	13.5	48.5	30.1	62.1
U2	6.5	275	145	20.8	2.2	27.2	1.9	25.2	22	30.8
U3	5.3	497	262	43.4	8.7	33.6	3.9	29.4	41.9	65.6
U4	6	460	380	36.5	2.5	70.6	19.8	52	38	98
U5	6.7	193	101	16.6	1.4	16	5.8	21	41.8	38.6
U6	6.8	661	349	47.1	9.1	0.1	51.5	96.6	23.4	77.1
U7	6.5	481	253	33.2	4.6	14.4	32.1	63	15.5	60.1
U8	5.5	119	62.9	9.9	0.1	30	11.5	36.8	22.3	43.1
U9	7.5	718	379	35.3	4.5	78.4	0.01	100.8	21.9	115.7
U10	6.5	449	238	46.3	13.3	48	0.01	79.8	20.6	54
U11	6.7	648	342	46.3	13.3	46.4	9.7	16.8	22.8	142.7
U12	6.8	532	282	41.5	10.5	56	3.9	138.6	12.4	61.7
U13	6.5	1600	840	228.8	22.8	112	27.2	310.8	48	285.3
U14	6.3	3580	1890	482.5	33.8	84.8	71.9	315	69.4	1349.6
U15	8.1	3518	2015	481.8	41.5	115.2	42.8	319.3	119.2	705.6
U16	6.3	130	75.2	13.8	1.6	25.6	3.9	7.6	15.3	64.8
U17	7.2	1240	760	141.3	11.3	120	12.6	231	25.3	212.1
U18	6.5	353	252	21.5	2.3	14.4	1	29.4	13.3	42.4

Laterite										
U19	6.5	270	141	20.7	2.6	22.2	4.8	50.4	11.5	27
U20	5.9	119	62.9	12	1.5	11.1	0.01	21	5	19.3
U21	7.2	832	440	82	6.9	81.6	15.6	141.8	61.4	106.4
U22	5.4	342	181	35.4	4.1	14.4	9.7	16.8	36.6	60.8
U23	5.3	320	169	26.6	12.3	19.2	4.9	16.8	20.5	54
U24	6.4	691	366	46.1	3.8	49.6	24.3	67.2	58.8	84.8
U25	7.3	423	223	24.7	1.9	42.1	12.6	95.4	24	38.7
U26	6.3	142	75.3	5.6	0.7	16	2.9	15.6	12.2	18.6
U27	6.4	137	72.3	9.7	2.5	11.2	5.8	50.4	0.6	19.3
U28	6	232	122	8.2	3.7	6.4	3.9	21	14.5	19.3
U29	5.3	85.9	45.1	11.4	1.7	6.4	1.9	12.6	2.4	23.1
U30	4.6	68	35.9	9.1	1.9	6.4	0.01	8.4	0.01	23.1
U31	5.2	94.9	50.3	14.9	1.4	6.4	3.9	12.6	7.4	23.1
U32	5.6	202	107	17.6	4.3	12.8	5.8	29.4	20.6	30.8
U33	5.1	111	58.9	14.8	1.3	6.4	1	8.4	0.8	27
U34	4.8	220	140.6	16.5	5.2	11.2	2.9	12.6	0.3	40.5
U35	6.8	202	104	15.5	1.2	70.4	0	67.2	7.1	19.3
U36	6.9	44.9	24.1	7.2	0.6	4.8	1.9	8.4	15	18.6
U37	5.8	122.6	59.4	11	1.3	9.6	1.9	19	0.8	22.9

Table 3.2 (b). Physico-chemical parameters of groundwater in urban phreatic aquifer during post-monsoon period (November- December-2015)

Sample code	pH	EC (µS/cm)	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	HCO_3^-+ CO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)
Alluvium										
U1	6.5	400	101	18.7	3.5	27.1	2.7	28	23.6	32
U2	6	212	111	15.8	2.4	24	2.9	32	28	24.9
U3	6.1	591	309	46.9	13.7	67.2	4.9	76	35.5	60.5
U4	6	260	137	16.8	2.6	35.2	2.9	36	35.4	49.8
U5	5	150	98	15.4	1.4	15.1	2.5	36	35.3	32
U6	5.1	206	109	15.7	4.6	19.4	4.9	20	14.9	46.3
U7	5.2	278	146	15.5	4.9	40.4	2	128	7.6	17.8
U8	6.2	309	160	8.4	3.4	32.3	17.7	20	14.2	60.5
U9	7	456	239	40.4	3.7	58.2	8.8	160	18.3	71.2
U10	6.1	370	195	33	3.7	30.7	8.8	112	22.5	46.3
U11	5.7	338	179	20.8	9.4	37.2	5.9	36	28	53.4
U12	6.8	532	245	30.4	6.9	33.6	7.8	44	39.4	121
U13	6.5	800	1300	215.6	18.4	64	5.8	96	38.6	601.5
U14	6.3	1200	1980	402.3	35.6	72	53.5	164	106.1	565.9
U15	7.9	657	1346	172.3	9.7	64.6	11.8	204	2.6	49.8
U16	8.3	1100	62	6.6	2.3	22.6	9.2	4	20.1	85.4
U17	6.7	1220	640	109.8	9.7	67.9	5.5	164	12.9	138.8
U18	7.4	363	210	149.4	9.6	85.6	20.6	20	22	284.7

Laterite										
U19	6.4	342	180	14.4	3.2	33.2	0.1	108	27.9	14.2
U20	4.9	93.7	56.4	10	1.1	9	1.8	16	4.6	17.8
U21	6.6	473	249	69.6	5.2	29.1	5.9	108	44.4	67.6
U22	5.3	204	107	24.9	3.1	14.5	2.9	12	17.6	35.6
U23	5.4	200	117	20.4	4.4	12.9	2	12	16.1	32
U24	6.7	469	247	42.2	1.8	46.9	16.7	136	48.4	46.3
U25	7.1	281	148	27.1	1	32.3	8.8	124	18	14.2
U26	5.7	71.7	37.6	8	1.1	27.1	0.1	20	2.3	14.2
U27	5.8	98.8	52	9.9	2.6	13.6	0.9	32	5.5	17.8
U28	5.1	150	110	7.5	3.1	4.8	3.9	28	2.1	10.7
U29	5.2	70.5	37	10.8	1.3	7.5	0.2	8	0.7	21.4
U30	4.5	61.3	32.3	9.5	1.9	4.5	0.9	12	3.4	14.2
U31	4.5	89.8	47.3	15.5	1.9	15.1	0.1	8	6.6	21.4
U32	5.7	136	71.9	14.4	2.9	11.3	2	24	17.4	21.4
U33	5	12.9	7.1	16.4	1.2	8.1	3.9	12	1.6	28.5
U34	4.8	220	125	12.5	4.5	6.5	4.9	36	11.6	35.6
U35	6.5	250	95	12.6	1	22.6	0.2	44	14.3	14.2
U36	7.1	70.6	21.2	5.3	0.4	6	0.9	8	0.8	14.2
U37	5.8	21.4	108.2	8.6	1.1	7.5	0.9	8	15.4	14.2

Table 3.2 (c). Physico-chemical parameters of groundwater in peri-urban phreatic aquifer during pre-monsoon period (March-April-2015)

Sample code	pH	EC (µS/cm)	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	HCO_3^-+ CO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)
Alluvium										
PU1	5.2	92.1	48.6	13.7	1.6	9.9	1	16.8	33.3	23.1
PU2	5.3	139	73.4	15.3	3.4	9.5	0.01	12.6	5	34.7
PU3	5.2	51.7	27.2	6.5	1.1	7.5	0.01	16.8	1.3	7.7
PU4	5.8	95.2	50.5	10.4	1	11.1	0.01	21	1.4	23.1
PU5	5.8	67.5	35.9	8.4	1.8	4.8	1.9	12.6	2.4	11.6
Laterite										
PU6	4.9	30.5	16	6.6	1.7	4.8	0.01	10.6	0.4	23.1
PU7	6.8	271	143	8.9	3.7	36.4	8.7	63	3.2	23.1
PU8	5.6	29.2	15.3	4.4	0.4	6.3	2	12.6	0.5	11.6
PU9	5.6	76.8	40.3	10.5	1.2	7.9	1	16.8	1.8	19.3
PU10	6	190	100	10.1	1.4	25.3	2.9	25.2	31.1	19.3
PU11	5.9	105	55.4	10.4	1	11.1	2.9	16.8	1.4	30.8
PU12	6.6	292	219	16.6	4.1	30.4	9.6	63	36.6	19.3
PU13	6.4	93.9	49.6	9.6	1.1	11.1	2	16.8	0.7	23.1
PU14	6.3	290	153	18.9	4.4	25.3	5.8	29.4	11.1	61.7
PU15	5.7	55.9	39.4	6.4	0.7	6.3	1	12.6	1.1	11.6
PU16	5.9	77	41	9.7	2.1	9.5	0.01	12.6	0.9	15.4
PU17	5	35.2	18.6	4.8	0.3	6.3	5.8	16.8	0.1	27

PU18	5.2	32.5	17.2	5.3	0.5	7.9	2	8.4	0.6	19.3
PU19	5.7	124	65.7	15.3	2.5	11.1	4.8	14.2	1.3	45.4
PU20	5.1	48.3	25.3	3.9	1	4.8	2.8	21	2.3	3.9
PU21	5.2	79.8	42.1	8.6	1.1	7.9	1.2	21	1.7	27
PU22	5.3	96.8	51	15.1	2	9.5	1	12.6	9.9	19.3
PU23	5.3	47.3	24.9	5.1	1.7	9.5	0.01	25.2	0.4	15.4
PU24	5.2	52.5	27.8	12.1	1.7	5	1	25.8	0.8	7.7
PU25	5.5	73.6	38.8	7.8	0.9	7.9	2.9	29.4	2.2	11.6
PU26	5.5	98.3	51.8	11.5	1.8	7.9	1.9	6.6	5.5	21.3
PU27	6.1	141	74.9	12.1	2.5	0.1	9.7	37.8	6.5	19.3
PU28	6.4	200	105	17.4	3.9	30.4	0.01	46.2	13	23.1
PU29	6	202	106	14.6	4.8	20.8	3.9	46.2	13.7	30.8
PU30	5	43.7	23.1	9.1	0.6	6.4	1	33.6	0.7	19.3
PU31	5.6	168	88.5	13.1	0.6	16	4.9	75.6	2.9	27
PU32	5.6	157	83.3	12.9	0.3	12.8	6.8	42	19.6	30.8
PU33	5.3	148	78.6	17.2	1.5	6.4	5.8	25.2	2.9	34.7
PU34	5.4	77.5	40.8	7.3	0.8	8	1.9	21	1.2	19.3
PU35	5.5	85.9	45.5	11	0.5	11.2	1.9	12.6	2.6	30.8
PU36	6.7	229	120	16	3	12.8	1.9	63	10.4	19.3
PU37	7.5	289	153	35.5	4.1	33.6	5.8	92.4	25.6	28.1
PU38	5.6	62.5	32.9	7.7	0.7	22.4	7.8	84	0.7	23.1
PU39	5.8	69.1	36.4	7.6	1	25.6	8.7	150.6	0.7	15.4
PU40	5.3	42.8	22.7	5.8	0.6	6.4	1.9	25.2	1.2	15.4
PU41	5.5	85.4	45	9	1.3	6.4	1	37.8	0.6	15.4
PU42	6.2	78.1	41.2	8.3	1.2	6.4	1.9	21	1	11.6
PU43	6.5	131	70.6	11.1	2.3	8	1.9	36.2	0.9	15.4

PU44	4.9	170	84.5	19.4	2.9	8	5.8	12.6	0.1	65.6
PU45	6.6	65.3	34.5	5.1	0.5	24	0.1	46.2	1.1	15.4
PU46	6	66.1	34.9	7.5	1.1	1.6	13.6	33.6	1.9	11.6
PU47	5.9	180.7	115.2	12.3	1.3	4.8	1.9	7.6	22.6	11.4
PU48	6.5	130	68.7	8	0.9	17.6	3.9	46.2	1.6	19.3

Table 3.2 (d). Physico-chemical parameters of groundwater in peri-urban phreatic aquifer during post-monsoon period (November - December-2015)

Sample code	pH	EC (μS/cm)	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	HCO_3^- + CO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)
Alluvium										
PU1	6.4	219	115	13.58	2.63	30.2	5.5	80	17.12	32.031
PU2	8.4	772	407	14.8	1.65	37.7	11.9	132	19.12	10.677
PU3	5.8	59.5	31.6	17.5	4.17	12.1	1.8	28	8.6	28.472
PU4	6	176	92.5	8.36	0.97	22.4	1.9	48	28.92	10.677
PU5	5.6	83.8	44.2	8.28	0.59	9.04	5.5	20	1.68	21.354
Laterite										
PU6	5.5	52.8	27.7	5.1	1.2	10.6	0.01	16	4.2	17.8
PU7	6.4	34.7	17.8	5	0.6	4.8	1	16	0.3	10.7
PU8	6.8	252	133	10.1	3.5	30.2	4.6	88	44	24.9
PU9	6.1	33.3	17.4	3.5	0.3	4.8	1	8	1	10.7
PU10	5.4	72.8	38.3	8.6	1.2	6.4	0.01	16	1.7	14.2
PU11	6.1	125	66.1	10.8	0.6	19.2	3.9	52	3.8	17.8

PU12	5.4	102.7	102.4	8.1	1.2	6	5.5	44	3.3	3.6
PU13	5.2	78.5	42.2	8.5	1.5	3	1.8	12	1.2	17.8
PU14	5.5	103.6	120	18.6	1.6	4.5	4.6	12	0.8	53.4
PU15	5.4	58.7	30.9	8	1.1	12.1	0.01	12	1	28.5
PU16	5.9	46.7	24.7	6	0.6	9	0.01	16	1	14.2
PU17	4.9	30.5	16.3	4.7	0.5	10.6	0.01	8	1.3	10.7
PU18	5.4	41.6	21.9	5.2	0.2	19.2	1.9	16	6.9	21.4
PU19	5.7	123	64.9	11.1	3	9.6	1.9	24	3.5	21.4
PU20	5	41.5	21.9	5.6	1.9	4.5	1.8	12	0.8	10.7
PU21	5.1	70.2	35.4	6.4	1.1	3	0.9	8	0.8	14.2
PU22	5.1	87.5	48	8.9	2	4.5	0.9	12	4.3	10.7
PU23	5.4	48.4	25.3	3	0.5	6.4	1.9	16	0.6	10.7
PU24	4.8	47.5	24.9	6.2	0.9	4.8	0.01	8	0.7	14.2
PU25	5.3	51.8	27.3	5.5	0.9	6.4	1	16	1.6	10.7
PU26	4.8	42.5	64.2	8.6	1.2	7.5	0.9	4	2.8	17.8
PU27	5.9	143	75.4	16	2.3	13.6	3.7	36	9.2	32
PU28	5.6	198	104	21	4	16.2	3.9	28	12.8	32
PU29	6.1	167	88.4	13.9	5.3	48.3	0.01	44	14.4	21.4
PU30	4.9	48.4	25.5	7.8	0.6	9	0.01	20	0.7	10.7
PU31	5.9	141	75.3	13.2	0.4	15.1	5.5	60	4.8	14.2
PU32	5.4	135	64	11.4	0.4	12.1	6.4	20	19.4	17.8
PU33	5.9	150	56	8.4	0.7	6	3.7	12	2.1	17.8
PU34	5.4	140	44	7.1	0.7	7.5	0.9	12	0.2	14.2
PU35	5.1	56.4	29.5	8.4	0.5	11.3	0.01	16	0.4	14.2
PU36	6.5	152.4	122	14.2	2.5	4.8	1	56	1.8	14.2
PU37	5.7	278	138	26.4	3.2	29.1	3.9	44	24.6	17.8

PU38	6.7	125.5	55	7.1	0.6	21	2	80	0.7	17.8
PU39	6.9	91.2	67	6.6	0.6	19.4	7.9	68	0.7	10.7
PU40	5.6	70.9	42	10.4	1.2	4.8	1	36	0.6	10.7
PU41	5.3	113.7	32	7.6	1.1	4.8	1	28	0.6	14.2
PU42	5.7	118.9	42.2	7.6	1.6	4.8	0.01	20	0.8	7.1
PU43	6.7	193.5	64	8.1	1.8	6.5	5.9	24	0.9	14.2
PU44	5.9	117	62.4	16.9	2	0.01	0.01	4	1.6	28.5
PU45	6.3	121	38	7	0.8	15.1	1.8	36	2.9	10.7
PU46	5.8	104.9	34	6.1	1	6	3.7	24	0.4	10.7
PU47	5.7	61.7	54.2	6.4	0.9	3	1.8	16	1.4	3.6
PU48	6.3	100.3	62.3	13.3	1.6	6.4	1.6	28	4.6	17.8

3.1.1.2. Electrical Conductivity (EC)

Electrical Conductivity (EC) of urban alluvial aquifers during pre-monsoon ranges from 119 µs/cm to 3580 µs/cm with a mean value of 884 µs/cm and in the post-monsoon period it ranges from 150 µs/cm to 1220 µs/cm with a mean value of 524 µs/cm (Table 3.1a). In urban lateritic aquifer, EC value ranges from 44.9 µs/cm to 832 µs/cm during pre-monsoon with a mean value of 245 µs/cm and in the post-monsoon period it ranges from 12.9 µs/cm to 473 µs/cm with a mean value of 174 µs/cm (Table 3.1 b). EC of peri-urban alluvial aquifers ranges from 51 µs/cm to 139 µs/cm with a mean value of 89 µs/cm during pre-monsoon and the value ranges from 59 µs/cm to 772 µs/cm with a mean value of 262 µs/cm during post-monsoon period (Table 3.1 c). In peri-urban lateritic aquifer, EC value ranges from 29.2µs/cm to 292 µs/cm with a mean value of 116 µs/cm and in the post-monsoon period it ranges from 30 µs/cm to 278 µs/cm with a mean value of 101 (Table 3.1 d).

The EC is a measure of an ability to conduct current so that the higher EC indicates the enrichment of salts in the groundwater. Thus EC of groundwater can be classified as Type I, if the enrichment of salts are low (EC = 1,500 µS/cm); type II, if the enrichment of salts are medium (EC = 1,500 and 3,000 µS/cm); and type III, if the enrichment of salts are high (EC = 3,000 µS/cm) (Prasanth et al. 2012). The spatial distribution maps of EC shows that majority of groundwater in the entire study area were observed with an EC value of < 600 µS/cm , i.e in type I category in both the seasons (Figure. 3.2 a & b). EC values were increased from lateritic zone to coastal alluvial area in both the seasons. Higher EC values along the coastal alluvial zone of the study area (western side) were indicated the increased enrichment of salts in groundwater. The permissible limit of EC in drinking water prescribed as 1,500 µs/cm. Since the EC value of the significant portion of the study area is below 600 µs/cm, groundwater is suitable for drinking purposes.

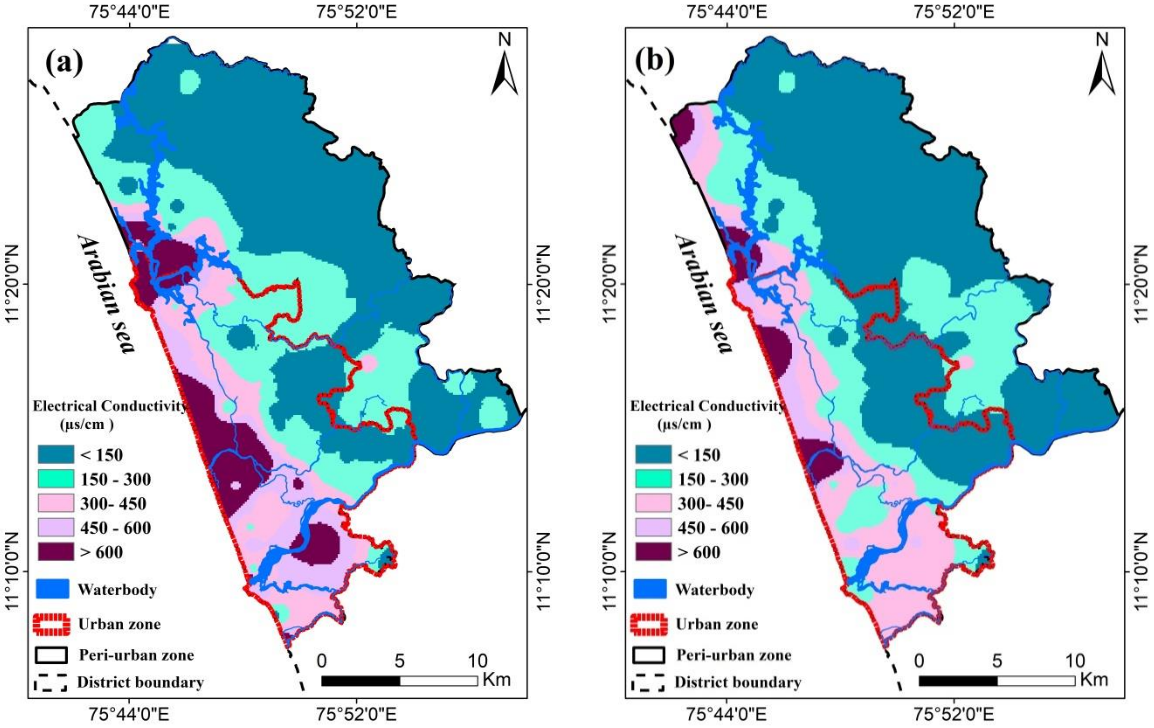

Figure 3.2. Spatial distribution of Electrical Conductivity (EC) in the study area (a) Pre- monsoon (b) Post-monsoon

The decrease in EC value from pre-monsoon to post-monsoon is due to dilution of soluble salts by rainfall. Assessment on seasonal variation of groundwater quality of phreatic aquifers in muvattupuzha river basin conducted by Laluraj and Girish, 2005 also confirmed the effect of rainfall on dilution of soluble salts and thereby decrease in EC values.

3.1.1.3. Total Dissolved Solids (TDS)

Total Dissolved Solids of urban alluvial aquifers during pre-monsoon ranges from 62.9 mg/L to 2015 mg/L with a mean value 492.7 mg/L of and in the post-monsoon period it ranges from 62 mg/L to 1980 mg/L with a mean value of 364.8 mg/L (Table 3.1 a). In urban lateritic aquifer, TDS value ranges from 24.1 mg/L to 440 mg/L during pre-monsoon with a mean value of 130.4 mg/L and in the post-monsoon period it ranges from 7.1 mg/L to 249 mg/L with a mean value of 97.3 mg/L (Table 3.1 b). TDS of peri-urban alluvial aquifers ranges from 27.2 mg/L to 73.4 mg/L with a mean value of 47.1 mg/L during pre-monsoon and the value ranges from 31.6 mg/L to 407 mg/L with a mean value of 138.1 mg/L during post-monsoon period (Table 3.1 c). In peri-urban lateritic aquifer, TDS value ranges from 15.3 mg/L to 219 mg/L with a mean value of 63.7 and in the post-monsoon period it ranges from 16.3 mg/L to 138 mg/L with a mean value of 54.6 mg/L (Table 3.1 d).

Groundwater quality can be classified as freshwater, if the TDS is less than 1,000 mg/L; brackish, if the TDS is between 1,000 and 10,000 mg/L; saline, if the TDS is varied from 10,000 to 1,000,000 mg/L; and brine, if the TDS is more than 1,000,000 mg/L (Todd and Mays,1980). Accordingly, the quality of groundwater in the entire study area is classified as freshwater type except some locations (U14 & U15) of urban coastal alluvium (Table 3.2 a &b) which are categorised as brackish. Spatial distribution of TDS values in urban and peri-urban phreatic aquifers show that the majority of the study area characterized by low TDS values (below 300 mg/L) (Figure 3.3 a & b). Where as high TDS value (> 600 mg/L) were observed in urban phreatic alluvial aquifers during both seasons. However, TDS distribution in urban and peri-urban were showed similar trend in both seasons. The hydro-geological properties of rocks have a strong influence on the extent of water-rock reaction. Areas with high groundwater flow velocities usually have relatively low dissolved solids because of shorter groundwater rock contact time and high water-rock ratios and vice-versa (Langmuir, 1997). On this basis, low TDS values observed in groundwater from lateritic region attributed to high rainfall. Furthermore, the urban alluvial coastal aquifer with highest

TDS value were occupied in the highly populated region with intense urban activities and the value due to the leaching of domestic sewage into the groundwater.

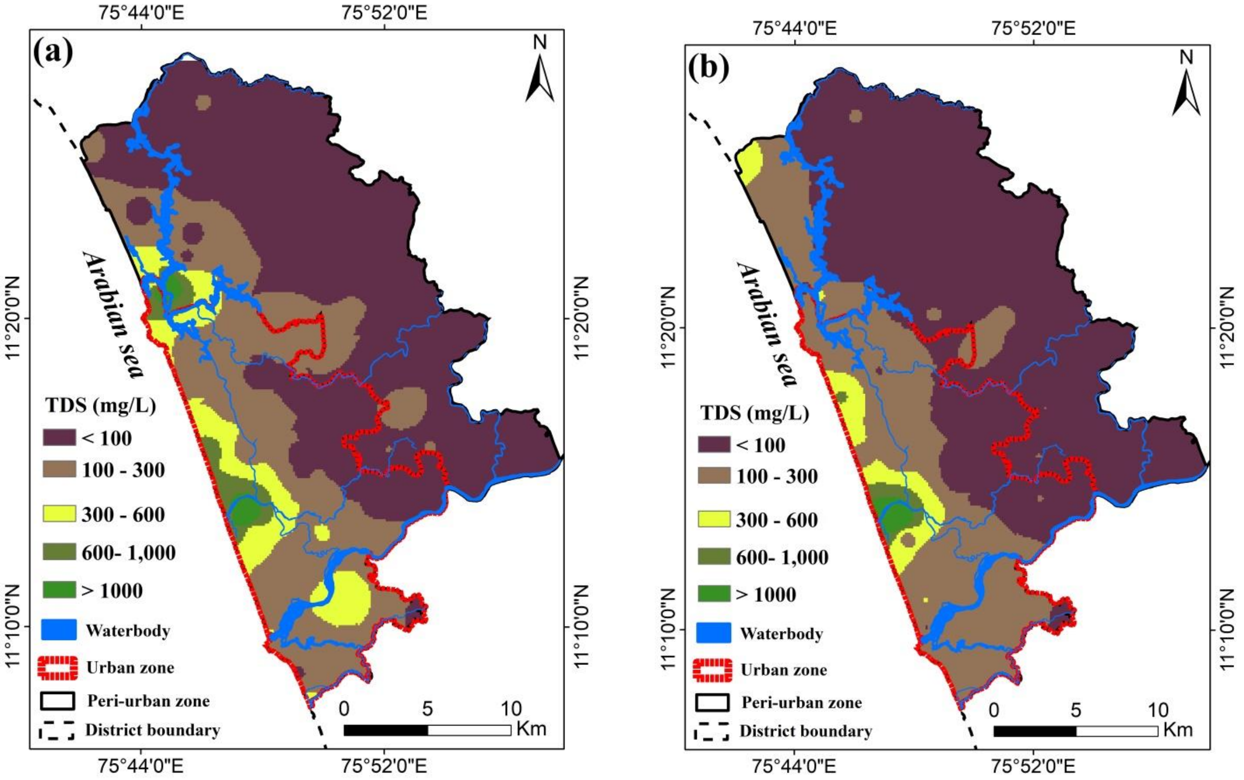

Figure 3.3. Spatial distribution of Total Dissolved Solids (TDS) in the study area (a) Pre-monsoon (b) Post-monsoon

According to BIS specification TDS up to 500 mg/L is the highest acceptable and up to 2000 mg/L is maximum permissible limit for drinking water and therefore a few urban alluvial aquifers with high TDS value (> 2000 mg/L) were not suitable for drinking water.

3.1.1.4. Total hardness

Spatial distribution of total hardness of the urban and peri-urban phreatic aquifers during both pre-monsoon and post monsoon period showed that the majority of the study area characterized by soft to moderately hard water type. Hard to very hard water types were observed in urban alluvial zone of the study area during pre-monsoon and post-monsoon period (Figure 3.4 a & b).

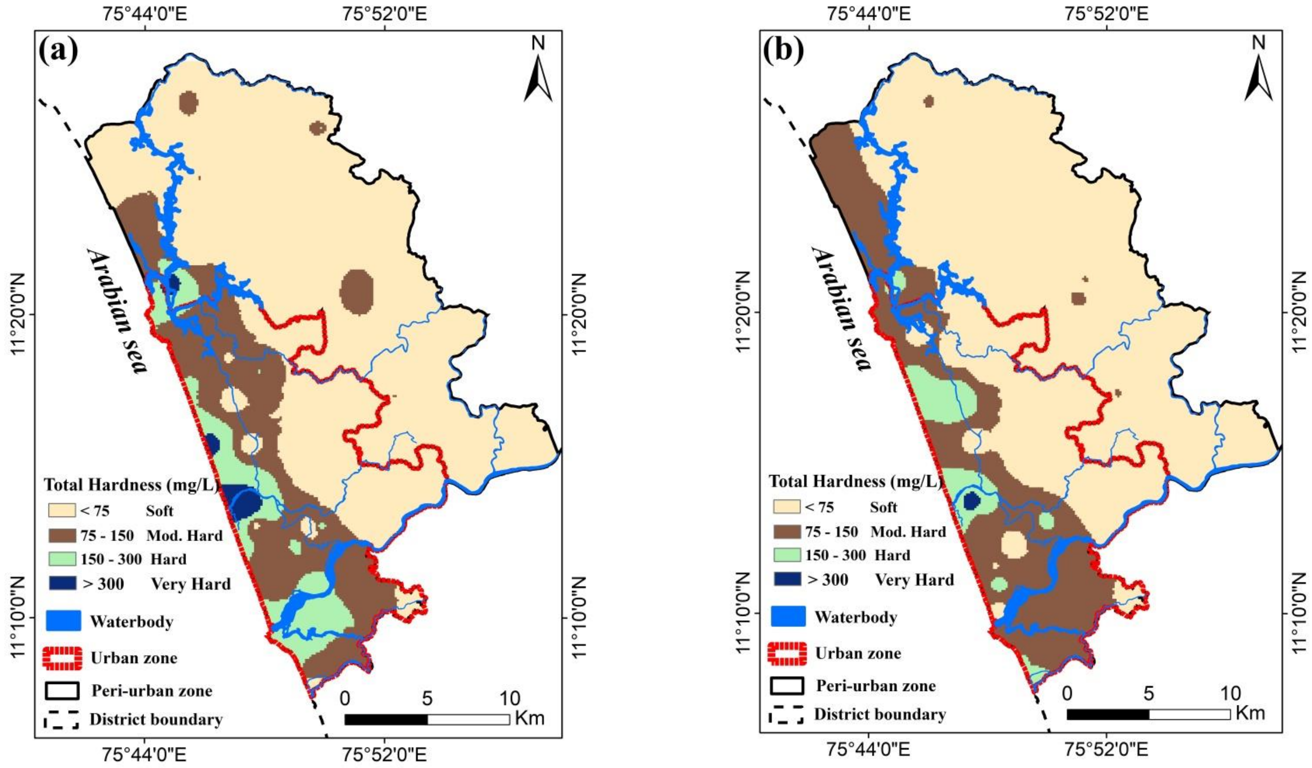

Figure 3.4. Spatial distribution of Total Hardness in the study area (a) Pre-monsoon (b) Post-monsoon

3.1.1.5. Major ions

The concentration of Na^+ ion in the urban alluvial phreatic aquifer ranged from 9.9 mg/L to 482.5 mg/L in pre-monsoon with a mean value of 98.3 mg/L and that of post-monsoon season, value varied from 6.6 mg/L to 402.3 mg/L with a mean value of 68.5 mg/L (Table 3.1 a). In urban lateritic aquifers value of sodium ion ranged from 5.6 mg/L to 82 mg/L with a mean value of 20.5 mg/L in pre-monsoon and that of post-monsoon season, value varied from 5.3 mg/L to 69.6 mg/L with a mean value of 17.9 mg/L (Table 3.1 b). Sodium ion concentration of peri-urban alluvial phreatic aquifer ranged from 6.5 mg/L to 15.3 mg/L in pre-monsoon with a mean value of 10.9 mg/L and that of post-monsoon season, value varied from 8.3 mg/L to 17.5 mg/L with a mean value of 12.5 mg/L (Table 3.1 c). In peri-urban lateritic aquifers sodium ion concentration ranged from 3.9 mg/L to 35.5 mg/L with a mean value of 10.9 mg/L in pre-monsoon and that of post-monsoon season, value varied from 3 mg/L to 26.4 mg/L with a mean value of 9.4 mg/L (Table 3.1d).

Spatial distribution of sodium ions in the study area shown that highest sodium ion concentration were observed in urban alluvium aquifers and the ionic concentration gets decreased from west to east direction in both seasons (Figure 3.5 a& b). Seasonal variation (pre-monsoon to post-monsoon) of sodium ion concentration were more visible in urban alluvial aquifers. Whereas less significant seasonal variation were visible in urban and peri-urban lateritic formation. However in both seasons, concentration of sodium in urban and peri-urban aquifers were within the maximum permissible limit, according to the WHO (2011) standard (200mg/L).

The concentration of K^+ ion in the urban alluvial phreatic aquifer ranged from 0.1 mg/L to 41.5 mg/L in pre-monsoon with a mean value of 10.6 mg/L and that of post-monsoon season, value varied from 1.4 mg/L to 35.6 mg/L with a mean value of 8.1 mg/L (Table 3.1a). In urban lateritic aquifers value of K^+ ion ranged from 0.6 mg/L to 12.3 mg/L with a mean value of 3.1 mg/L in pre-monsoon and that of post-monsoon season, value varied from 0.4 mg/L to 5.2 mg/L with a mean value of 2.3 mg/L (Table 3.1 b). Potassium ion concentration of peri-urban alluvial phreatic aquifer ranged from 1 mg/L to 3.4 mg/L in pre-monsoon with a mean value of 1.8 mg/L and that of post-monsoon season, value varied from 0.6 mg/L to 4.2 mg/L with a mean value of 2 mg/L (Table 3.1 c). In peri-urban lateritic aquifers potassium ion concentration ranged from 0.3 mg/L to 4.8 mg/L with a mean value of 1.7 mg/L in pre-monsoon and that of post-monsoon season, value varied from 0.2 mg/L to 5.3 mg/L with a mean value of 1.4 mg/L (Table 3.1 d). According to WHO guidelines, the maximum permissible limit for K^+ is 12 mg/L. In the study area a few samples from urban alluvial aquifers exceeds this maximum permissible limit for potassium ion during both seasons (Table 3.2 a & b).

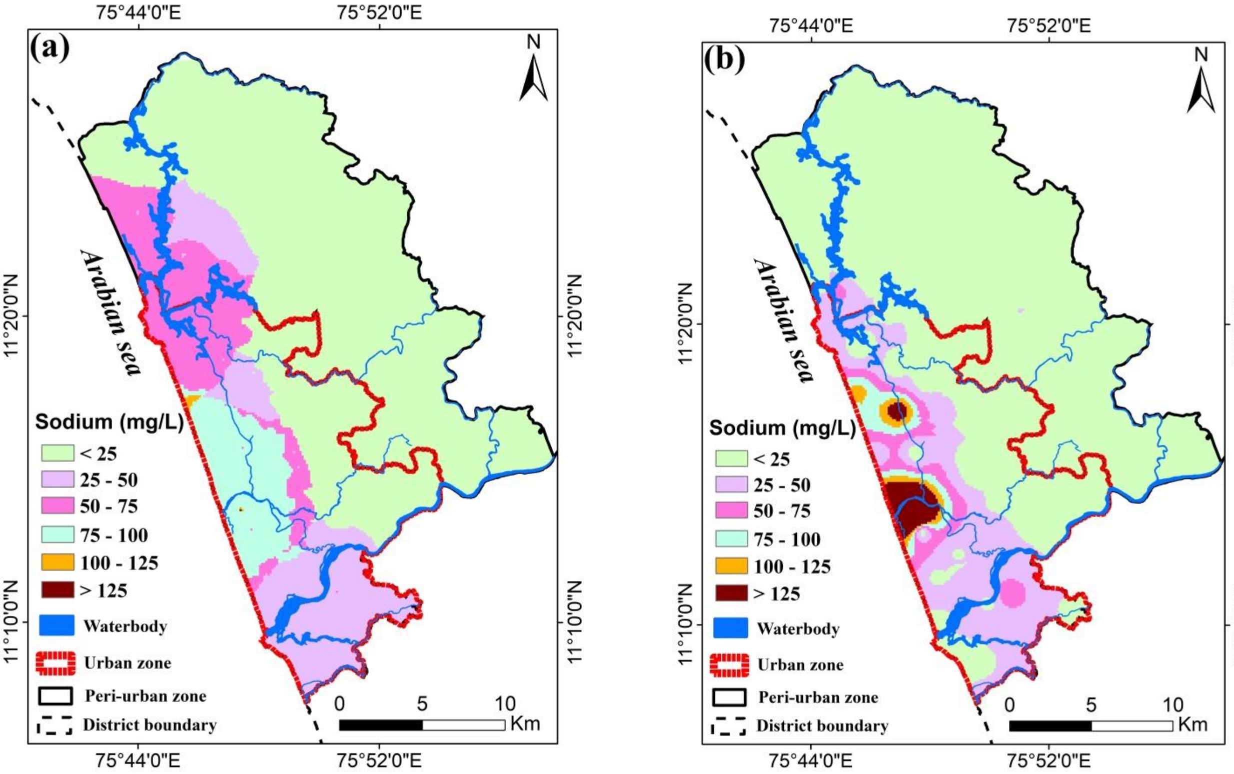

Figure 3.5. Spatial distribution of Sodium in the study area (a) Pre-monsoon (b) Post-monsoon

Calcium concentration of groundwater in the urban alluvial phreatic aquifer ranged from 0.1 to 120 mg/L in pre-monsoon with a mean value of 52 mg/L and that of post-monsoon season, value varied from 15.1 mg/L to 85.6 mg/L with a mean value of 44.3 mg/L (Table 3.1 a). In urban lateritic aquifers value of calcium ion ranged from 4.8 mg/L to 81.6 mg/L with a mean value of 21.5 mg/L in pre-monsoon and that of post-monsoon season, value varied from 4.5 mg/L to 46.9 mg/L with a mean value of 16.5 mg/L (Table 3.1 b). Calcium ion concentration of peri-urban alluvial phreatic aquifer ranged from 4.8 mg/L to 11.1 mg/L in pre-monsoon with a mean value of 8.6 mg/L and that of post-monsoon season, value varied from 9 mg/L to 37.7 mg/L with a mean value of 22.3 mg/L (Table 3.1 c). In peri-urban lateritic aquifers calcium ion concentration ranged from 0.1 mg/L to 36.4 mg/L with a mean value of 12.6 mg/L in pre-monsoon and that of post-monsoon season, value varied from 0.1 mg/L to 48.3 mg/L with a mean value of 10.5 mg/L (Table 3.1 d).

The acceptable limit of calcium concentration for drinking water is specified as 75 mg/L (BIS 2012 &WHO 2011). Figure 3.6 (a) & (b) shows that a few groundwater samples fall beyond the acceptable limit and concentration gets decreases from pre-monsoon to post-monsoon. Spatial distribution of calcium ion in peri-urban lateritic aquifer remains in the same class (> 25mg/l - 50 mg/L) both in pre-monsoon and post-monsoon period. Groundwater samples from the entire study area were occurred below the permissible limit of 200 mg/L as per BIS.

Magnesium concentration of groundwater in the urban alluvial phreatic aquifer ranged from 0.1 to 71.9 mg/L in pre-monsoon with a mean value of 17.4 mg/L and that of post-monsoon season, value varied from 2 mg/L to 53.5 mg/L with a mean value of 9.9 mg/L (Table 3.1 a). In urban lateritic aquifers value of magnesium ion ranged from 0.1 mg/L to 24.3 mg/L with a mean value of 5.5 mg/L in pre-monsoon and that of post-monsoon season, value varied from 0.1 mg/L to 16.7 mg/L with a mean value of 3 mg/L (Table 3.1b). Magnesium ion concentration of peri-urban alluvial phreatic aquifer ranged from 0.1 mg/L to 1.9 mg/L in pre-monsoon with a mean value of 0.6 mg/L and that of post-monsoon season, value varied from 1.8 mg/L to 11.9 with a mean value of 5.3 mg/L (Table 3.1 c). In peri-urban lateritic aquifers magnesium ion concentration ranged from 0.1 mg/L to 13.6 mg/L with a mean value of 3.5 mg/L in pre-monsoon and that of post-monsoon season, value varied from 0.1 mg/L to 7.9 mg/L with a mean

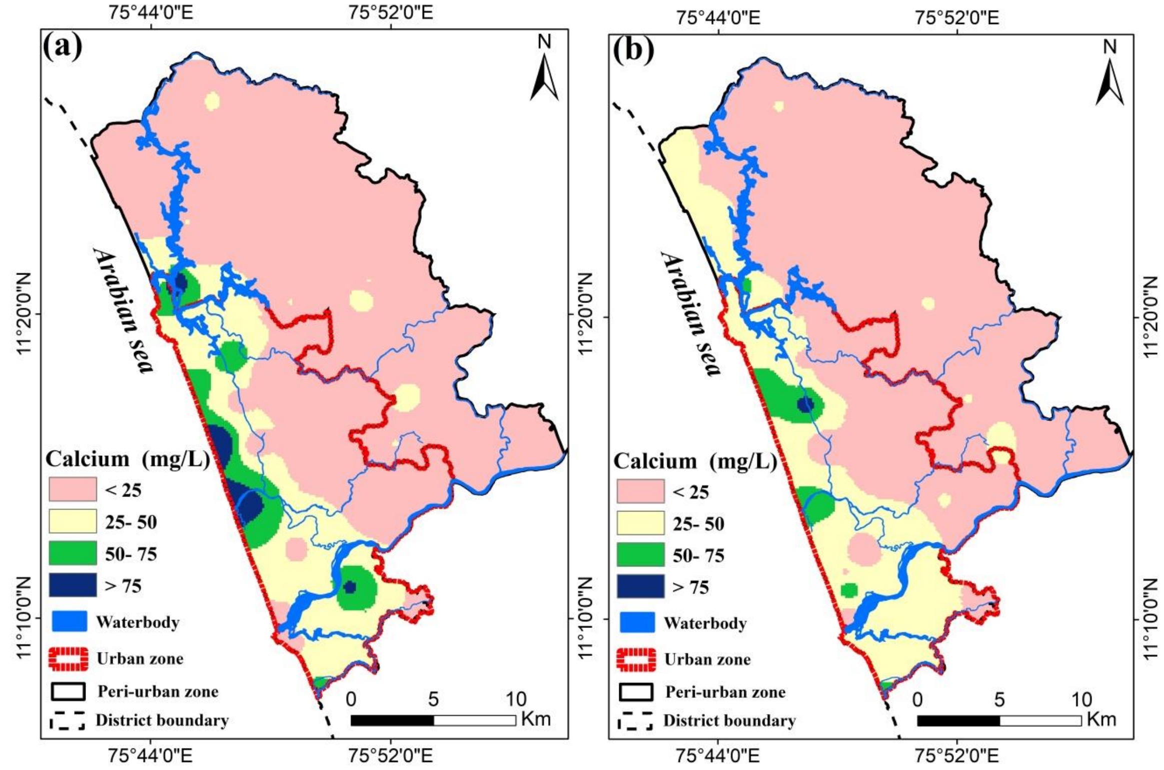

Figure 3.6. Spatial distribution of Calcium in the study area (a) Pre-monsoon (b) Post-monsoon

value of 2.1 mg/L (Table 3.1d). The maximum permissible limit of the Mg^{2+} concentration of drinking water is specified as 100 mg/L (BIS 2012).

All the samples from the urban and peri-urban aquifers of the study area were laid within the permissible limit of BIS.Calcium and magnesium ions in drinking water are important for the bone health, human nervous system, cardiovascular health and in coagulation of blood. Low content of calcium in drinking water causes diseases like rickets and teeth defects (WHO 2011). Calcium and magnesium are the most abundant elements in the natural surface and groundwater and exist mainly as bicarbonates and to a lesser degree in the form of sulphate and chloride. The principal sources of calcium in groundwater are silicate minerals like feldspars, pyroxenes, and amphiboles among igneous and metamorphic rocks and limestone, dolomite and gypsum among sedimentary rocks (Hem, 1959). In addition to this, the disposal of sewage and industrial waste are also contributing calcium to groundwater.

The concentration of $HCO_3 + CO_3$ ion in the urban alluvial phreatic aquifer ranged from 7.6 mg/L to 319.3 mg/L in pre-monsoon with a mean value of 106.8 mg/L and that of post-monsoon season, value varied from 4 mg/L to 204 mg/L in pre-monsoon with a mean value of 76.7 mg/L (Table 3.1 a). In urban lateritic aquifers value of $HCO_3 + CO_3$ ion ranged from 8.4 mg/L to 141.8 mg/L with a mean value of 35.5 mg/L in pre-monsoon and that of post-monsoon season, value varied from 8 mg/L to 136 mg/L with a mean value of 39.8 mg/L (Table 3.1 b). $HCO_3 + CO_3$ ion concentration of peri-urban alluvial phreatic aquifer ranged from 12.6 mg/L to 21 mg/L in pre-monsoon with a mean value of 16 mg/L and that of post-monsoon season, value varied from 20 mg/L to 132 mg/L with a mean value of 61.6 mg/L (Table 3.1 c). In peri-urban lateritic aquifers $HCO_3 + CO_3$ ion concentration ranged from 6.6 mg/L to 150.6 mg/L with a mean value of 33.9 mg/L in pre-monsoon and that of post-monsoon season, value varied from 4 mg/L to 88 mg/L with a mean value of 26.2 mg/L (Table 3.1 d).

Bicarbonates represent the dominant form of alkalinity in natural waters; its source is the partitioning of CO_2 from the atmosphere and the weathering of carbonate minerals in rocks and soil. The spatial distribution map of bicarbonate as total alkalinity (Figure 3.7 a & b) shows that majority of the area falls within the permissible limit (600mg/L) of BIS drinking water standards. Highest concentration of bicarbonate were visible in western side of the study area, particularly in coastal urban phreatic zone. Concentration of bicarbonate in majority of urban and peri-urban lateritic aquifers were remains in constant class (< 50) during pre-monsoon and post-monsoon. Where as in urban and peri-urban coastal zone, slight increase in bicarbonate concentration were observed from pre-monsoon to post monsoon period.

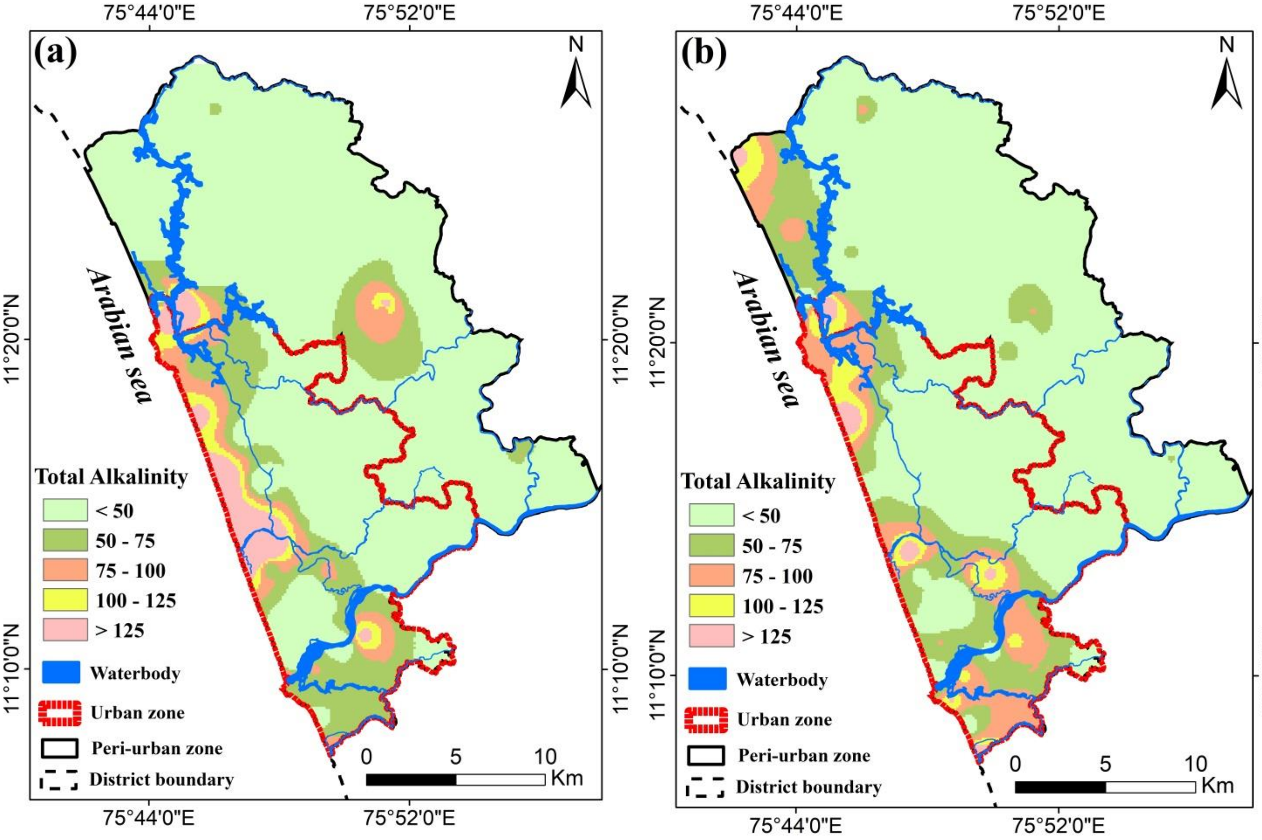

Figure 3.7. Spatial distribution of Total Alkalinity in the study area (a) Pre-monsoon (b) Post-monsoon

The concentration of sulphate ion in the urban alluvial phreatic aquifer ranged from 12.4 mg/L to 119.2 mg/L in pre-monsoon with a mean value of 33.5 mg/L and that of post-monsoon season, value varied from 2.6 mg/L to 106.1 mg/L in pre-monsoon with a mean value of 28 mg/L (Table 3.1 a). In urban lateritic aquifers value of sulphate ion ranged from 0.1 mg/L to 61.4 mg/L with a mean value of 15.8 mg/L in pre-monsoon and that of post-monsoon season, value varied from 0.7 mg/L to 48.4 mg/L with a mean value of 13.6 mg/L (Table 3.1 b). sulphate ion concentration of peri-urban alluvial phreatic aquifer ranged from

1.3 mg/L to 33.3 mg/L in pre-monsoon with a mean value of 8.7 mg/L and that of post-monsoon season, value varied from 1.7 mg/L to 28.9 mg/L with a mean value of 15.1 mg/L (Table 3.1 c). In peri-urban lateritic aquifers sulphate ion concentration ranged from 0.1 mg/L to 36.6 mg/L with a mean value of 5.7 mg/L in pre-monsoon and that of post-monsoon season, value varied from 0.2 mg/L to 44 mg/L with a mean value of 4.4 mg/L (Table 3.1 d).

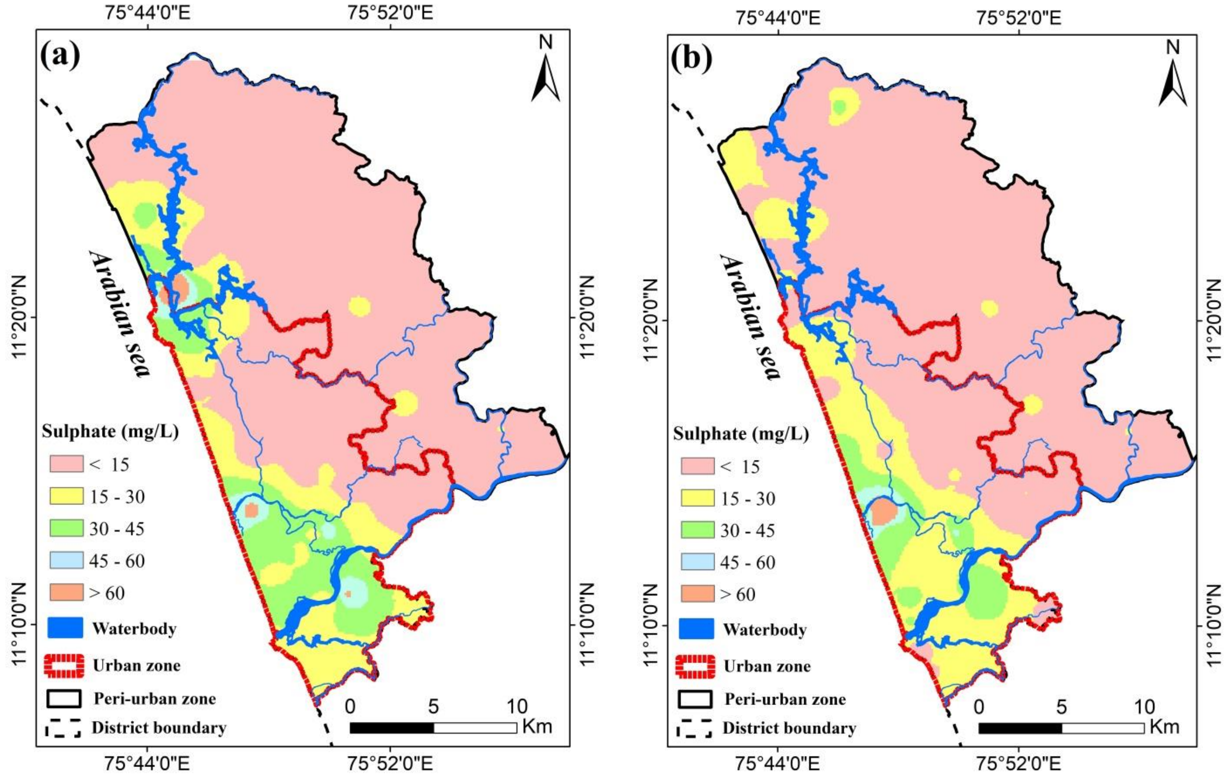

Figure 3.8. Spatial distribution of Sulphate in the study area (a) Pre-monsoon (b) Post-monsoon

From figure 3.8 (a &b) it is clear that the entire study area falls within the acceptable limit for the drinking water (< 200 mg/L) suitability specified by WHO (2011) & BIS standards. Natural sources for sulphate in the groundwater are oxidation of sulphide ores, gypsum and anhydrite and its composition is usually less than 300 mg /L, except in wells influenced by acid mine drainage having up to 200,000 mg/L in some brines (Chapman and WHO, 1996).

The concentration of chloride ion in the urban alluvial phreatic aquifer ranged from 30.8 mg/L to 1349.6 mg/L in pre-monsoon with a mean value of 195 mg/L and that of post-monsoon season, value varied from 17.8 mg/L to 601.5 mg/L in pre-monsoon with a mean value of 130.1 mg/L (Table 3.1 a). In urban lateritic aquifers value of chloride ion ranged from 18.6 mg/L to 106.4 mg/L with a mean value of 35.6 mg/L in pre-monsoon and that of post-monsoon season, value varied from 10.7 mg/L to 67.6 mg/L with a mean value of 24 mg/L (Table 3.1 b). Chloride ion concentration of peri-urban alluvial phreatic aquifer ranged from 7.7 mg/L to 34.7 mg/L in pre-monsoon with a mean value of 20.1 mg/L and that of post-monsoon season, value varied from 10.7 mg/L to 32 mg/L with a mean value of 20.6 mg/L (Table 3.1 c). In peri-urban lateritic aquifers chloride ion concentration ranged from 3.9 mg/L to 65.6 mg/L with a mean value of 22.3 mg/L in pre-monsoon and that of post-monsoon season, value varied from 3.6 mg/L to 53.4 mg/L with a mean value of 16.5 mg/L (Table 3.1 d).

The chloride concentration in groundwater of the entire study area was classified into very oligohaline (< 5 mg/L), oligo haline (5- 30 mg/L) , fresh (30 – 150 mg/L), fresh-to-brackish (150-300 mg/L), brackish (300-100 mg/L) and brackish salt (> 1000 mg/L) types based on Stuyfzand, (1989) procedure. Its spatial distribution in both seasons shown in figure 3.9 (a & b). Majority of the sample were came under the oligohaline class followed by the freshwater type. In the post-monsoon period, some freshwater type areas were transformed to oligohaline water type. Fresh-to-brackish to brackish type groundwater were observed in urban alluvial zone and as per the WHO (2011) & BIS (2012) Specifications for drinking water, majority of the study area falls within the permissible limit, except a few samples from the coastal zone. This highest value in groundwater is due to domestic sewage percolation and saline water intrusion. Salaj et al. (2018 a) study on assessment of coastal change impact on vulnerability in Kozhikode coastal stretch was also pointed out that the seawater intrusion and sewage percolation are the reason for highest concentration of chloride ion in groundwater.

Some water containing as much as 250 mg Cl^-/L may have a detectable salty taste if the cation is sodium. On the other hand, the typical salty taste may be absent in water, containing as much as 1000 mg/L when predominant cations are Ca and Mg (APHA, 2012). The chloride in groundwater may be from sources such as leaching of sedimentary rocks & soil, and from domestic & municipal effluents (Prasanth et al. 2012).

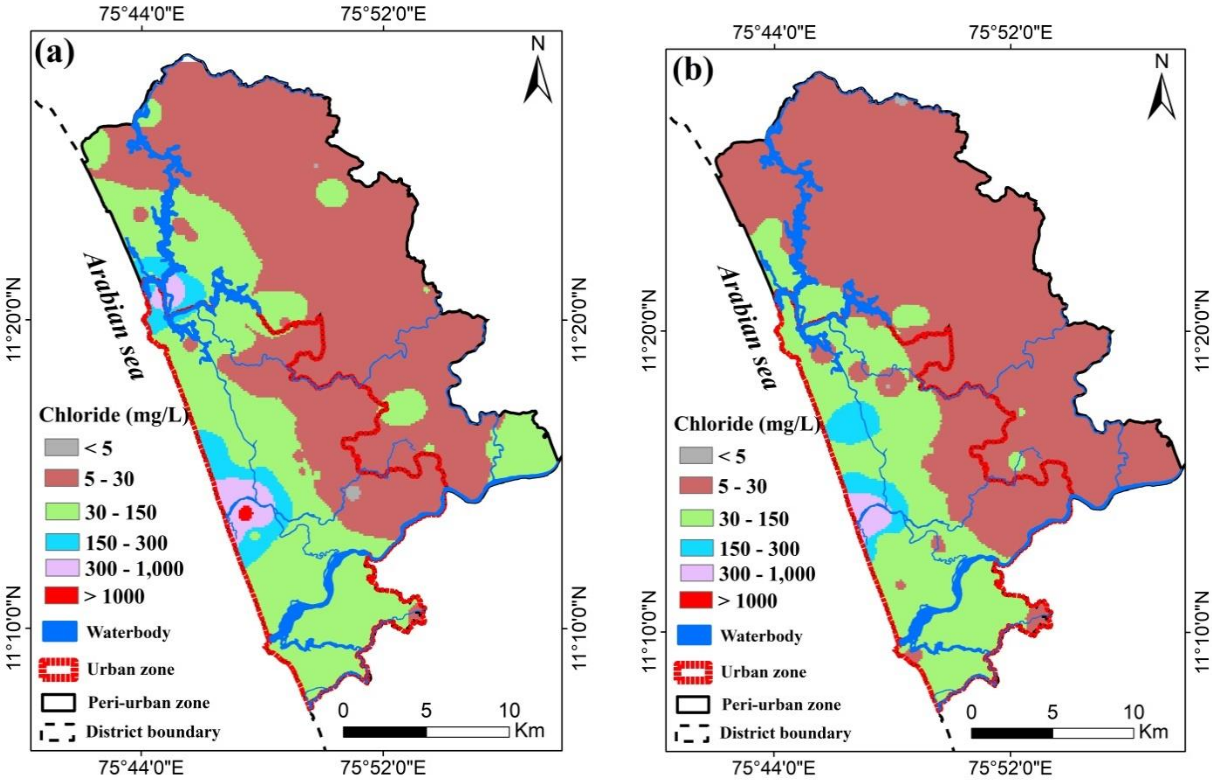

Figure 3.9. Spatial distribution of Chloride in the study area (a) Pre-monsoon (b) Post-monsoon

Physico-chemical parameters were showed significant variation from urban to peri-urban phreatic aquifers than that during pre-monsoon to post-monsoon seasons. Also, the seasonal change in groundwater composition were comparatively more visible in urban alluvial phreatic coastal aquifers than in peri-urban lateritic aquifers. Majority of the urban cluster in the study area situated in the low land alluvial plain with a slope of 0-15% and the depth to water level is in the range of 0.7- 6 mbgl during the peak summer season (Jesiya and Gopinath, 2015). Studies on spatial and temporal variation in chemical quality of the Madras aquifer conducted by Elango and Manickam, 1987, pointed out seasonal variation in physico-chemical parameters of coastal aquifers may be due to the frequent mixing of sea, river, and rainwater with groundwater. In addition to this, the disposal of sewage also contributing elevated concentration of physico-chemical parameters in urban phreatic aquifers. Majority of peri-urban phreatic aquifers of the study area were located in moderate to steep slope, highly vegetated terrain with valley fills and alternating laterite & alluvial strips. This undulating topography and vegetation cover may be responsible for the least variant groundwater chemistry in peri-urban zone.

3.1.2. Box- Whisker plot

Box plots drawn for representing the spatial and temporal variation of concentration of the major ions in groundwater of the urban and peri-urban aquifers of the study area (Figure 3.10) . The upper and lower quartiles of the data are define the top and the bottom of a rectangle box. The line with a red dot inside the box represents the median value, and the size of the box represents the spread of the central value (Tizro and Voudouris 2008). Seasonally averaged concentrations of major ions in the groundwater samples were permit to identify their abundance. Figure 3.10 shown that the concentration of physico-chemical parameters in phreatic aquifers were decreases from pre-monsoon to post-monsoon.

Dissolution of minerals deposited during the pre-monsoon season were caused an elevated concentration of water quality parameters in pre-monsoon than post-monsoon period (Rajmohan, and Elango, 2004; 2006). And during post-monsoon, dilution of groundwater by rainwater recharge were took place and thereby reduces the ionic concentration in the groundwater through the mixing of fresh infiltrated water with groundwater. Study on

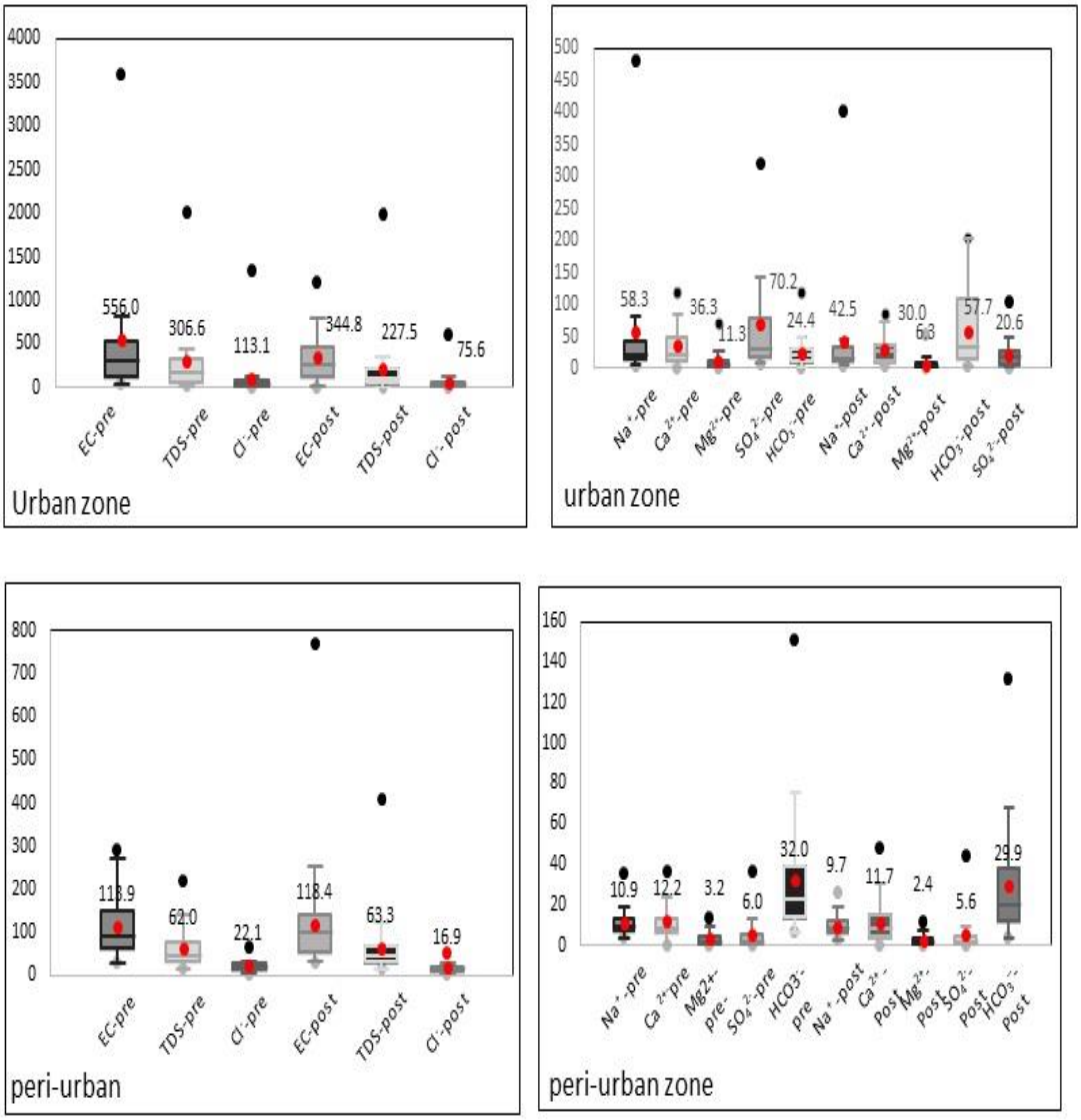

Figure 3. 10. Box-Whisker plot for the maximum, minimum and average of the chemical constituents in groundwater during pre-monsoon and post-monsoon (all values in mg/L except pH, EC (µS/cm)

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relationship between hydrogeochemistry and groundwater level fluctuation in the Palar and Cheyyar river basins conducted by Rajmohan, and Elango, (2004) were proved the influence of recharge process on seasonal variations.

3.1.3. Mann-Whitney U test for identifying degree of spatial variation

A non-parametric test-Mann Whitney U test based on ranked sums were used to distinquish the distribution of two independent samples (McBean and Rovers, 1998). Groundwater samples from urban and peri-urban phreatic aquifers during pre-monsoon and post monsoon seasons were undergone Mann Whitney U test and thereby confirmed the significant ($P \leq 0.05$) spatial variation between urban and peri-urban groundwater quality variables.

Table 3.3. Mann-Whitney U test for urban and peri-urban water quality parameters in pre-monsoon and post-monsoon period

Variable\Test	**Urban [Pre-monsoon & Post-monsoon]**	**Peri-Urban- [Pre-monsoon & Post-monsoon]**	**Pre-monsoon [Urban & Peri Urban]**	**Post-monsoon [Urban & Peri Urban]**
pH	0.178	0.971	**0.002**	**0.001**
EC(µS/cm)	0.323	0.846	**< 0.0001**	**< 0.0001**
TDS(mg/L)	0.177	0.769	**< 0.0001**	**< 0.0001**
Na(mg/L)	0.270	0.154	**< 0.0001**	**< 0.0001**
K(mg/L)	0.642	0.283	**< 0.0001**	**< 0.0001**
Ca (mg/L)	0.892	0.385	**< 0.0001**	**< 0.0001**
Mg(mg/L)	0.272	0.114	**0.004**	**0.005**
HCO_3^- + CO_3(mg/L)	0.721	0.327	0.066	0.056
SO_4^{2-}(mg/L)	0.627	0.300	**< 0.0001**	**< 0.0001**
Cl^-(mg/L)	0.074	0.06	**< 0.0001**	**< 0.0001**

For this test, the null hypothesis states that the two samples taken from a common population will have no consistent differences between the two sets of ranking. This hypothesis rejected when the calculated p-value is less than 0.05. In other words, when the p-value is less than 0.05, the two groups are significantly different. The Mann–Whitney U test were performed in order to quantify the significance of the differences in water quality parameters distribution between two differently urbanised zones, and also between pre and post-monsoon seasons. As explained above, the data used in the Mann–Whitney U test does not need the normality assumption. The Mann–Whitney U test (Table 3.3) were confirmed that concentration of physic-chemical parameters other than HCO_3^-+ CO_3^- shows significant differences (p-value < 0.05) between urban and peri-urban phreatic aquifers. Whereas physico-chemical parameters of groundwater in both urban and peri-urban phreatic zone were showing a less significant difference between of pre and post-monsoon period.

3.1.4. Nitrate - An urban pollution indicator

The concentration of nitrate in the entire study area ranges from 0 mg/l to 66 mg/l with an average value of 0.23 mg/l during pre-monsoon. While considering urban and peri-urban zone separately, the concentration ranges from 0 mg/l to 66 mg/l in urban groundwater with an average value of 5.96 mg/L. Peri-urban groundwater samples having nitrate concentration in the range of 0 to 5.72 mg/L with an average of 0.14 mg/L. Average nitrate concentration of both urban and peri-urban groundwater samples were indicated that all groundwater samples except two urban alluvial groundwater samples having nitrate concentration below the acceptable limit (> 45 mg/L) specified by the drinking water standard (BIS, 2012). The concentration of nitrate remains same during both pre-monsoon and post-monsoon period. Therefore the spatial distribution of nitrate (mg/L) concentration for urban and peri-urban aquifers during pre-monsoon season were shown in figure 3.11. Sources of nitrate in groundwater are mainly from agricultural/farming, anthropogenic activities, etc. There is neither agricultural nor farming activities are going on the urban coastal alluvial zone where nitrate concentration were exceeding the value of > 45mg/L. Whereas these groundwater samples were located in the vicinity of the densely populated region of the study area. Therefore intense urban activities such as dumping of animal wastes, seepages from waste water system are the potential source of nitrate contamination in the corresponding groundwater.

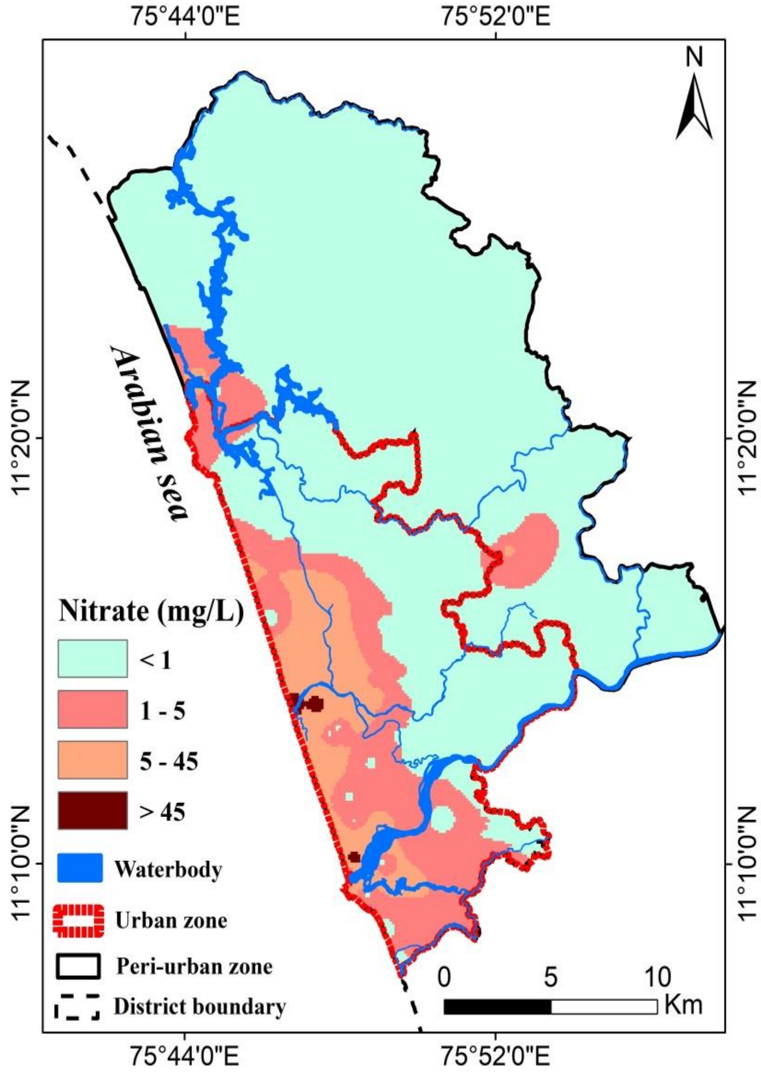


Figure 3.11. Spatial distribution of Nitrate in the study area during pre-monsoon period

3.1.5. Biological parameters

Groundwater samples were collected and analyzed for bacterial contamination such as Total Coliform Counts (TCC), Fecal Coliform Counts (FCC) and *Escherichia coli*.

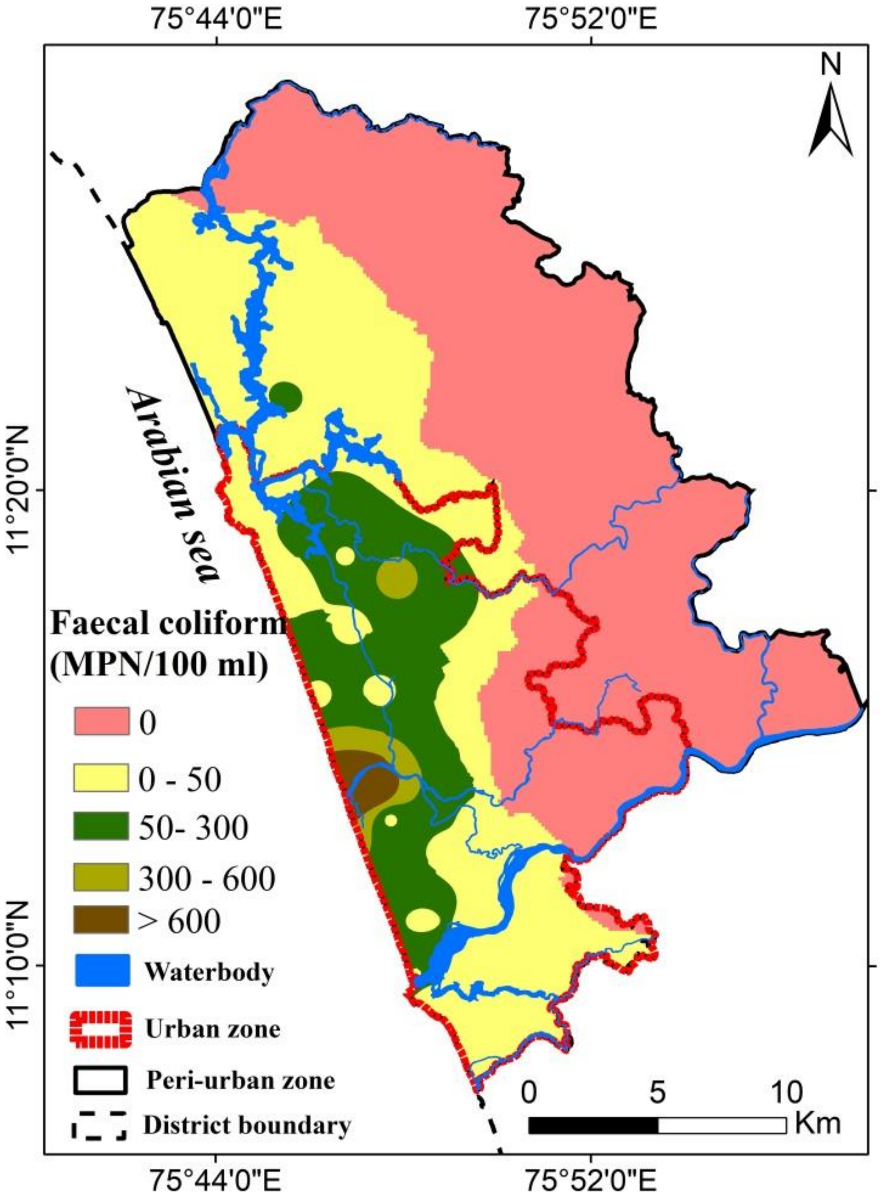


Figure 3.12. Spatial distribution of Faecal coliform along the study area during pre-monsoon period

The greatest microbial risks associated with ingestion of water that contaminated with human or animal faeces. In the study area, the presence of faecal coliforms detected is in the range of 0-1098 in a 100 ml sample. Major bacterial contamination occurred in urban groundwater especially in well water collected from the coastal urban region (Figure 3.12). E. coli is the more precise indicator of faecal pollution and urban coastal wells in the study area were observed with the high faecal contamination, detected the presence of *Escherichia coli*. According to the BIS guidelines for drinking water, the presence of faecal coliforms must not be detectable in any 100 ml sample. Peri-urban phreatic aquifers having the depth to water level in the range of > 6mbgl shows good bacteriological quality compared to urban zone. This may be due vertical percolation of water through soil results in the removal of microbial pollutants (Harikumar and Chandran, 2013). Since urban zone facing a severe space limitation for necessary infrastructure, leach pits are not in proper distance from the wells and thereby leading to high bacterial contamination. Megha et al. (2015) study on bacterial contamination in groundwater of rural village of Kozhikode were explained that the present distances between wells and latrines coupled with the level of hygiene of these wells are insufficient to prevent groundwater contamination in the atudy area. From figure 3.11 and 3.12, it can be see that heavy contamination of faecal coliforms (> 600 MPN/100 ml) and high nitrate concentration (> 45 mg/L) in groundwater were observed from the same area and thereby confirmed the influence of anthropogenic activities on the urban alluvial aquifers. Studies conducted by Sreekala et al. 2018 on Thermotolerant Coliforms and *E.coli* in the groundwater of central Kerala also explained the influence anthropogenic factors on heavy contamination of coliforms in groundwater.

3.2. Hydrogeochemical processes

3.2.1. Hill-Piper diagram for hydrogeochemical facies

In Hill–Piper diagram (Piper, 1944), data plotted on the subdivisions of diamond-shaped field were expressed the water types / hydrochemical facies occured in the urban and peri-urban phreatic groundwater of the study area (Figure 3.13 i) . These hydrogeochemical facies present in the groundwater of the study area were enlightened the geochemical processes functioned at the region. The concentration of cations and anions were plotted as a percentage in meq/L so that the total of cations (Ca + Mg and Na + K) and anions (Cl, SO_4,and CO_3+HCO_3) made to 100 %.

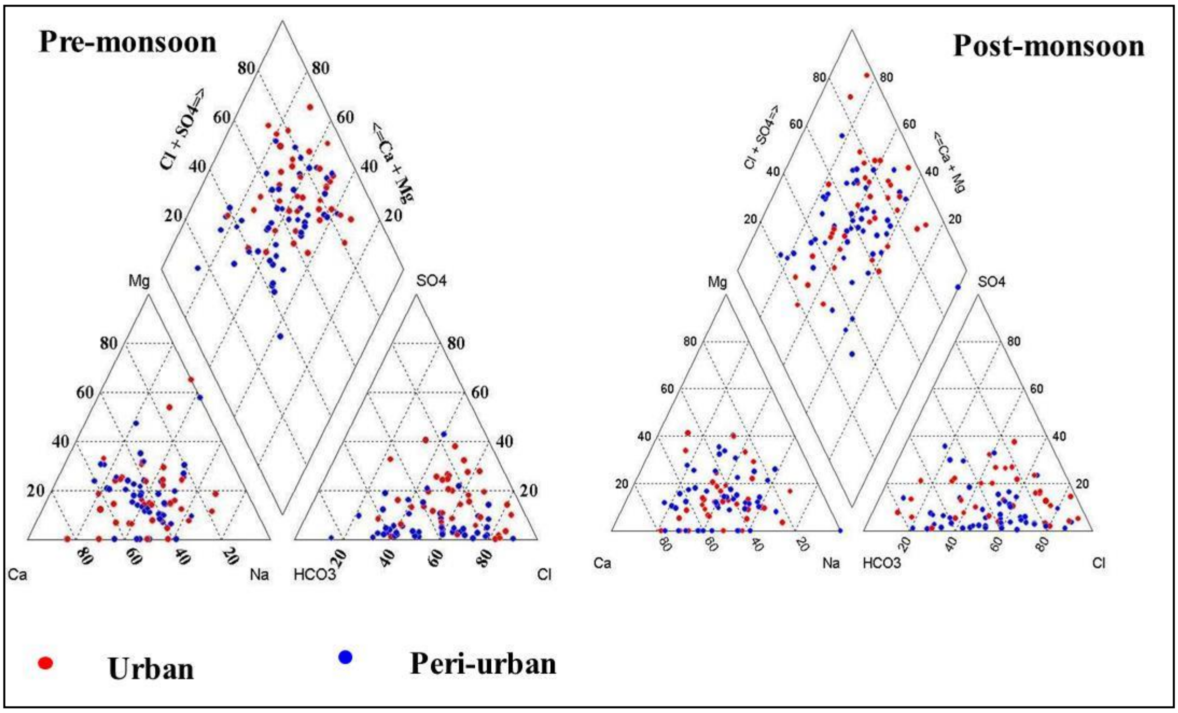


Figure 3.13 (i). Piper tri-linear diagram for pre-monsoon and post-monsoon period

Groundwater in urban and peri-urban zone of the total study area classified into three facies such as Ca-Mg-HCO_3 (14%), Na-K- Cl-SO_4 (24%) and Ca-Mg-Cl-SO_4 (62%) type during the pre-monsoon period. While comparing the study area into urban an peri-urban zones separately, it could be seen that in the pre-monsoon period, of the 36 urban groundwater samples, 61% of the groundwater have a Ca-Mg-Cl-SO_4 water type, 30% with Na-K-Cl- SO_4, and the rest 9% with Ca-Mg-HCO_3 hydrogeochemical facies. In peri-urban zone 60% are characterized by Ca-Mg-Cl-SO_4 type, 25% of groundwater with Ca-Mg-HCO3 and 15% with Na-K-Cl-SO_4 hydrogechemical types. Spatial distribution of major water types occurred in the study area shown in Figure 3.13 (ii).

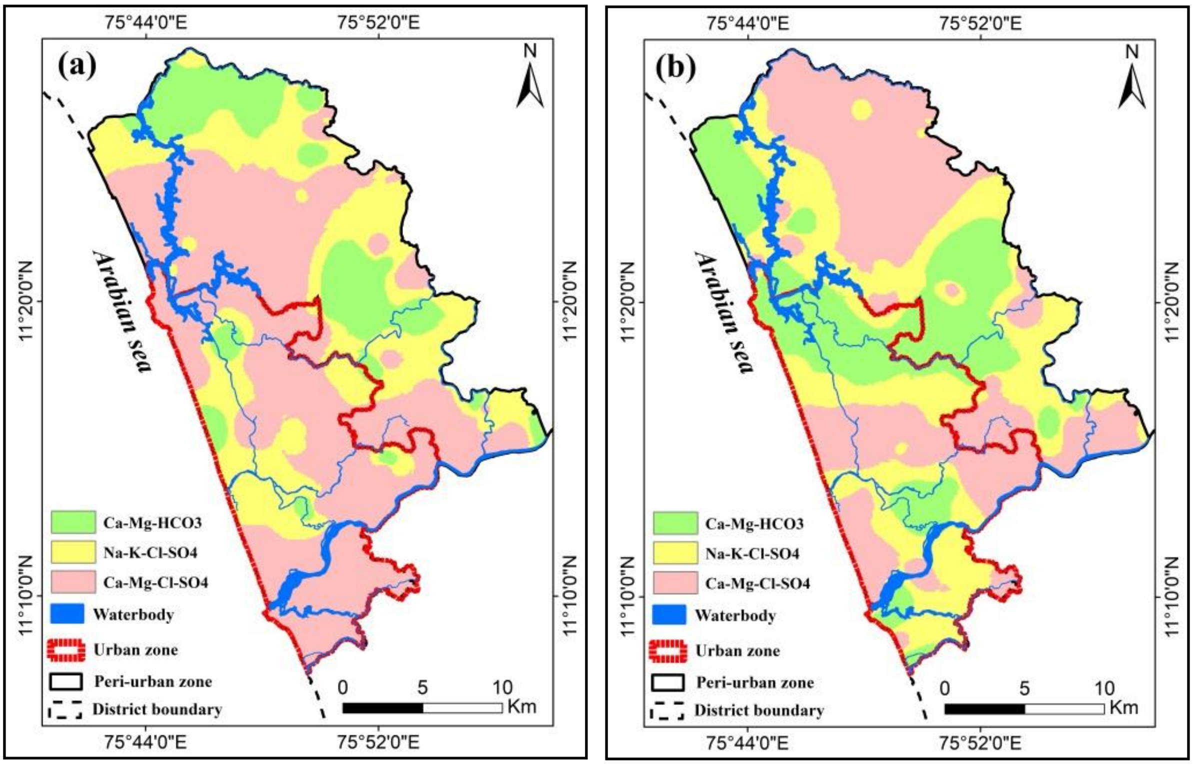
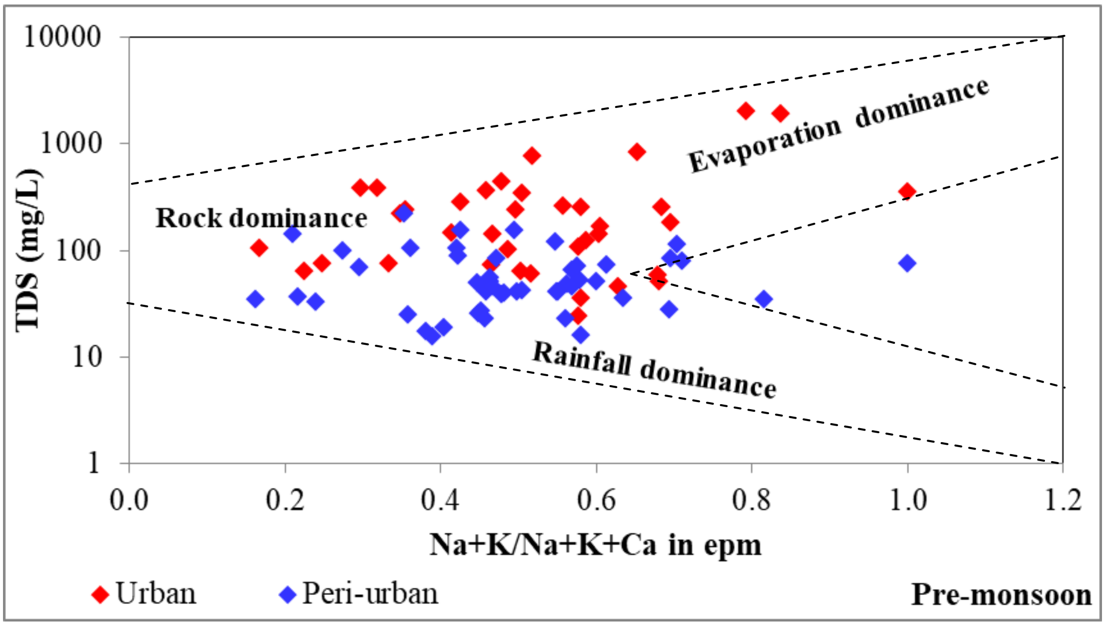


Figure 3.13 (ii). Spatial distribution of water types in the study area (a) Pre-monsoon (b) Post-monsoon

Groundwater in urban and peri-urban phreatic aquifers were showed slight deviation in relative occurrence of hydrochemical facies during the post-monsoon period. Urban groundwater characterized by three major water types such as Ca-Mg-Cl-SO_4 (49%), Ca-Mg-HCO_3 (24%) and Na-K-Cl-SO_4 (27%). Simultaneously peri-urban groundwater comprised of Ca-Mg-Cl-SO_4 (59%), Ca-Mg-HCO_3 (23%) and Na-K-Cl-SO_4 (18%) type. In the total study area, the majority of the sample dominated with alkaline earth metals (i.e., Ca^{2+} and Mg^{2+}) and followed by alkalies (i.e., Na^{+}+ K^{+}). In the entire study area an increase in Ca-Mg-HCO_3 water type was observed from pre-monsoon to post monsoon. Handa (1979) reported that presence of such water facies were indicated sufficient recharge from freshwater.

3.2.2. Gibbs diagram

The diagram which expressed the mechanism that controls the chemical composition of major dissolved salts in water is termed as Gibbs Diagram. The plot could provide information on the relative importance of three major natural mechanisms controlling groundwater chemistry such as 1) atmospheric precipitation 2) rock weathering and 3) evaporation and fractional crystallization. The chemical data of groundwater samples from urban and peri-urban phreatic aquifers were plotted in the Gibbs diagram (Figure 3. 14). Gibb's analysis showed that majority of the samples from urban alluvial aquifers were located in the rock dominant zone both in pre-monsoon and post-monsoon period indicated that groundwater chemistry of urban alluvial aquifers mainly controlled by rock-water interaction. Whereas samples from urban–lateritic and peri-urban aquifers were laid in precipitation dominant zone during both seasons depicted that groundwater chemistry of these aquifers were mainly influenced by rainfall. Urban alluvial samples of the study area such as U14 and U15 were located in evaporation dominant zone during pre-monsoon and post-monsoon period. For both urban and peri-urban groundwater samples , there is a shift towards rainfall dominance zone were observed from pre-monsoon to post-monsoon season. Gibb's analysis on groundwater in coastal phreatic aquifers of Allappuzha district showed similar observation that groundwater were influenced by both the rock-water interaction and precipitation dominance (Manjusree et al. 2009).



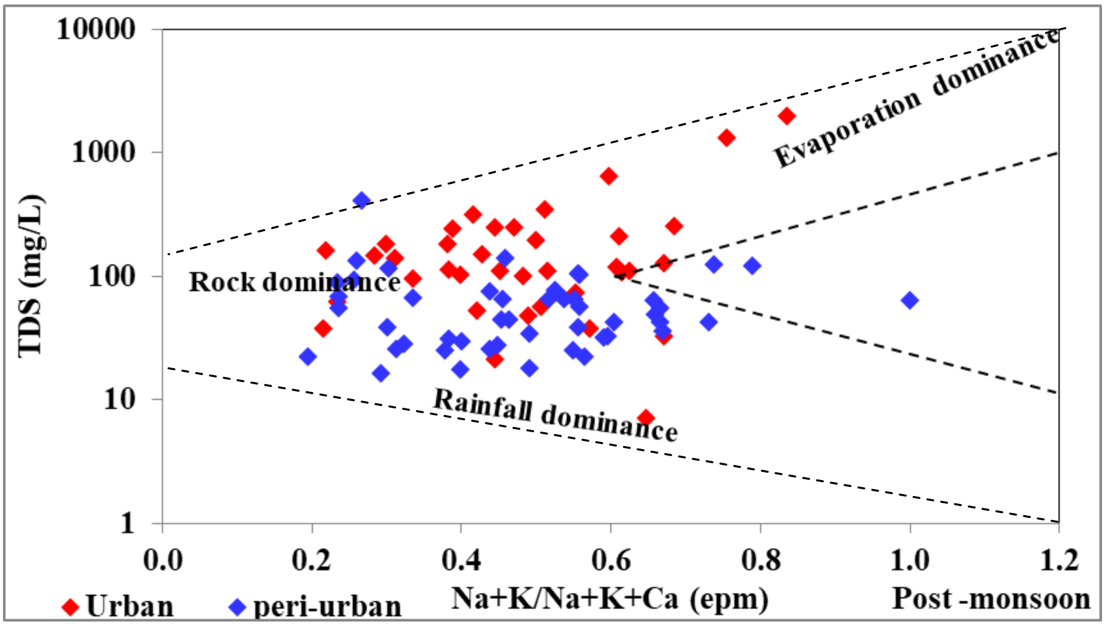


Figure 3. 14. Variations of the weight ratio of Na+K / Na+K+Ca as a function of Total Dissolved Solids (TDS) of urban and peri-urban phreatic aquifers (After Gibbs, 1970).

3.2.3. Inter-ionic relationships

3.2.3.1. Inter-ionic relationships–Urban groundwater

Hydrogeochemical compositional relationships among various dissolved ions deciphered the innate hydrogeochemical processes occurred in the groundwater system. Geochemical processes revealed from Gibb's plot was further verified using the inter-ionic relationships of various geochemical components present in the groundwater.

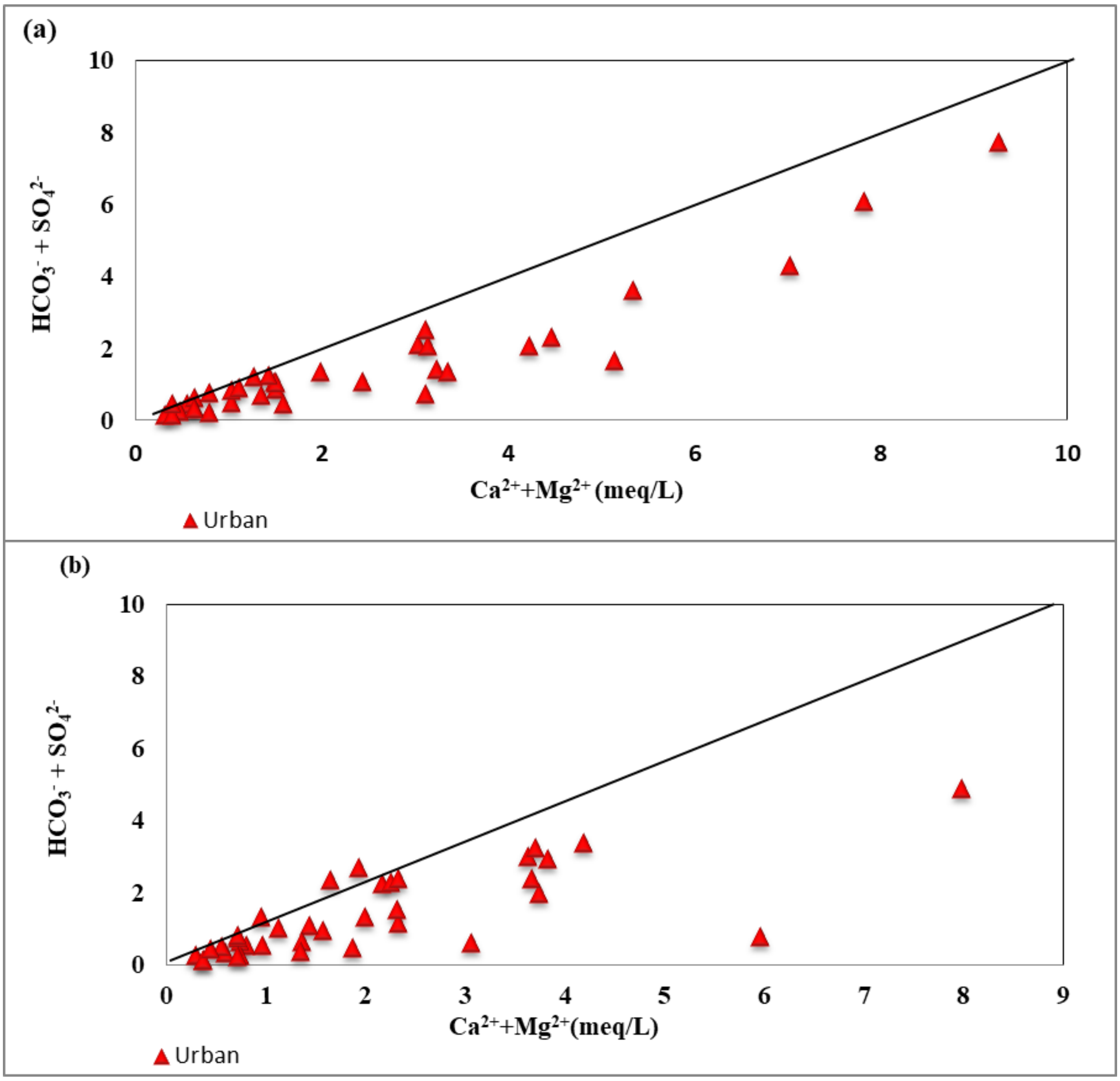


Figure 3.15. Relationship between (Ca^{2+}+Mg^{2+}) with (HCO_3^-+SO_4^{2-}) of the urban groundwater during (a) pre-monsoon and (b) post-monsoon seasons in the study area

The scatter plot of (Ca^{2+}+Mg^{2+}) vs. (HCO_3^-+SO_4^{2-}) was depicted that ionic concentration of all urban samples falls below the equiline in pre-monsoon (Figure 3.15). Moreover, in the post-monsoon, some urban samples move to above the line. The Ionic concentration below the equiline indicates silicate weathering process in groundwater (Datta and Tyagi, 1996). According to Datta and Tyagi (1996), if the primary source of Ca+Mg assumed to be silicate weathering, the dominant geological formation is alkaline earth silicate.

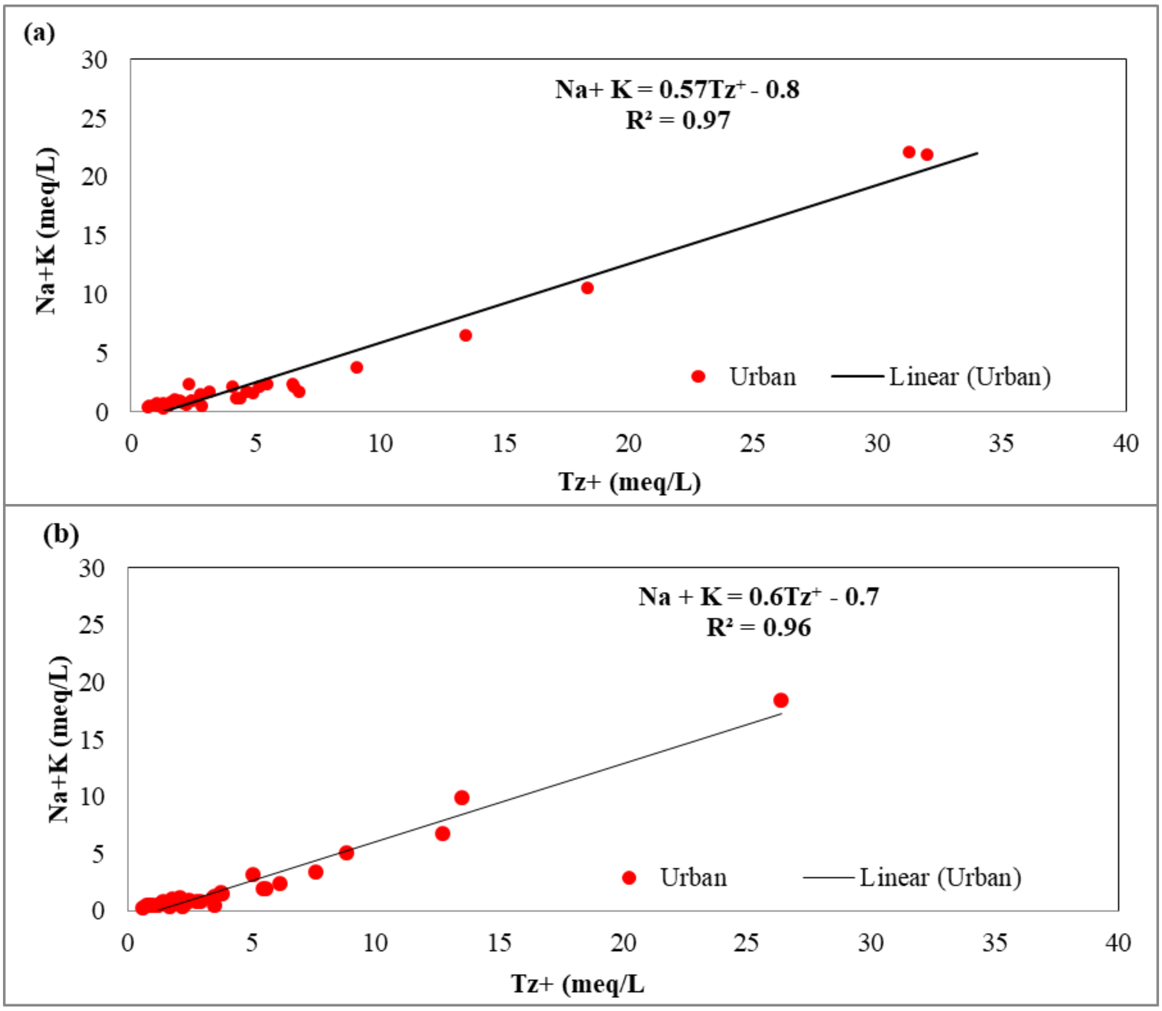


Figure 3.16. Relationship between Na^++K^+ with Tz^+ of the urban groundwater during (a) pre-monsoon and (b) post-monsoon seasons in the study area

Silicate weathering in urban alluvial groundwater were confirmed through a scatter diagram of (Na+K) and Tz^+. Trend analysis shows that majority of ions falls along and below the trend line and (Na+K): Tz^+ have a high ratio of > 0.5 for both in pre-monsoon and post-monsoon which indicated the cation contribution could be through silicate weathering (Figure 3.16).

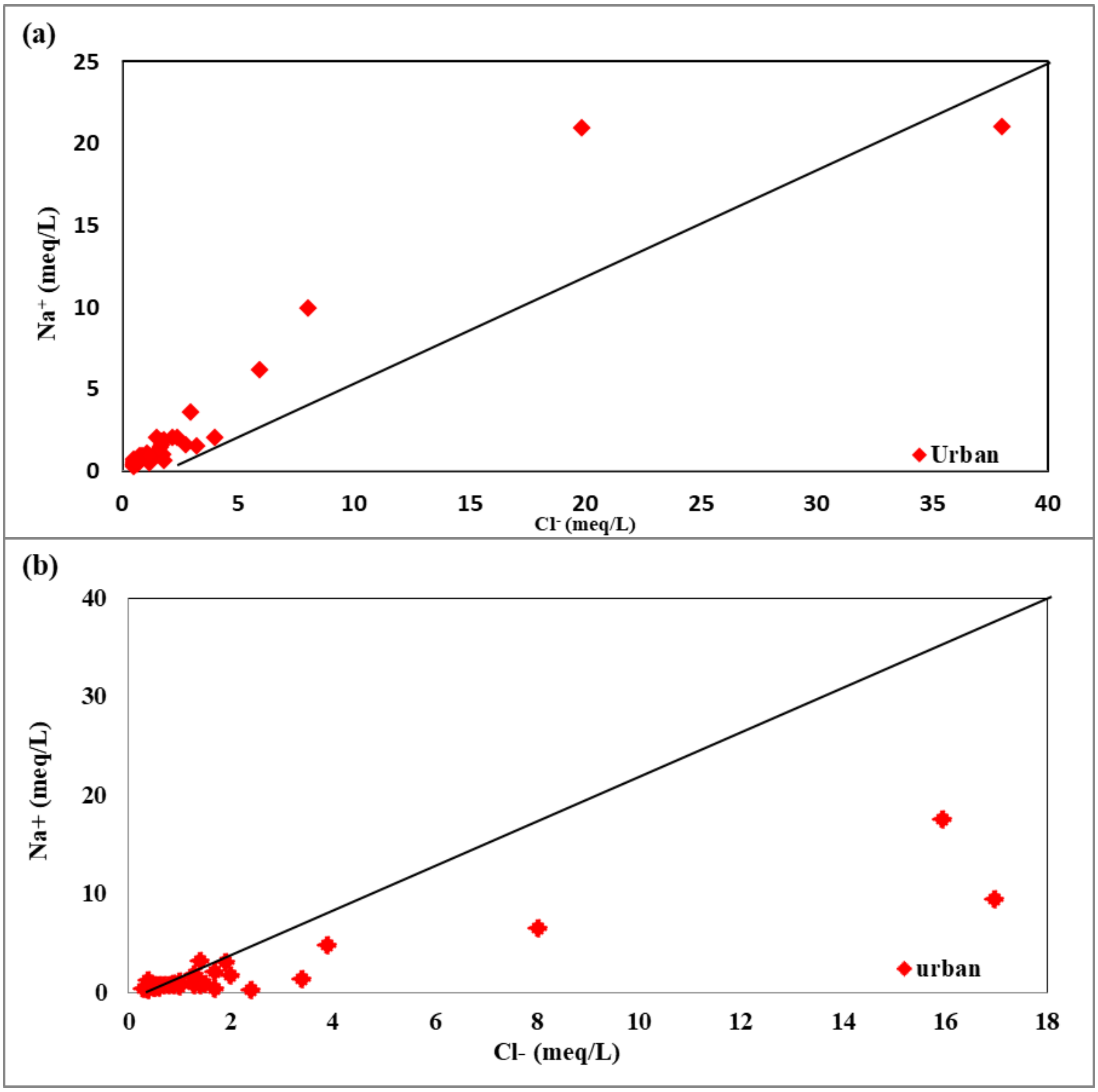


Figure 3.17. Relationship between Na^+ with Cl^- of the urban groundwater during (a) pre-monsoon and (b) post-monsoon seasons in the study area

All urban groundwater except few were showed 1:1 ionic relationship between sodium and chloride with a significant correlation ($R^2 > 0.8$), during both seasons due to the common source of origin(Figure 3.17). Few samples from urban alluvial aquifers (U14 & U15) shows a divergence from the equiline explains that Na^+ derived from different sources / due to the addition of Cl^- as a result of evaporation. Similar ionic radii between Na^+ and Ca^{2+} was confirmed an ionic exchange between groundwater and clay minerals happened frequently

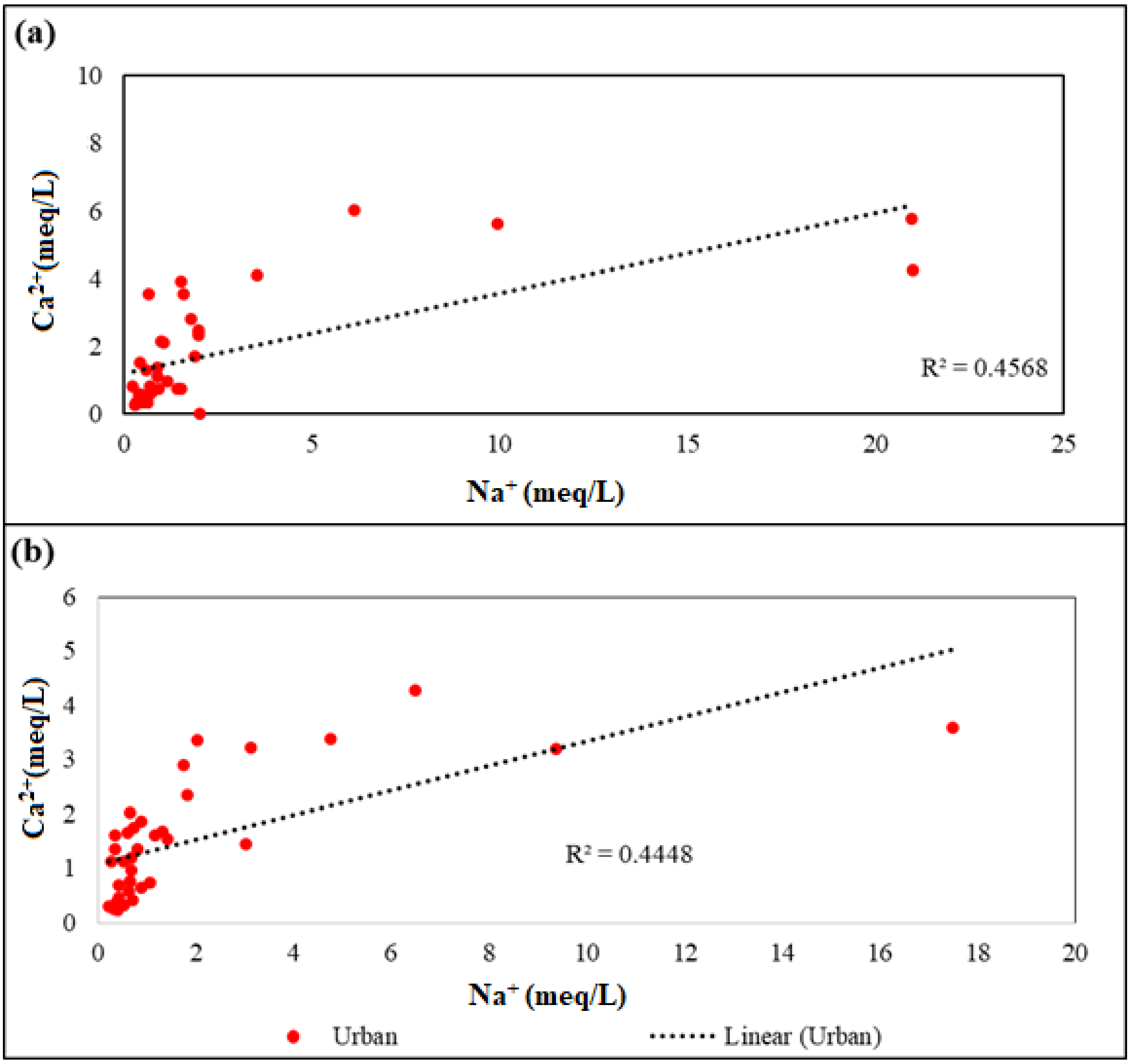


Figure 3.18. Relationship between Na^+ with Ca^{2+} of the urban groundwater during (a) pre-monsoon and (b) post-monsoon seasons in the study area

In the plot for Na^+ vs Ca^{2+}, slight deviation of calcium ions from the regression line was indicated the ion exchange process (Figure 3.18). To further confirm the ion-exchange, the scatter plot of $(Na^+ + K^+) - (Cl^-)$ Vs $(Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-})$ was plotted (Figure 3.19).

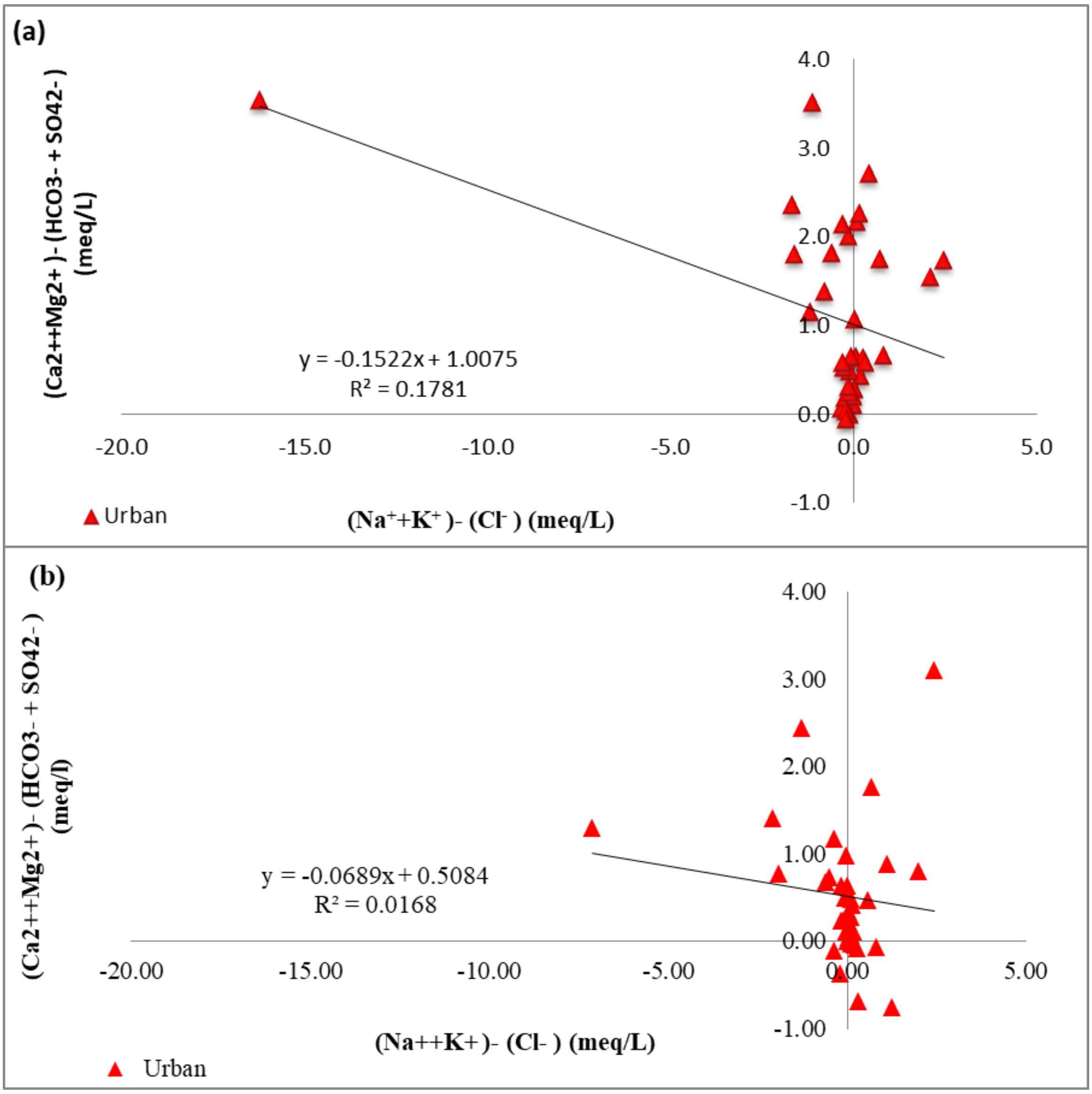


Figure 3.19. Relationship between $(Na^+ + K^+) - (Cl^-)$ with $(Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-})$ of the urban groundwater during (a) pre-monsoon and (b) post-monsoon seasons in the study area

Fisher and Mullican, 1997 explained that negative slope for groundwater samples in (Na^++K^+)- (Cl^-) Vs (Ca^{2+}+Mg^{2+})- (HCO_3^- + SO_4^{2-}) scatter plot were indicated the exchange in the hydrochemical process. Negative slope of -0.06 and -0.15 observed during pre-monsoon and post-monsoon respectively were substantiated the cation exchange process. Urban samples which shifted to the positive abscissa and negative ordinate was explained by the Na^+ and K^+ enrichment relative to Ca and Mg. Also, the discharge of Na^+ and K^+ ions.

3.2.3.2. Inter-ionic relationships - Peri-urban groundwater

In the scatter plot of (Ca^{2+}+Mg^{2+}) vs. (HCO^{3-}+SO_4^{2-}) of peri-urban groundwater majority were fall below the equiline, and some fall both along and above the line (Figure 3.20).

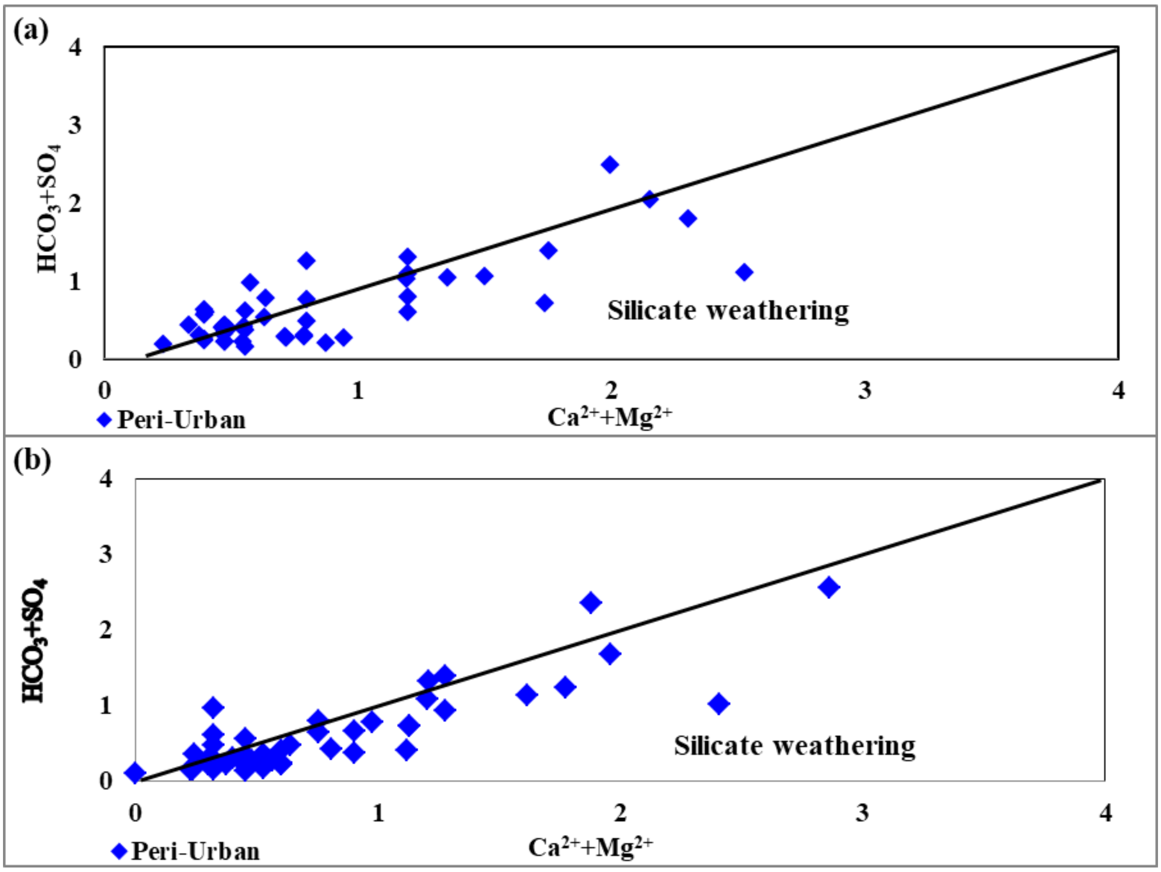


Figure 3.20. Relationship between (Ca^{2+}+Mg^{2+}) with (HCO_3^-+SO_4^{2-}) of the peri-urban groundwater during (a) pre-monsoon and (b) post-monsoon seasons in the study area

Thus the plot was depicted the dominance of silicate weathering process in peri-urban phreatic aquifers of the study area. The infiltration of rainwater and increase in recharge from pre-monsoon to post-monsoon period were enhanced the weathering process thereby release of Ca^{2+} and bicarbonate ions. In relationship between Na +K with Tz^{+}, not all peri-urban zone groundwater samples fall below the regression line and shows low Na +K: Tz^{+} ratio of 0.2, which indicated that Ca is dominant than Na (Figure 3.21).

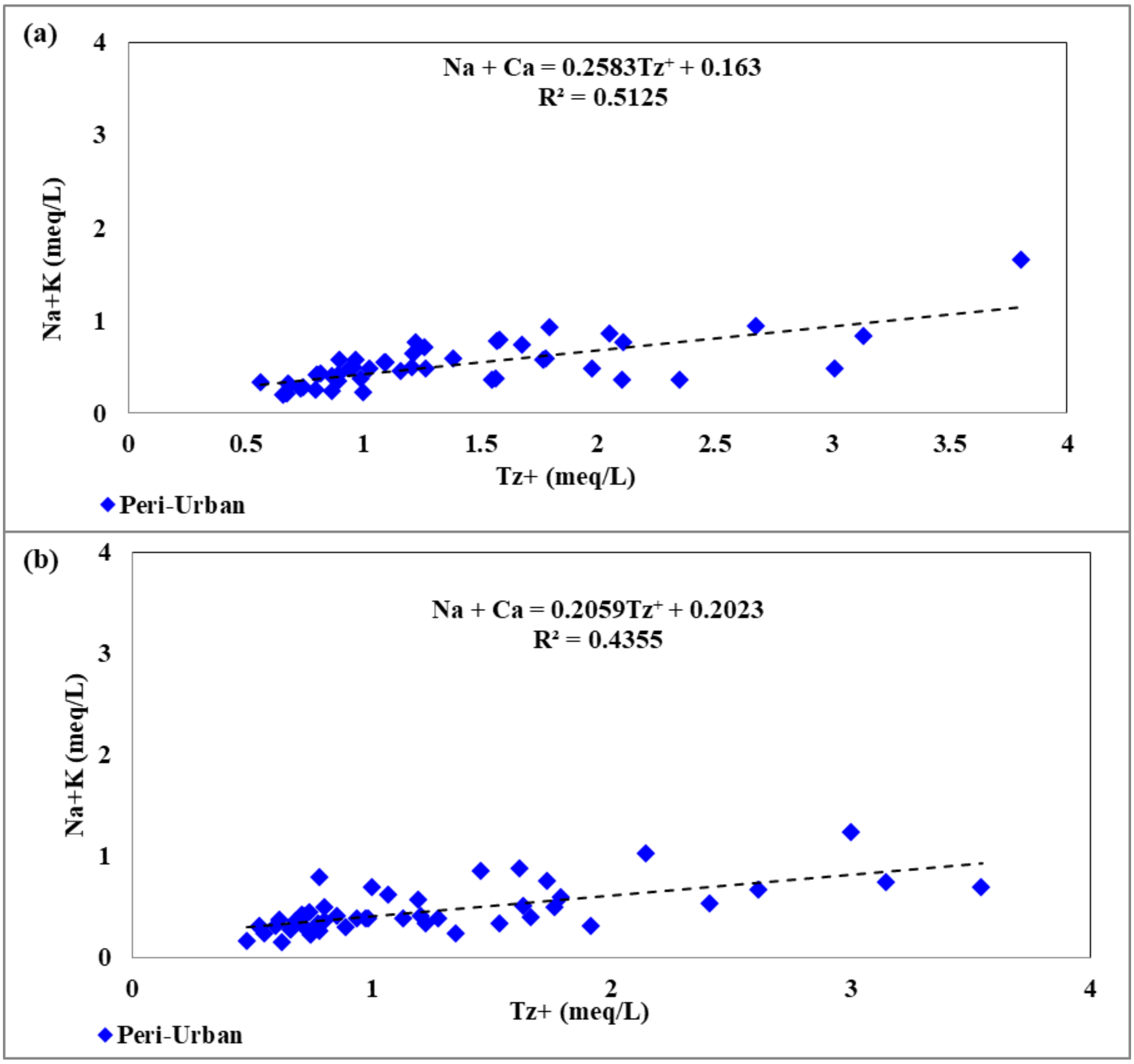


Figure 3.21. Relationship between (Na^{+}+K^{+}) with Tz^{+} of the peri-urban groundwater during (a) pre-monsoon and (b) post-monsoon seasons in the study area

For peri-urban zone, Na-Cl correlation is very poor (R^2 <0.3) in both pre-monsoon and post-monsoon period (Figure 3.22) and some peri-urban samples were show increased

Na concentration than chloride. According to Stallard and Edmond, 1983 ; Elango and Kannan, 2007, this increased Na concentration may be due to release of Na^+ ion from silicate weathering.

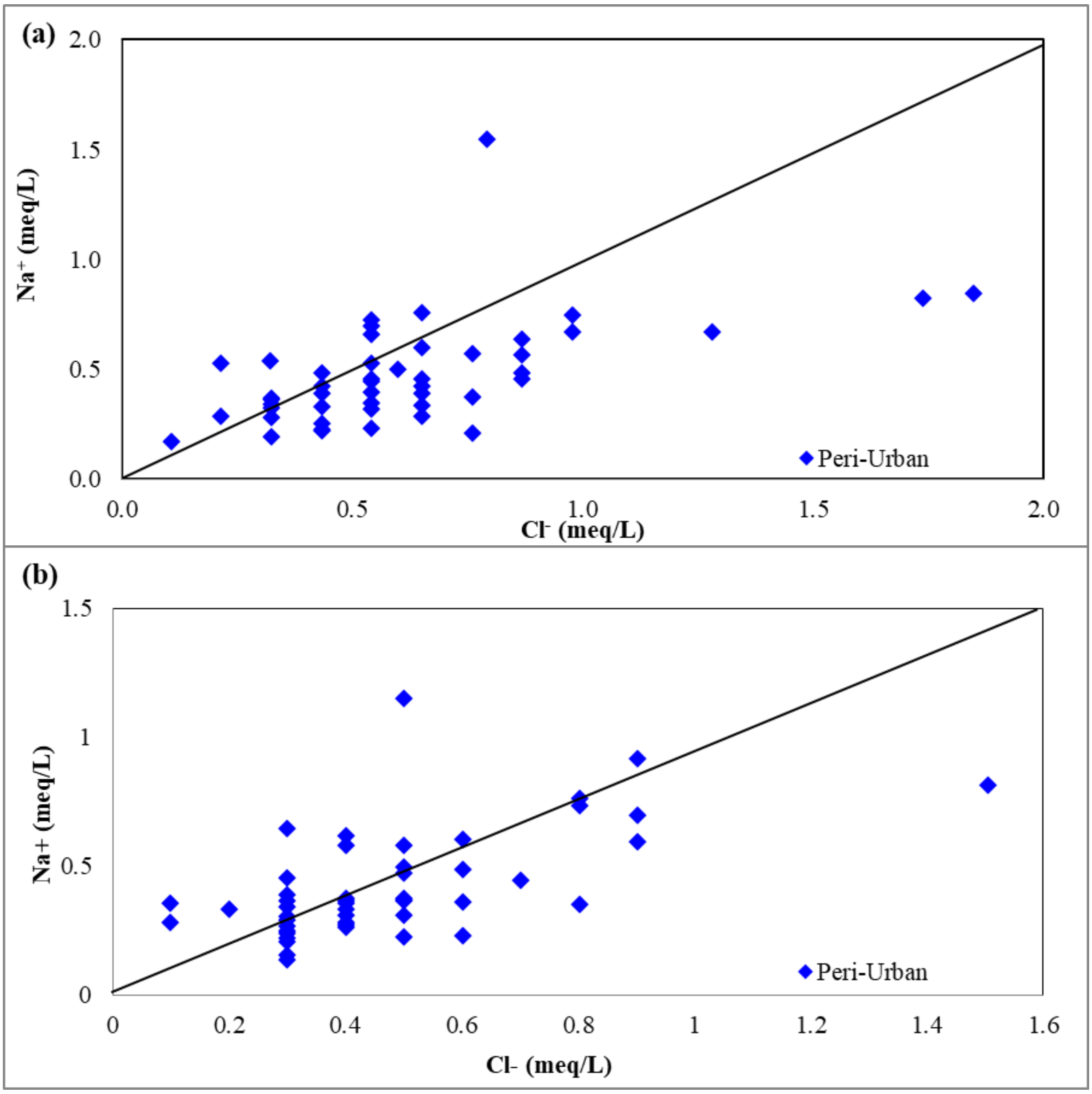


Figure 3.22. Relationship between Na^+ with Cl^- of the peri-urban groundwater during (a) pre-monsoon and (b) post-monsoon seasons in the study area

A significant deviation of ions from the regression line of the plot of Na^+vs Ca^{2+} were depicted the ion exchange process (Figure 3.23) and lower concentration of Na+K due to

Ca/Na exchange process.. Negative slope for groundwater during both seasons in Figure 3.24 was depicted the occurrence of cation exchange in the hydrochemical process.

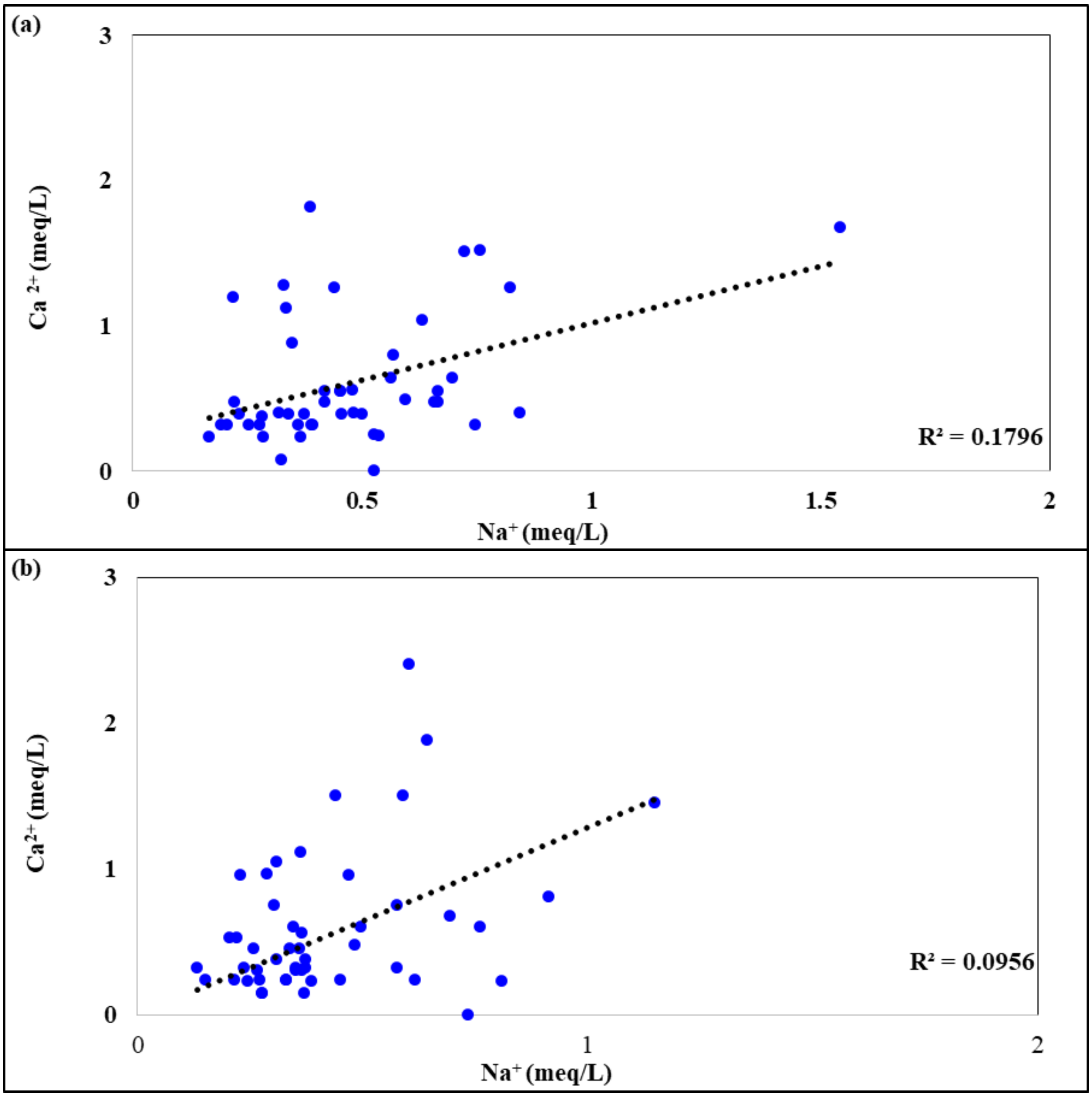


Figure 3.23. Relationship between Na^+ with Ca^{2+} of the peri-urban groundwater during (a) pre-monsoon and (b) post-monsoon seasons in the study area

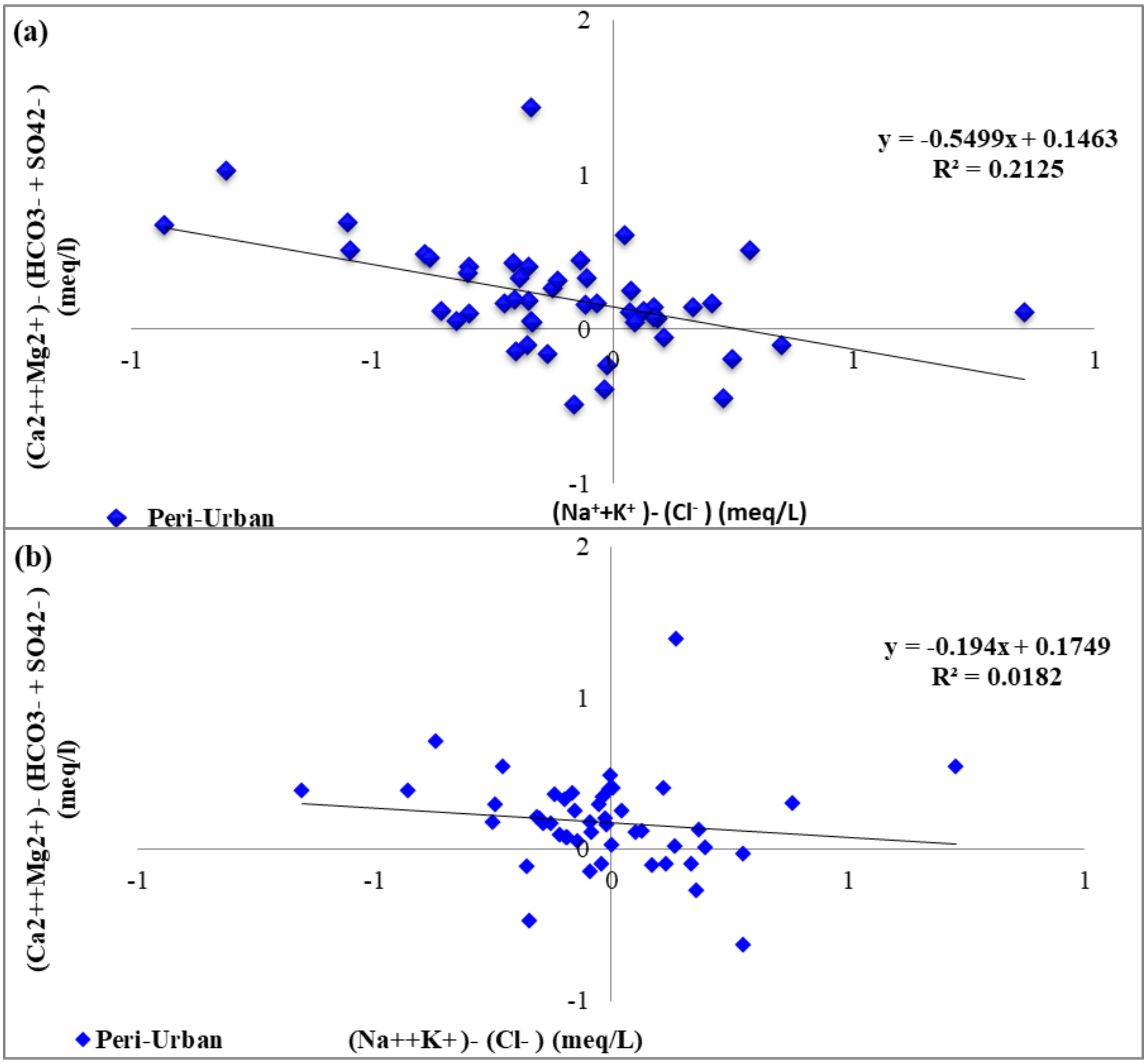


Figure 3.24. Relationship between $(Na^+ + K^+)$- (Cl^-) with $(Ca^{2+} + Mg^{2+})$- $(HCO_3^- + SO_4^{2-})$ of the peri-urban groundwater during (a) pre-monsoon and (b) post-monsoon seasons in the study area

Visible scattering of peri-urban groundwater samples in negative abscissa and positive ordinate during pre-monsoon were shifted to the positive abscissa and negative ordinate and the process were explained by the alkaline earth metal enrichment relative to alkalies.

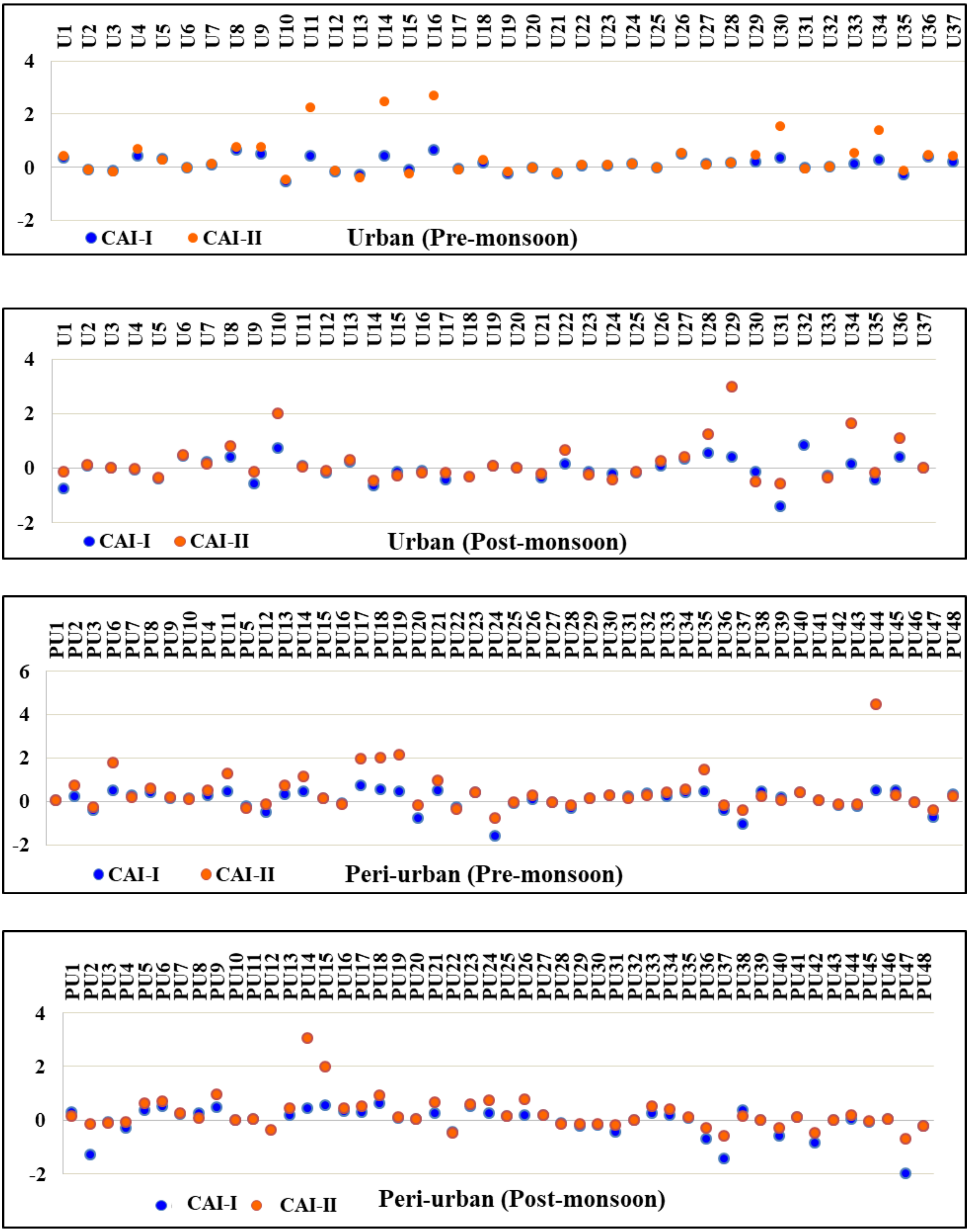
3.2.4. Index of base exchange (Chloro-Alkaline Indices-CAI)

Chloro-alkaline indices/ Indices of Base Exchange (IBE) were enabled to confirm the ion-exchange process between the groundwater and the aquifer material during the residence or travel (Schoeller, 1967) and these two chloro alkaline indices CAI and CAII (in meq/L) can be expressed as:

CAI-I = [Cl-(Na+K)] / Cl

CAI-II = [Cl-(Na+K)] / (SO4+HCO_3)

When there is an exchange between Na or K in groundwater with Mg or Ca in the aquifer material, both of the indices(CAI-I and CAI-II) are positive, indicating direct ion exchange. If the exchange takes place between the Ca and Mg in groundwater with Na or K in the aquifer material, the indices will be negative, indicating reverse ion exchange (Schoeller, 1967). In both seasons 60% of urban samples were showing positive CAI-I and CAI-II index values indicating the dominance of direct ion exchange process. The remaining urban groundwater having negative index values showed the occurrence of reverse ion-exchange process. A negative value indicates lack of long residence time in the aquifers (Freeze and Cherry, 1979). In peri-urban zone, 67% and 60% of samples during pre-monsoon and post-monsoon seasons respectively were showed direct ion -exchange process. Figure 3.25 represents the status of CAI-I and CAI-II of the study area. Reverse ion-exchange mainly observed in samples from both in alluvial and charnockite rock formation.


Urban (Pre-monsoon)

Urban (Post-monsoon)

Peri-urban (Pre-monsoon)

Peri-urban (Post-monsoon)

Figure 3.25. CAI-I and CAI-II for urban and peri-urban aquifers of the study area during pre-monsoon and post-monsoon seasons

3.3. Multivariate statistical analysis

Meaningful prediction, ranking analysis or pattern recognition of the water quality requires multivariate projection methods (Ayoko et al. 2007; Rao et al. 2013; Vinayachandran, 2014) which provide simultaneous and systematic interpretation. Taking this into consideration the multivariate statistical techniques such as factor analysis and hierarchical cluster analysis are used to interpret important factors contributing to the groundwater hydrochemical processes (Davis and Sampson, 1986; El- Alfy et al. 2017).

3.3.1. Co-variance of ionic species

Correlation analysis illustrated the closeness of the relationship of components/chemical parameters and enabling to explain the primary reactions that have formed groundwater chemistry (Helena et al. 2000; Singh et al. 2005; Hassen et al. 2016). Correlation coefficient (r) of correlation matrix is a measure of interrelationship for all pairs of constituents were determined in correlation analysis and it was expressed the extent to which two variables are statistically associated (Ashley and Lloyd, 1978). Correlation coefficient (r) of < 0.5 was indicated the poor correlation between ions in groundwater. Whereas Correlation coefficient of 0.5 to 0.7 was termed as good correlation and that of ≥ 0.7 for strong correlation. Strong correlations ($r \geq 0.7$) exist between electrical conductivity and Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^- and SO_4^{2-} ions of groundwater in urban and peri-urban phreatic zone indicating that electrical conductivity increases with dissolution of metals. Subba Rao (2002) explained that increase in dissolution of metals through ion exchange or oxidation-reduction reaction in a groundwater aquifer system increases the electrical conductivity, hence strong correlation exist in phreatic aquifers.

Table 3.4. Correlation matrix for the hydrogeochemical parameters occur in phreatic groundwater samples during pre-monsoon and post-monsoon period

Pre-monsoon										
	pH	**EC**	**TDS**	**Na**	**K**	**Ca^{2+}**	**Mg^{2+}**	**CO_3^-+ HCO_3^-**	**So_4^{2-}**	**Cl^-**
pH	1.00									
EC	0.47	1.00								
TDS	0.47	1.00	1.00							
Na	0.38	**0.98**	**0.98**	1.00						
K	0.42	**0.94**	**0.94**	**0.93**	1.00					
Ca^{2+}	0.63	**0.75**	**0.76**	**0.69**	**0.71**	1.00				
Mg^{2+}	0.35	**0.81**	**0.80**	**0.78**	**0.72**	0.50	1.00			
CO_3^-+ HCO_3^-	0.55	**0.87**	**0.86**	**0.85**	**0.82**	**0.84**	**0.72**	1.00		
So_4^{2-}	0.53	**0.81**	**0.81**	**0.76**	**0.76**	0.71	0.66	**0.67**	1.00	
Cl^-	0.28	**0.93**	**0.91**	**0.94**	**0.84**	0.58	0.80	**0.75**	0.64	1.00
Post-monsoon										
	pH	**EC**	**TDS**	**Na**	**K**	**Ca^{2+}**	**Mg^{2+}**	**CO_3^-+ HCO_3^-**	**So_4^{2-}**	**Cl^-**
pH	1									
EC	0.62	1.00								
TDS	0.29	**0.74**	1.00							
Na^+	0.25	**0.67**	**0.95**	1.00						
K^+	0.23	**0.71**	**0.92**	**0.93**	1.00					
Ca^{2+}	0.57	**0.76**	**0.64**	**0.66**	**0.70**	1.00				
Mg^{2+}	0.39	**0.65**	**0.77**	**0.81**	**0.76**	**0.60**	1.00			
CO_3^-+ HCO_3^-	0.60	**0.68**	**0.68**	0.50	0.50	**0.73**	0.51	1.00		
So_4^{2-}	0.32	**0.66**	**0.74**	**0.71**	**0.74**	**0.65**	**0.71**	0.51	1.00	
Cl^-	0.24	**0.64**	**0.90**	**0.93**	**0.86**	**0.62**	**0.68**	0.36	0.64	1.00

The correlations between various ions in groundwater of the entire study area are presented in Table 3.4. In hydrogeochemical process, there are three major relationships were exist between cations and anions of groundwater (Douglas and Leo, 1977) and these are ,

1. **The highly competitive relationships** between ions having same charge but a different valence number (e.g. Ca^{+2} and Na^{+1}, Na^{+1} and Mg^{2+}) .

2. **The affinity ion relationshi**p between ions having different charges but same valence number e g. Na^{+} and Cl^{-}

3. **The non-competitive relationship** between ions having the same charge and the same valence number e.g. Ca^{2+} and Mg^{2+} .

The correlation analysis of ions in urban and peri-urban phreatic aquifers of the total study area were showed the following relationships:

1. The highly competitive ion relationship: Na^{+} with Ca^{2+} & Mg^{2+} , K^{+} with Ca^{2+} & Mg^{2+}, and SO_4^{-2} with HCO_3^{-1} are in a strong positive correlation ($r \geq 0.7$) during both pre-monsoon and post monsoon period. Whereas SO_4^{2-} with Cl^{-} (0.6) have good positive correlation.
2. The affinity ion relationship- Most of the ionic pairs in groundwater of the total study area under this category (SO_4^{2-} with Ca^{2+} & Mg^{2+}, Cl^{-} with Na^{+} & K^{+}) were in strong significant positive correlation ($r \geq 0.7$) during both seasons. Whereas, HCO_3^{-} +CO_3^{-} with Na^{+} & K^{+} were showing good positive correlation during post-monsoon.
3. The non-competitive relationships- Non-competitive ions like Na^{+} & K^{+} were showing strong positive correlation and Ca^{2+} and Mg^{2+} shows good positive correlation ($r \geq 5$) during both seasons.

Therefore, most of the ions in groundwater of urban and peri-urban zones of the total study area were strongly correlated ($r \geq 0.7$) with each other, during pre-monsoon and post-monsoon seasons, indicated that these ions are from the same source and play a vital role in the mineralization of groundwater in study area through its continuous addition along the groundwater flow path. Chidambaram , 2000 study on hydrogeochemistry of groundwater in Periyar district, Tamilnadu was also explained the correlation between ions and its common origin.

3.3.2. Factor analysis

The characterization & interpretation of various groundwater parameters is often a complex problem and factor analysis offers a powerful means of identifying the similarities among the variables present in the chemical budget of water (Okiongbo and Douglas, 2015). In factor analysis, factor loadings and eigenvalues were examined to evaluate the variables belonging to a specific chemical process and also to find out the dominance and contribution of the total data set. Kaiser-Mayer-Olkin test (KMO) was performed prior to factor analysis for the checking of sampling adequacy. KMO was showed a value of 0.8, indicated the meritorious adequacy for factor analysis. The extraction of the factors was achieved using varimax criteria.

Table 3.5 a. Factor pattern after varimax rotation for urban groundwater

Urban	Pre-monsoon		Post-monsoon	
	Factor 1	***Factor 2***	***Factor 1***	***Factor 2***
pH	0.160	**0.654**	0.263	**0.727**
EC(µS/Cm)	**0.893**	0.450	**0.687**	0.581
TDS(mg/L)	**0.880**	0.472	**0.975**	0.012
Na(mg/L)	**0.916**	0.384	**0.972**	0.061
K(mg/L)	**0.832**	0.411	**0.952**	0.038
Ca (mg/L)	0.372	**0.848**	0.380	**0.704**
Mg(mg/L)	**0.773**	0.223	**0.789**	0.192
HCO_3^-+ CO_3^- (mg/L)	0.661	**0.672**	0.212	**0.588**
SO_4 (mg/L)	**0.644**	0.515	**0.764**	0.085
Cl(mg/L)	**0.930**	0.202	**0.863**	0.116
Variability (%)	58.010	26.320	55.944	17.151
Cumulative %	58.010	84.330	55.944	73.095

For urban aquifers, two factors were chosen as the principal factors and in pre-monsoon and post- monsoon period and two factors together accounts for 84.3% and 73.1 % of the Total Data Variability (TDV) (Table 3.5 a). In pre-monsoon, a mixed factor loaded heavily (> 0.6) with Na^+, K^+, Cl^- and TDS indicated the dominance of aforementioned variables on groundwater chemistry and suggested a similar source for such ions. The Na^+ and Cl^- ions have the highest loading in factor 1 and mixed nature of factor 1 were denoted the contribution of the dissolution of chlorides and sulfates process. Factor 2 represented by the presence of Ca^{2+} and HCO_3^- + CO_3^- ions reflected the signatures of both natural water recharge and rock-water interaction.

Factor 1 components of urban groundwater during post-monsoon, representing similar variables as in pre-monsoon. However, 17% variance observed in factor 2, represented by high loadings of Ca^{2+}, HCO_3^-, and pH implies that the pH of the groundwater is mainly controlled by HCO_3^- influx. The significantly high positive content of Ca^{2+}indicated the variables associated with the rock-water interaction. From the components presents in the in factor 2, high factor loading for Ca^{2+}, HCO_3^-, and pH were assumed the rock-water interaction process.

Table 3.5 b. Factor pattern after varimax rotation for peri-urban groundwater

Peri-urban	**Pre-monsoon**		**Post-monsoon**	
	Factor 1	***Factor 2***	***Factor 1***	***Factor 2***
pH	0.357	**0.647**	**0.811**	-0.044
EC(µS/Cm)	**0.861**	0.504	**0.913**	0.142
TDS(mg/L)	**0.828**	0.525	**0.883**	0.208
Na(mg/L)	**0.757**	0.248	0.332	**0.798**
K(mg/L)	**0.720**	0.290	0.226	**0.739**
Ca (mg/L)	0.399	**0.678**	**0.668**	0.319
Mg(mg/L)	0.188	**0.411**	**0.736**	0.006
HCO_3^-+ CO_3^- (mg/L)	-0.071	**0.915**	**0.919**	0.031
SO_4(mg/L)	**0.528**	0.335	**0.558**	0.404
Cl (mg/L)	**0.723**	-0.237	0.019	**0.631**
Variability (%)	37.332	25.741	41.610	17.726
Cumulative %	37.332	**63.072**	41.610	**59.337**

For peri-urban aquifers, two factors were chosen as the principal factors and in pre-monsoon and post-monsoon period and two factor together accounts for 63.1% and 59.3 % of the Total Data Variability (TDV)(Table 3.5 b). Similar to urban aquifers, factor 1 loaded heavily (> 0.6) with Na^+, K^+, Cl^-, and TDS in peri-urban aquifers during pre-monsoon, indicated the dominance of aforementioned variables on groundwater chemistry. SO_4 having moderate loading in factor 1. Factor 2 represented by the presence of Ca, Mg and HCO_3^- ions reflected the signatures of natural water recharge and rock-water interaction. In post-monsoon, 41% variance is noticed in factor 1 represented by Ca, Mg and HCO_3^- with heavy loading and SO_4 with moderate loadings. In post monsoon peri-urban groundwater, factor 2 with 17% variance and represented by the variables Na, K and Cl. Factor analysis for urban and peri-urban phreatic aquifers during pre-monsoon and post –monsoon seasons were bring out relative significance of the combinations of chemical variables and these associations were substantiated that the groundwater interaction with aquifer matrix and rainfall recharge were the major factors responsible for hydrogeochemical characteristics of groundwater.

3.3.3. Cluster Analysis

The dendrogram after Agglomerative Hierarchical Cluster (AHC) grouped groundwater samples of the entire study area into three significant clusters (Table 3.6). The cluster 1 includes 38 no of samples, i.e. 44% of the total groundwater sample of the study area. The ionic abundance of groundwater in the cluster is Na> Ca> Mg> K and HCO_3>Cl> SO_4. Majority of groundwater samples in the cluster I belonging to the peri-urban zone. Cluster II constitutes equal no of samples from both urban and peri-urban zone having a chemical composition of Ca> Na> Mg>K and HCO_3>Cl>SO_4. It contains 36% of the total groundwater samples. Cluster III contains 18% of the groundwater of the study area, and all are belonging to the urban zone of the study area. The ionic abundance of groundwater in cluster III is in the order of Ca> Na> Mg> k and Cl^->HCO_3^->SO_4^{2-}.

Table 3.6. Cluster analysis for groundwater in urban and peri-urban aquifers of the study area

Class	EC (µS/Cm)	TDS (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	HCO3- + CO3- (mg/L)	SO42- (mg/L)
1	73.3	38.8	9.1	1.2	8.9	2.1	23.8	3
2	208.5	115.6	16.1	2.9	19.2	3.7	36.3	14.4
3	570.8	313	42.1	7.2	47	12.2	77.5	30.9
4	1420	800	185	17	116	19.9	270.9	36.7
5	3580	1890	482.5	33.8	84.8	71.9	315	69.4
6	3518	2015	481.8	41.5	115.2	42.8	319.3	119.2

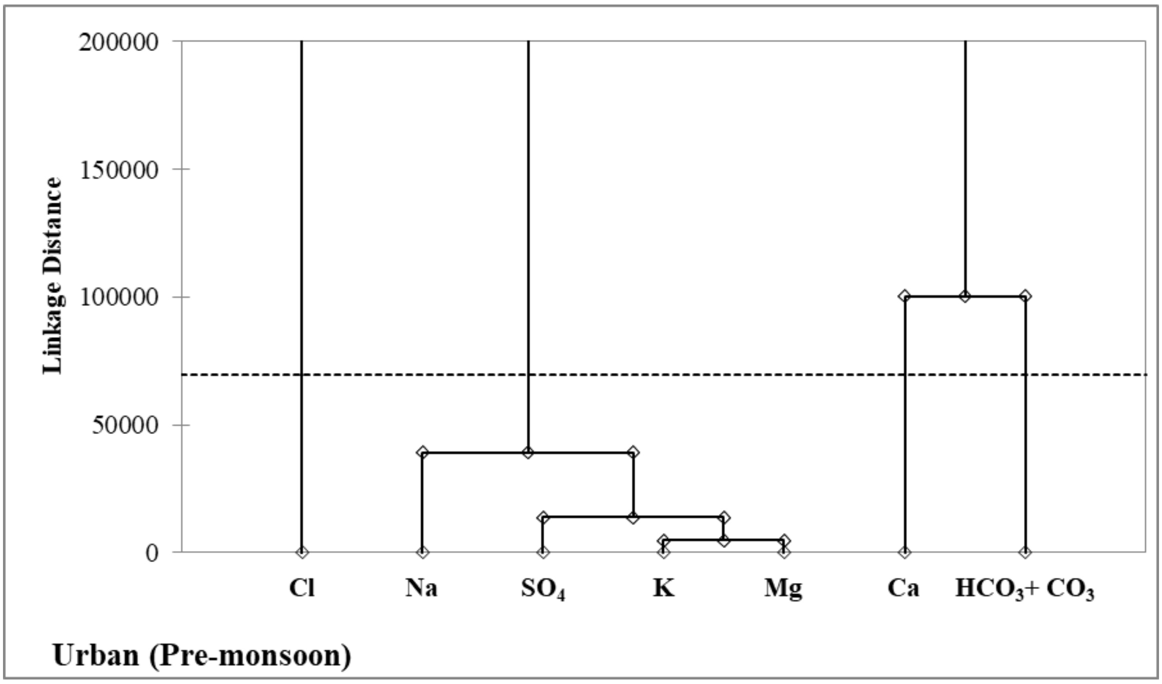


Figure 3.26(a). Cluster analysis for urban groundwater during pre-monsoon

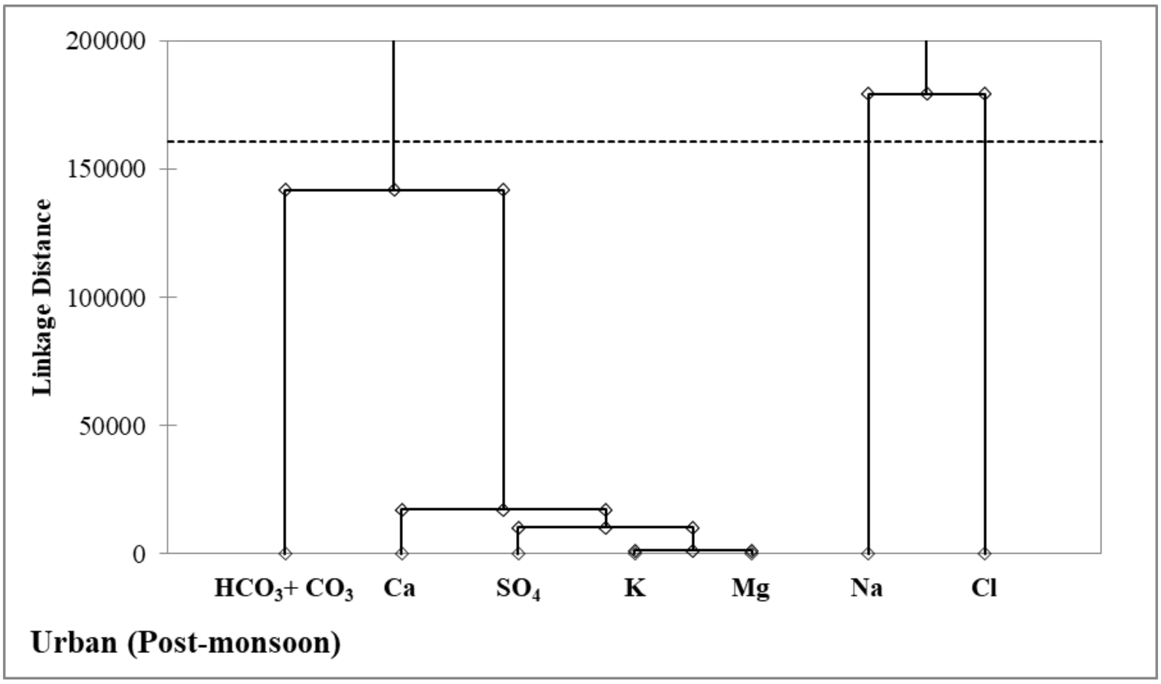


Figure 3.26(b). Cluster analysis for urban groundwater during post-monsoon

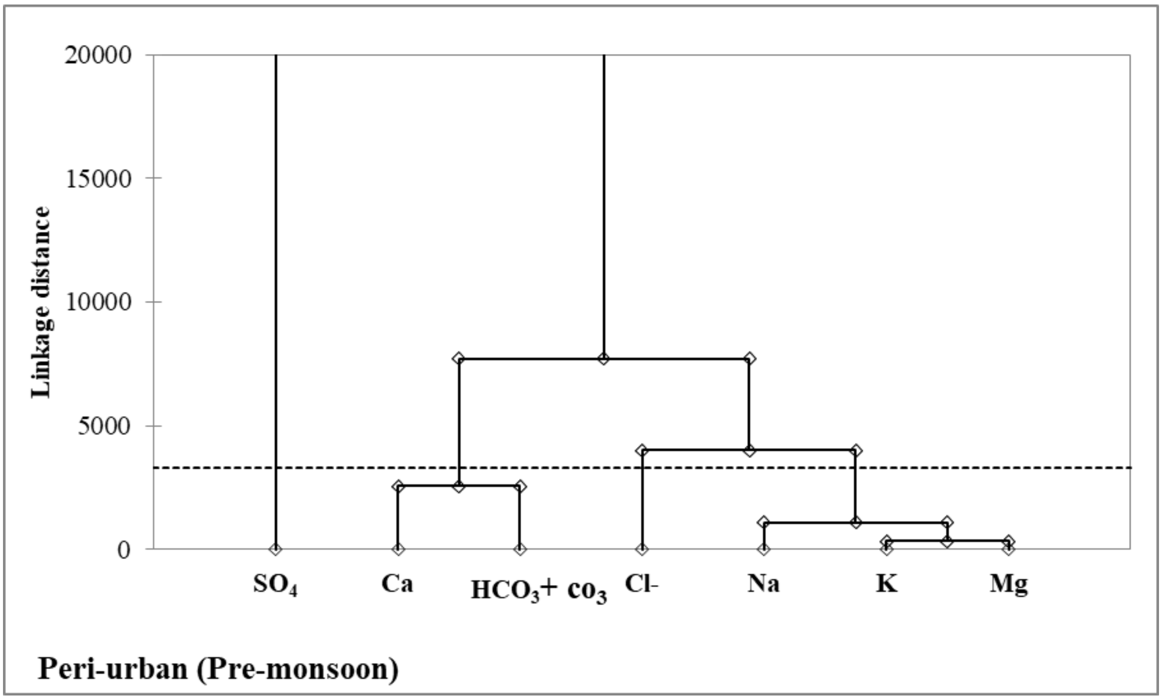


Figure 3.26 (c). Cluster analysis for peri-urban groundwater during pre-monsoon

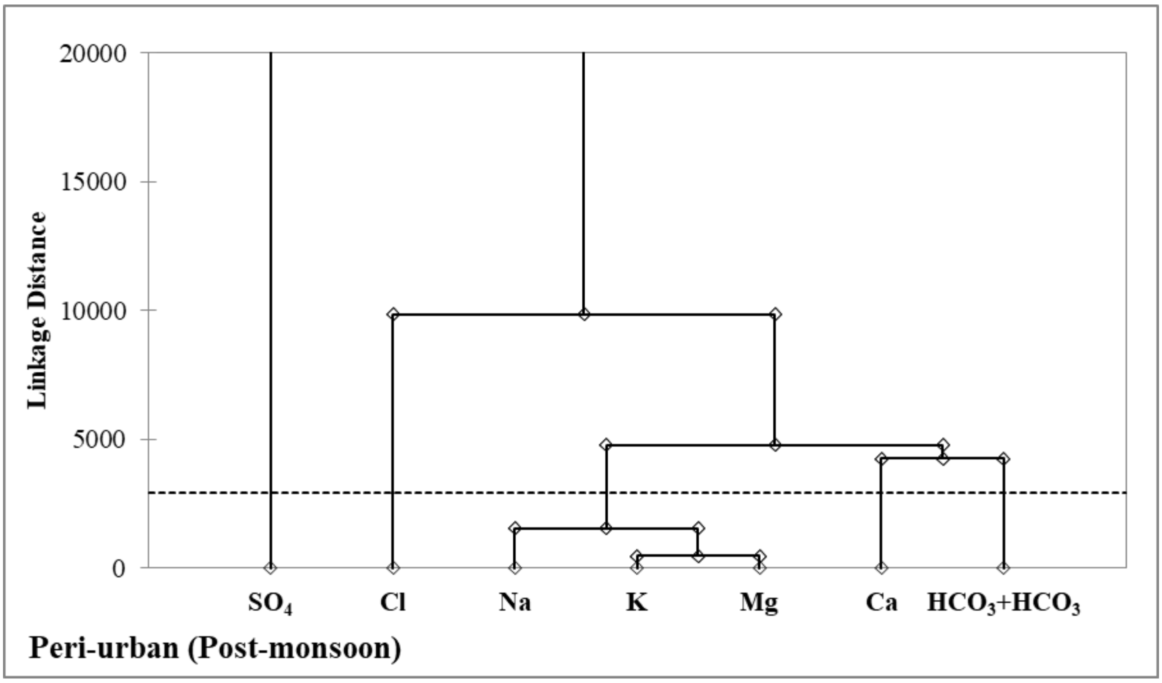


Figure 3.26 (d). Cluster analysis for peri-urban groundwater during post-monsoon

The dendrogram of the groundwater samples in urban and peri-urban phreatic aquifer during pre-monsoon and post-monsoon period after Agglomerative Hierarchical Cluster (AHC) analysis were explained that there is a strong associations between the variables such as Na^+, K^+, Cl^- and also between Ca-HCO_{3^-} Therefore, the clusters shown in the dendrogram (Figure 3.26 a-d) were significantly substantiated with the inherent hydrogemical processes explained in factor analysis.

CHAPTER 4

ISOTOPIC CHARACTERISATION OF GROUNDWATER AND IDENTIFICATION OF RECHARGE MECHANISM

Introduction

Stable isotopes of oxygen (^{16}O and ^{18}O) and hydrogen (^{1}H and ^{2}H or D) forming water molecule are inert and conservative in mixing relationship. Hence these are used worldwide as a potential tracer to understand dynamics of hydrological processes. The processes are include characterization of various H_2O reservoirs within the hydrological cycle, groundwater recharge, surface-water groundwater interaction, advection/ diffusion rate estimation in the unsaturated/ saturated zone, evaporation on groundwater systems, factors controlling the geographical distribution of isotopes in groundwateretc. (Gat and Gonfiantini,1981; Deshpande et al. 2003; Hoefs and Hoefs, 2009;Gat, 2010;Deshpande and Gupta, 2012; Clark and Fritz, 2013;Grimmeisen et al. 2017, Eastoe and Towne, 2018; Deshpande, 2018; Matiatos and Wassenaar, 2019). The mechanism of mixing relationship between saline water bodies and surrounding freshwater in many coastal aquifers and migration pathways of the fresh–saltwater interface (Gonfiantini et al. 1974; Han et, 2011; He et al. 2018) were illustrated well within the domain of stable isotope geochemistry.

The important application of stable isotope tracer techniques in hydrometeorology include identifying the origin of vapour source of precipitation and its spatio-temporal variation in monsoon systems & atmospheric vapour content (Bouchaou et al. 2008; Hameed et al. 2015, 2016; Deshpande, 2018; Thivya et al. 2016) and understanding the post-precipitation evaporation.The chapter 4 discussed the isotope characterisation of groundwater in urban and peri-urban aquifers and identification of recharge mechanism occurred in the study area .

4.1. δD and $\delta^{18}O$ isotopic composition of rainwater

Rainwater samples were collected from two rainwater collection units located at Kozhikode and Balussery stations which are representing urban and peri-urban zones respectively. Figure 4.1 showed the sampling location of rainwater, groundwater and surface water for stable isotope study.

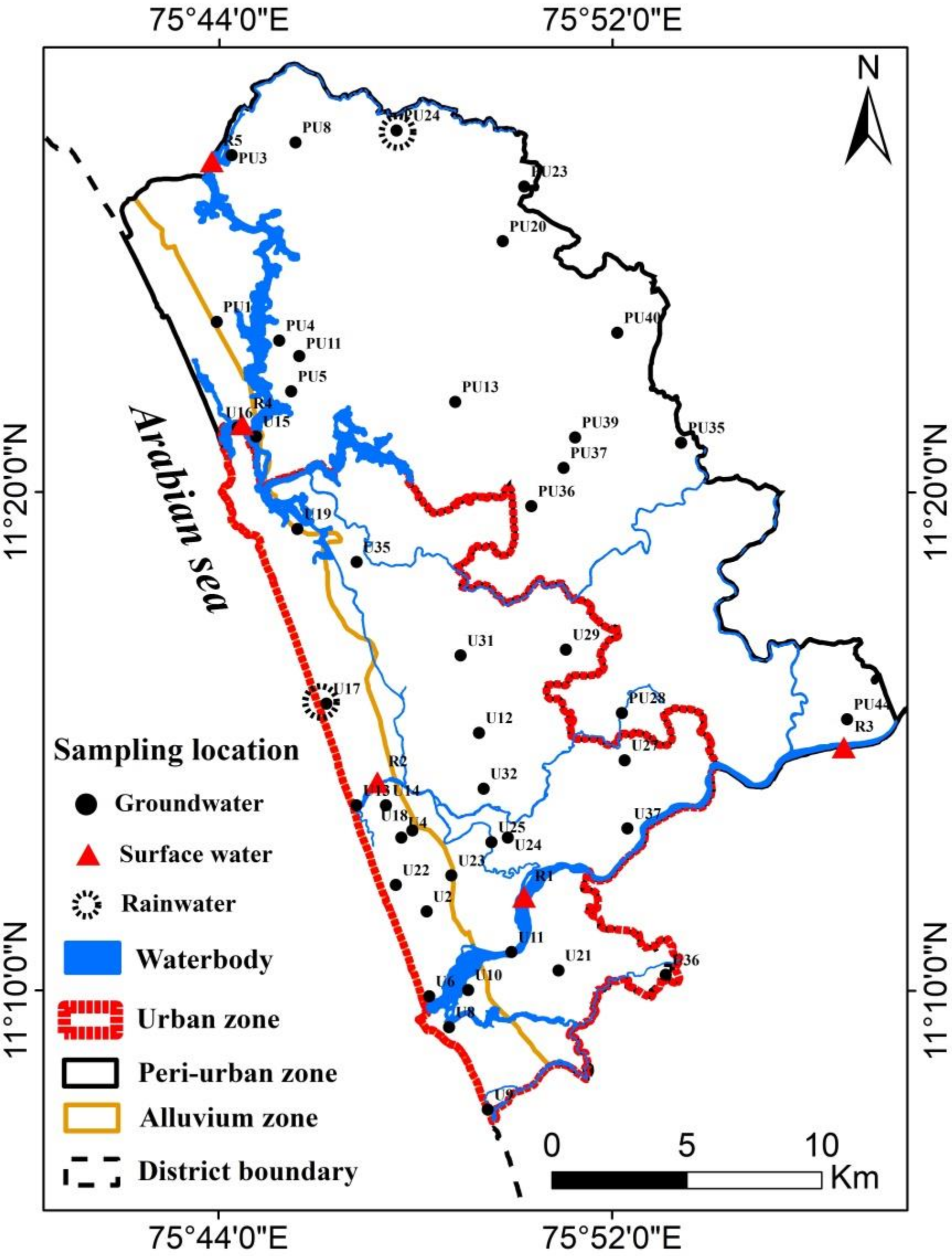


Figure 4.1. Sampling location map of the study area for stable isotope investigation

The urban and peri-urban sampling locations were also representing two physiographic regions of the study area such as low and mid land region respectively. The values of stable isotopic composition (δD and $\delta^{18}O$) of rainwater in the study area from July to November are as follows. At the urban (low land region), δD value ranged from -34.1 to -4.2‰ and $\delta^{18}O$ values from -5.8 to -1.6 ‰. At the peri-urban (midland region), δD value ranged from -35.6 to 0.4 ‰ and $\delta^{18}O$ values from -6.0 to -1.0 ‰ (Table 4.1).

Table 4.1. Stable isotopic composition of rainwater collected from Kozhikode (Urban/low land) and Balussery (Peri-urban/ mid land) stations of the study area.

Month	Kozhikode (low land)			Balussery (mid land)		
	$\delta^{18}O$ (‰)	δD (‰)	d-excess	$\delta^{18}O$ (‰)	δD (‰)	d-excess
July	-1.6	-4.2	11.2	-1.0	0.4	15.0
August	-3.3	-16.3	9.0	-2.3	-8.9	12.0
September	-2.6	-11.1	5.2	-3.3	-16.3	5.7
October	-5.8	-34.3	12.9	-6.0	-35.7	14.5
November	-5.8	-34.1	12.0	-6.0	-35.6	14.0

In the southwest (SW) monsoon period, the mean value of $\delta^{18}O$ of the rain water at Kozhikode station(Low land) is -2.5‰ and that in Balussery (mid land) station is -2.2‰. At the same time, δD for rainwater in Kozhikode(Low land)and Balussery (mid land) stations are -10.52‰ and -8.28‰ respectively. The relatively enriched isotopic values of most of the southwest monsoon samples revealed that the southwest monsoon in Kozhikode derives its moisture from the Arabian Sea branch of southwest monsoon and it was also confirmed by isotopic characterization studies on dual monsoon precipitation of Kerala by Warrier et al. 2010. In the NE monsoon period, the mean value of $\delta^{18}O$ for the rain water in Kozhikode station(Low land) is -5.8‰ and that in Balussery (mid land) station is -6 ‰. The depleted isotopic values of the northeast monsoon samples further verified with previous studies such as Deshpande et al. (2003); Warrier et al. (2010, 2016) that it was due to the effect of northeast monsoon winds which is originating from the central Asia can draw moisture from depleted continental vapour sources and oceanic sources like South China Sea and Bay of Bengal during its southward journey and the subsequent rainout effect.

Simultaneously δD for rainwater in Kozhikode (Low land) and Balussery (mid land) stations are -34.2‰ and -35.6‰ respectively. The abovesaid values indicated less significant spatial variation among rainwater at the two locations. While comparing the isotopic signatures of SW and NE monsoon precipitation, the mean composite values of SW monsoon precipitation are considerably enriched than NE monsoon period samples. Investigation on isotopic characterization of dual monsoon precipitation of Kozhikode district carried out by Warrier et al; 2010 explained that these variation in mean composite values of rainwater during SW and NE monsoon is the evidence for different vapour sources of monsoon periods. The time series plot for δD and δ^{18}O values shows that similar trend was observed for δD and δ^{18}O values over a period of SW and NE monsoon (Figure 4.2 & 4.3). However, from June to November both δD and δ^{18}O values were gradually depleting at the low land and midland stations.

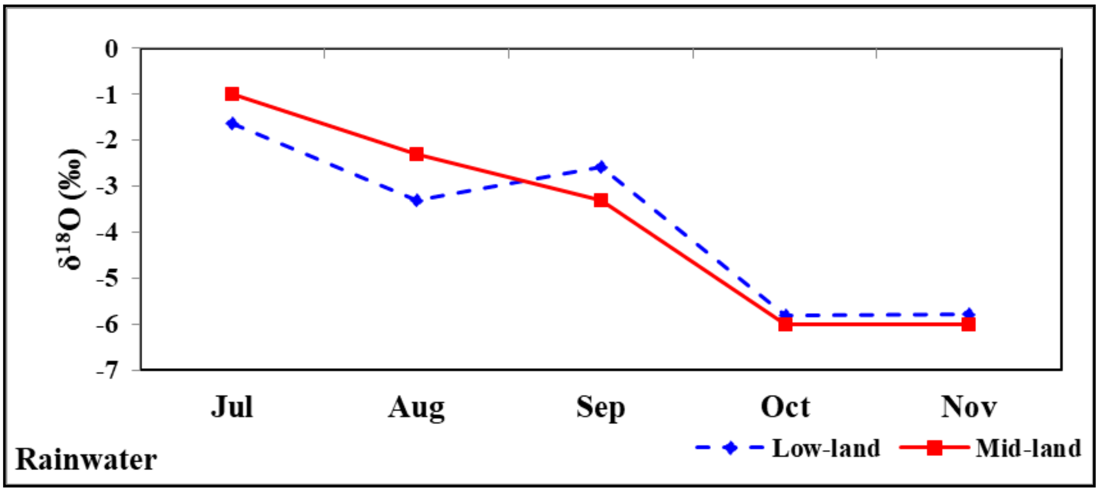


Figure 4.2. Time series plot of δ^{18}O value in rainwater at low land and mid land of the study area

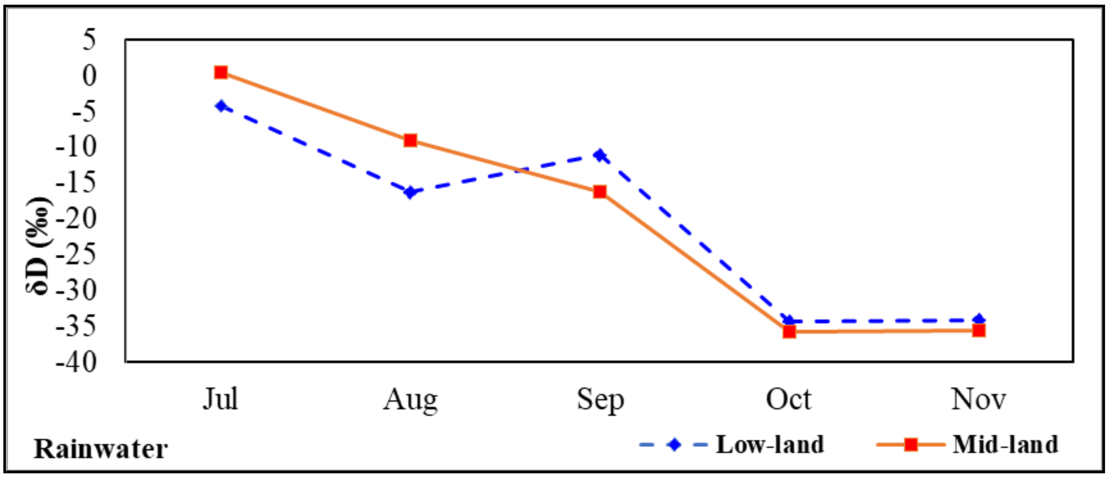


Figure 4.3. Time series plot of δD value in rainwater at low land and mid land of the study area.

4.2. Local Meteoric Water Line (LMWL) of the study area

The Global Meteoric Water Line (GMWL) described the relation between δ^2H and δ^{18}O in global meteoric water (derived from precipitation) developed by Craig (1961) and expressed by the equation: $\delta^2H = 8\ \delta^{18}O + 10$ ‰. This relation was developed as an average of many local water lines which differ from the GMWL as a result of climatic and geographic factors. Differential fractionation of δ^2H and δ^{18}O occurs as a function of humidity during primary evaporation of water vapor from the ocean and as a function of temperature during secondary evaporation as rain falls from a cloud. GMWL plotted in the Figure 4.4 as a reference for interpreting the hydrological processes and origin of different water masses in the study area. Linear-regression analysis was carried out using the δ^2H and δ^{18}O composition of the monthly composite rainwater samples collected during the period of SW and NE monsoons to determine the local meteoric water line (LMWL) for the study area (Figure 4.4). Defining the LMWL for precipitation is an important part of ground-water investigations that will compare isotopic ratios in ground water or surface water with precipitation at specific locations. The LMWL for the entire study area for one hydrological year was computed as:

$$\delta D = 7.2\delta^{18}O + 7.6 \quad R^2 = 0.99 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

For both low and mid-land LMWL shows similar regression values and the LMWL was more or less followed the GMWL.

This high correlation coefficient of 0.99 was reflected the close association of oxygen and hydrogen stable isotopes in water molecules. The slope of LMWL, slightly lower than the GMWL and with a lower intercept. This is due to the existence of precipitation which has undergone evaporation in the lowest part of the cloud, during its route towards the rainfall site, and also to the partial evaporation of the water drops before their arrival at the land surface (Plata, 1994).

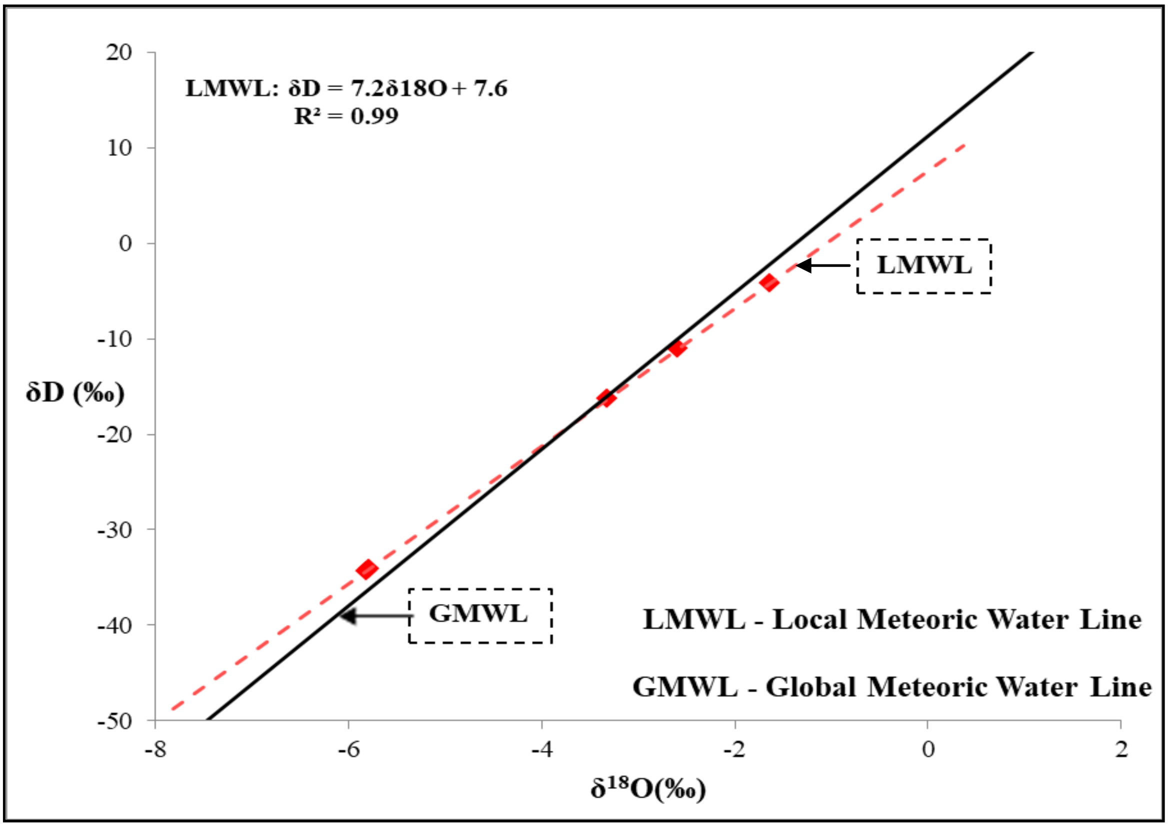


Figure 4.4. δD-$\delta^{18}O$ regression plot for rainwater samples collected from urban (low land) and peri-urban (mid land) during the period of SW and NE monsoons

4.3. Temporal variation in d-excess of rainwater

d-excess value defined as the excess deuterium value that cannot be accounted for equilibrium fractionation between water and vapor (Deshpande et al. 2003). The d-excess value reflects the conditions that lead to kinetic isotope fractionation between water and vapour during primary evaporation in the ocean. A bar diagram of the weighted monthly average d-excess values of the rainwater samples collected from mid – land and low-land region of the study area is shown in Figure 4.5. The average d-excess values of rainwater at low-land location of the study area is 10‰ and that of mid-land location is 12‰, which is slightly higher than the global average (~10).The low value of d-excess and its lowest amplitude of seasonal variation implied that the smaller magnitude of vapour recycling at two locations of the study area. As per Warrier et al. 2010 this comparatively high d-excess value of northeast monsoon samples (12‰ -14.5‰) observed is probably due to continental vapour contribution.

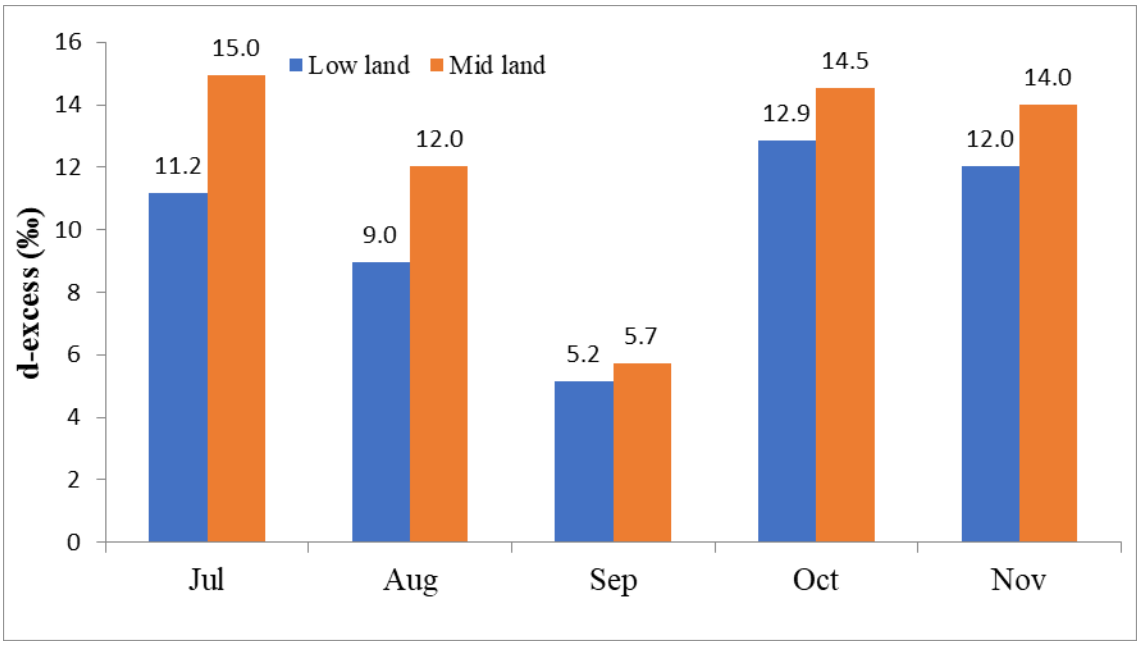


Figure 4.5. Bar diagram of the weighted monthly average d-excess values of the rainwater samples collected from mid – land and low-land region of the study area

4.4. Distribution of δD and $\delta^{18}O$ in the urban and peri-urban groundwater

In the entire study area, the groundwater occurred under two phreatic aquifer types such as laterite, alluvium formations. The urban groundwater samples selected for the study occurred in both in laterite and alluvium formations where as in peri-urban zone groundwater occurred mainly in laterite aquifer formation.

Table 4.2.a. Stable isotope composition of groundwater samples from the urban alluvium zone of the study area during pre-monsoon and post monsoon period.

Sample Code	Pre-monsoon			Post-monsoon		
	$\delta^{18}O$	δD	d-excess	$\delta^{18}O$	δD	d-excess
U2	-1.7	-5.9	8.0	-1.8	-4.1	10.2
U4	-0.6	1.6	6.7	-2.1	-6.1	10.3
U6	-1.8	-5.3	8.8	-2.4	-7.2	12.0
U8	-2.0	-6.0	9.7	-3.0	-13.8	10.5
U9	-2.0	-4.7	11.0	-2.3	-10.1	8.2
U10	-2.6	-10.8	9.9	-2.8	-14.4	7.7
U11	-2.8	-12.4	10.0	-2.7	-14.4	7.3
U12	-2.2	-8.6	9.2	-2.7	-10.0	11.2
U13	-2.5	-11.1	8.6	-2.3	-7.8	10.4
U14	-3.8	-20.8	9.8	-2.3	-8.3	10.1
U15	-1.7	-4.9	8.9	-3.7	-22.2	7.6
U16	-1.1	-2.7	6.1	-2.6	-12.0	9.0
U17	-3.0	-13.9	10.3	-2.0	-4.5	11.5

Therefore, for the detailed investigation on recharge characteristics of groundwater, samples collected from study area again divided in to three category viz urban alluvium and urban laterite, peri-urban laterite.

Stable isotope composition of groundwater samples collected from the urban alluvium urban laterite, peri-urban laterite zone of the study area during pre-monsoon and post monsoon period shown in Table 4.2.(a, b & c) respectively.

Table 4.2.b. Stable isotope composition of groundwater samples from the urban laterite zone of the study area during pre-monsoon and post monsoon period.

Sample Code	Pre-monsoon			Post-monsoon		
	$\delta^{18}O$	δD	d-excess	$\delta^{18}O$	δD	d-excess
U19	-2.3	-9.4	9.1	-3.5	-20.3	7.6
U21	-2.7	-11.1	10.6	-2.9	-15.1	8.2
U22	-2.6	-9.1	11.9	-2.4	-12.1	7.1
U23	-2.5	-6.9	12.9	-2.4	-13.1	6.4
U24	-2.4	-8.4	10.9	-2.4	-9.4	9.9
U25	-1.6	-3.9	8.7	-2.8	-11.3	11.2
U27	-3.1	-12.4	12.2	-2.9	-11.5	11.9
U29	-2.3	-8.5	9.9	-2.6	-9.3	11.3
U31	-3.0	-11.9	11.9	-3.0	-11.7	12.1
U32	-2.0	-7.6	8.7	-2.7	-12.2	9.7
U18	-3.4	-16.6	10.5	-2.0	-7.2	9.7
U35	-2.9	-12.8	10.4	-2.1	-7.5	9.2
U36	-1.8	-4.1	10.3	-2.3	-13.6	4.9
U37	-3.1	-14.1	10.5	-2.1	-11.6	9.9

Table 4.2.c. Stable isotope composition of groundwater samples from the peri-urban laterite zone of the study area during pre-monsoon and post monsoon period.

Sample Code	Pre-monsoon			Post-monsoon		
	$\delta^{18}O$	δD	d-excess	$\delta^{18}O$	δD	d-excess
PU1	-2.1	-5.9	10.6	-2.2	-6.8	10.7
PU3	-0.9	-2.8	4.0	-2.6	-10.5	10.5
PU4	-2.3	-6.3	12.2	-2.6	-11.2	9.6
PU5	-3.2	-14.1	11.6	-2.6	-11.2	9.9
PU8	-1.6	-6.2	6.5	-2.3	-8.3	10.3
PU11	-2.6	-7.8	12.9	-2.8	-12.3	10.2
PU13	-2.0	-7.2	8.8	-2.5	-13.0	7.0
PU20	-2.6	-10.1	10.7	-2.7	-13.0	8.9
PU23	-3.4	-12.8	14.1	-3.0	-11.0	12.7
PU24	-2.5	-9.6	10.3	-2.5	-9.8	10.0
PU28	-2.8	-11.0	11.0	-3.5	-17.9	10.4
PU35	-2.5	-9.7	10.6	-2.5	-11.1	9.2
PU36	-2.4	-10.1	9.3	-2.4	-8.6	10.5
PU37	-2.9	-14.8	8.5	-2.7	-11.5	10.1
PU39	-2.1	-5.8	11.3	-2.71	-11.06	10.10
PU40	-2.5	-10.2	10.1	-3.1	-13.9	11.0
PU44	-2.6	-10.1	10.9	-2.7	-10.8	10.7

The groundwater occurred in the urban alluvial aquifer zone , deuterium (δD) value ranged from -20.81‰ to 1.6‰ with an average value of -8.1‰ during the pre-monsoon season and from -22.2‰ to -4.1‰ with an average of -10.4‰ during the post-monsoon season. The $\delta^{18}O$ values of groundwater from the same zone, ranged from -3.8 ‰ to -0.6 ‰

with an average value of -2.1‰ during the pre-monsoon season and from -3.7‰ to -1.8 ‰ with an average of -2.5‰ during the post-monsoon season (Table 4.3).

In groundwater of the urban laterite region, deuterium (δD) value ranged from -16.6‰ to -3.9‰ with an average value of -9.8‰ during the pre-monsoon season and from -20.3‰ to -7.5‰ with an average of -12.3‰ during the post-monsoon season. $\delta^{18}O$ varied from -3.4 ‰ to -1.6 ‰ with an average value of -2.5‰ during pre-monsoon and -3.5 ‰ to -2.1 ‰ with an average of -2.7‰ during post –monsoon (Table 4.3).

Table 4.3. Summary statistics of stable isotope composition of urban and peri-urban aquifers

			Urban		**Peri-urban**
			Alluvium	**Laterite**	**Laterite**
Average	Pre-monsoon	$\delta^{18}O$	-2.1	-2.5	-2.4
		δ D	-8.1	-9.8	-9.1
	post-monsoon	$\delta^{18}O$	-2.5	-2.7	-2.7
		δ D	-10.4	-12.3	-11.3
Minimum	Pre-monsoon	$\delta^{18}O$	-3.8	-3.4	-3.4
		δ D	-20.81	-16.6	-14.8
	post-monsoon	$\delta^{18}O$	-3.7	-3.5	-3.5
		δ D	-22.2	-20.3	-17.9
Maximum	Pre-monsoon	$\delta^{18}O$	-0.6	-1.6	-0.9
		δ D	1.6	-3.9	-2.8
	post-monsoon	$\delta^{18}O$	-1.8	-2.1	-2.2
		δ D	-4.1	-7.5	-6.8

The groundwater occurred in the peri-urban laterite aquifer zone, deuterium (δD) value ranged from -14.8 ‰ to 2.8 ‰ with an average value of -9.1‰ during the pre-monsoon season and from -17.9 ‰ to -6.8 ‰ with an average of -11.3‰ during the post-monsoon season (Table 4.3). The $\delta^{18}O$ values of groundwater from the peri-urban laterite aquifer zone , ranged from -3.4 ‰ to -0.9 ‰ with an average value of -2.4‰ during the pre-monsoon season and from -3.5‰ to -2.2 ‰ with an average of -2.7‰ during the post-monsoon season.

The summary statistics of groundwater from both the urban and peri-urban phreatic aquifers in the pre-monsoon and post-monsoon period are shown in Table 4.3**.** It is seen that samples from the entire study area have a rather narrow (-3.4‰ to -0.6‰) range of δ^{18}O values and broad range (-22.2 ‰ to 1.6‰) of δD values. This observed value range for phreatic aquifers of the total study area were confirmed by previous observations on distribution of oxygen and hydrogen isotopes in shallow groundwater from Southern India conducted by Deshpande et al. 2003.

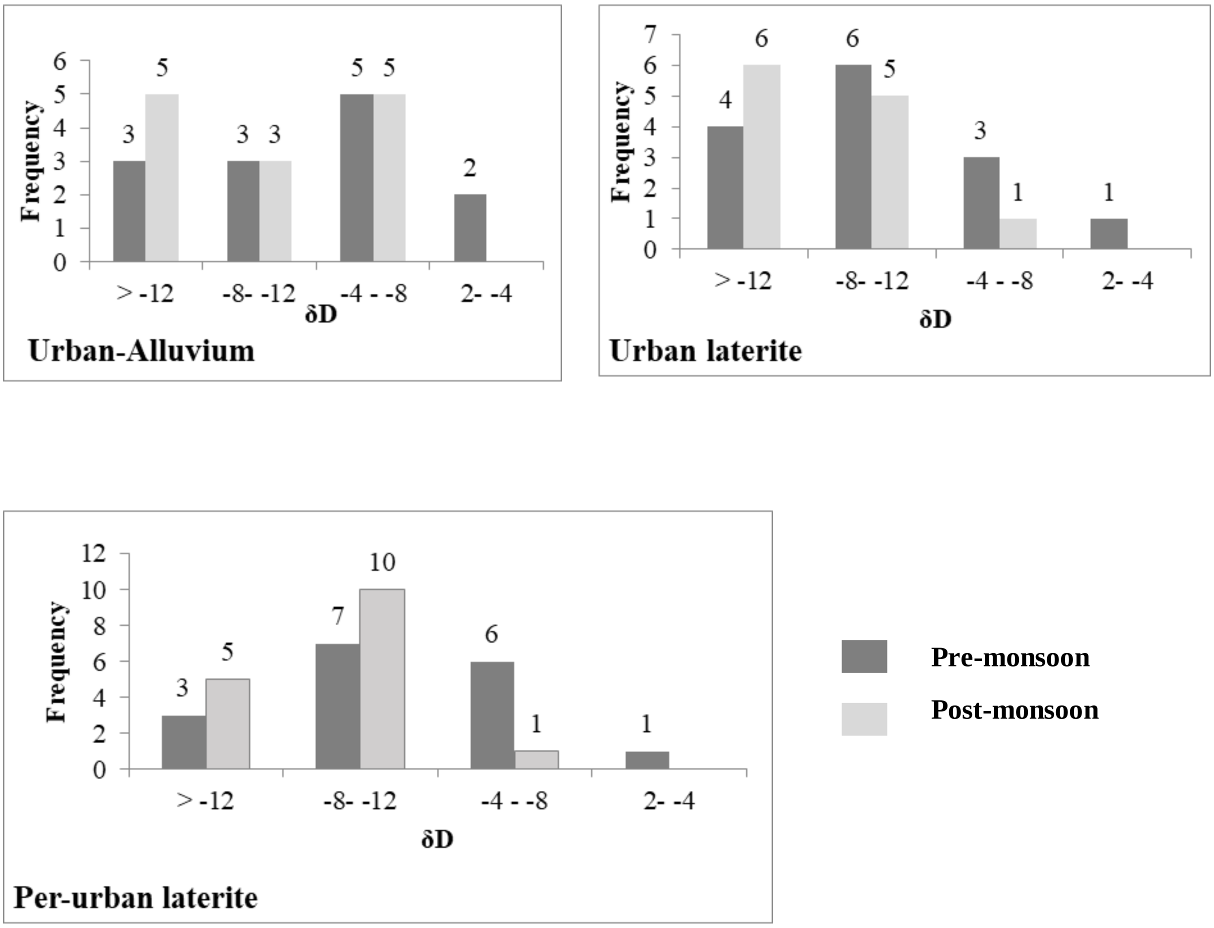


Figure 4.6. Frequency distribution of δD values of groundwater collected from urban alluvium, urban laterite and peri-urban laterite zones of the study area during pre-monsoon and post -monsoon period

The frequency distribution of the δD and $\delta^{18}O$ values of groundwater samples in urban lateritic, urban alluvium and peri-urban laterite were shown in Figure. 4.6 & 4.7. Frequency of urban alluvium groundwater samples distributed in relatively low δD values such that -8 ‰ to > -12‰.Whereas urban laterite and peri-urban laterite aquifers also shows a maximum frequency in -8‰ to > -12‰ with a large scattering in values. This observation was supported by Deshpande et al. 2003 studies on shallow aquifers of Kozhikode, observed that all coastal samples of Kozhikode with altitude less than, 100 m (amsl) , shows a large scatter with no discernable altitude effect.

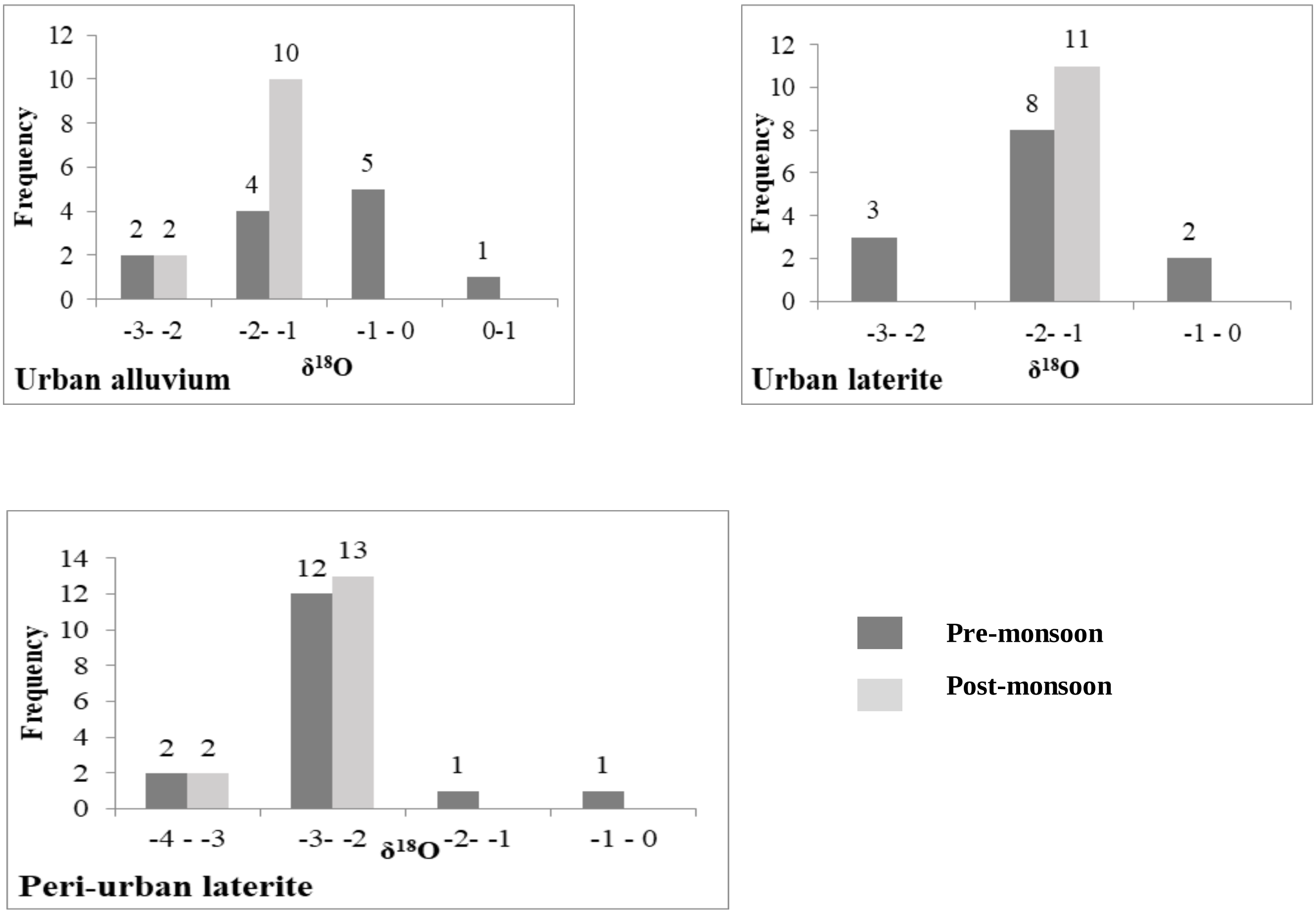


Figure 4.7. Frequency distribution of $\delta^{18}O$ values of groundwater collected from urban alluvium , urban laterite and peri-urban laterite zones of the study area during pre-monsoon and post -monsoon period

In the above three zones, relatively low frequency was occurred at enriched δD values. Similarly, for urban alluvium and laterite aquifers the maximum frequency occurred at relatively enriched $\delta^{18}O$ values of -2 ‰ to -1‰ whereas in peri-urban laterite aquifers zone, maximum frequency occurred at depleted $\delta^{18}O$ values of -3‰ to-2‰. The maximum frequency values were confirmed the recharge index from rainfall with $\delta^{18}O$ value range of -3 ‰ to -2 ‰ to groundwater. According to Deshpande et al. 2003, this relative depletion in groundwater may be due to the consecutive rainout of moisture from the Arabian sea during Southwest monsoon which in turn led depleted rainwater composition and consequently groundwater.

4.5. Relationship between $\delta^{18}O$ and δD of groundwater and rain water

The relationship between $\delta^{18}O$ and δD of groundwater and rainwater from urban and peri-urban phreatic aquifers of the study area during both pre-monsoon and post-monsoon seasons shown in Figure 4.8, 4.9, 4.10 & 4.11.

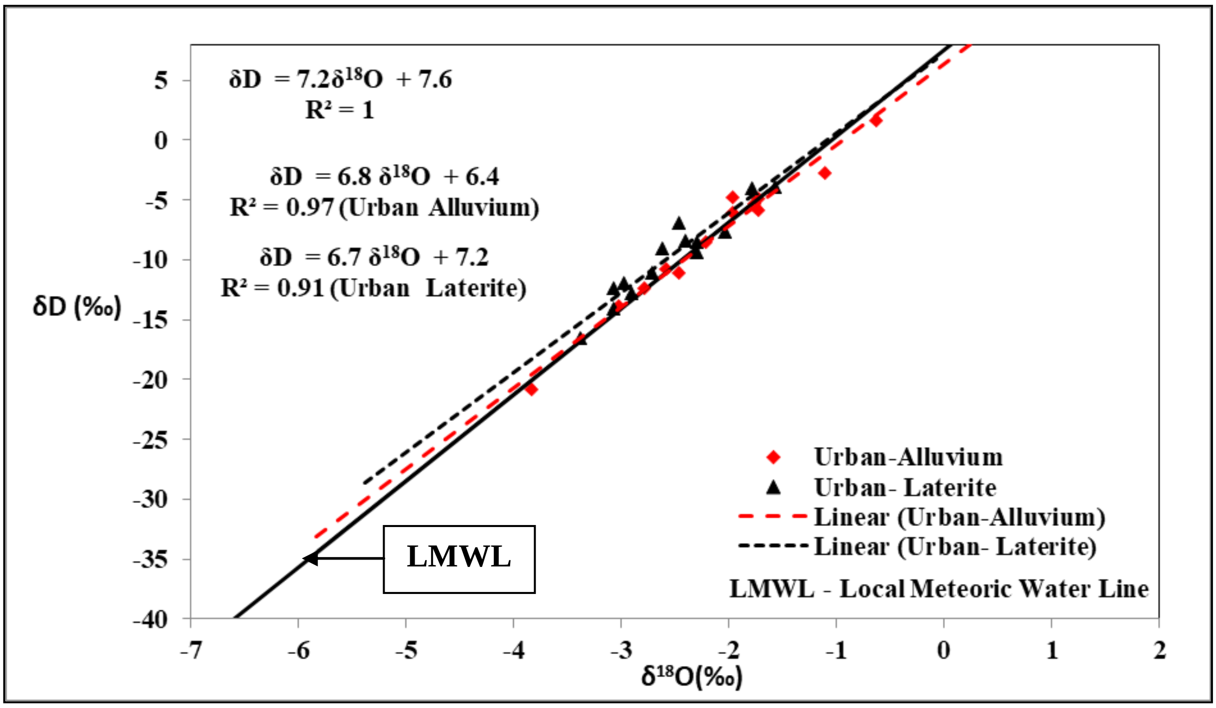


Figure 4.8. The relationship between $\delta^{18}O$ and δD of groundwater and rain water in the urban (alluvium &laterite) phreatic aquifer during pre-monsoon

The δD and $\delta^{18}O$ values of the groundwater samples collected from both urban and peri-urban zones during pre-monsoon and post-monsoon period positioned closely around the LMWL. Thus it can be confirmed that the groundwater most probably recharged by the recent precipitation

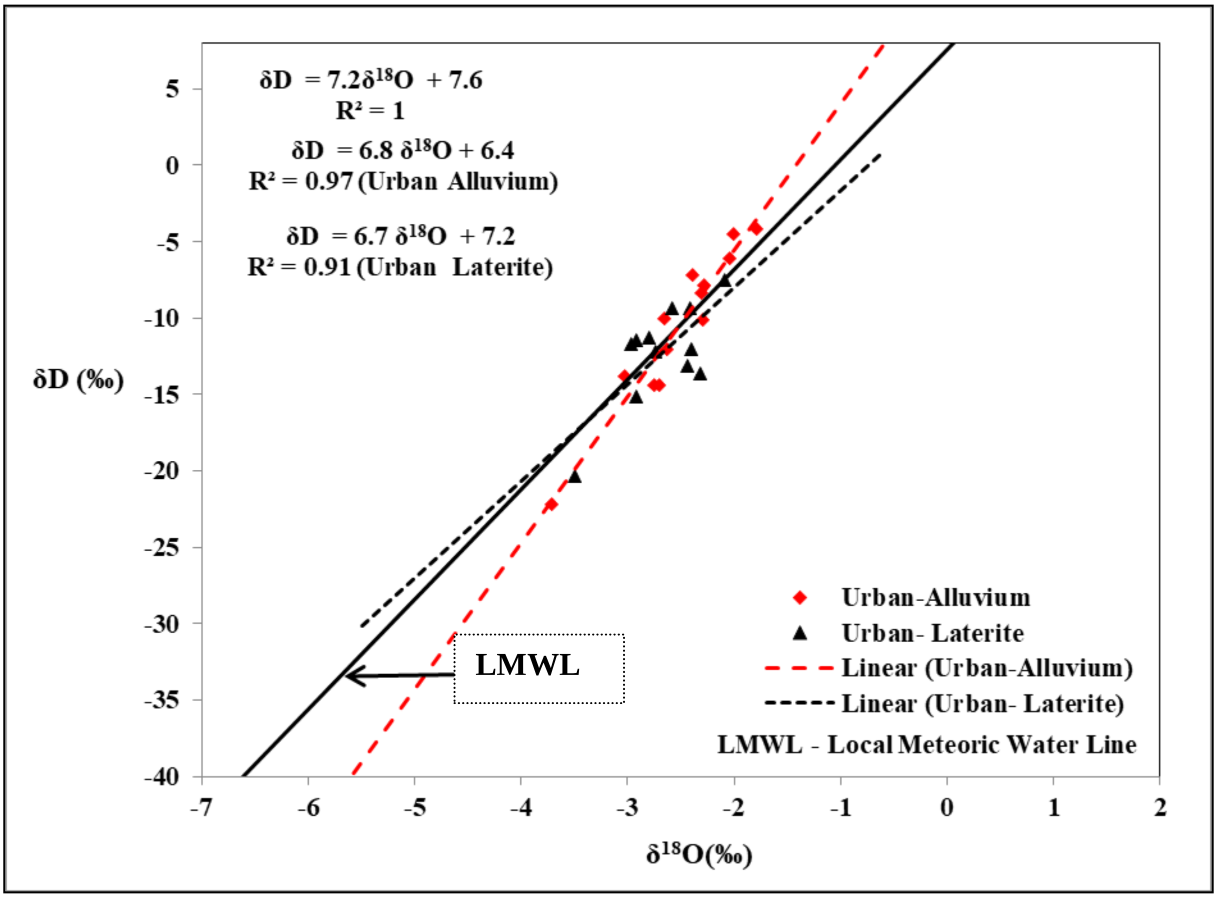


Figure 4.9. The relationship between $\delta^{18}O$ and δD of groundwater and rain water in the urban phreatic aquifer (laterite & alluvium) during post- monsoon

In post monsoon period, some urban and peri-urban groundwater laid slight away from LMWL shows a slight enrichment process in isotopic composition. It is mainly visible in samples from alluvial aquifers. Farid et al. 2013 explain that this enrichment process in isotopic composition may be due to surface water seepage or rainfall. Some peri-urban samples such as PU3 & PU8 during pre-monsoon fall slightly below the LMWL reveals the evaporative enriched isotopic composition.

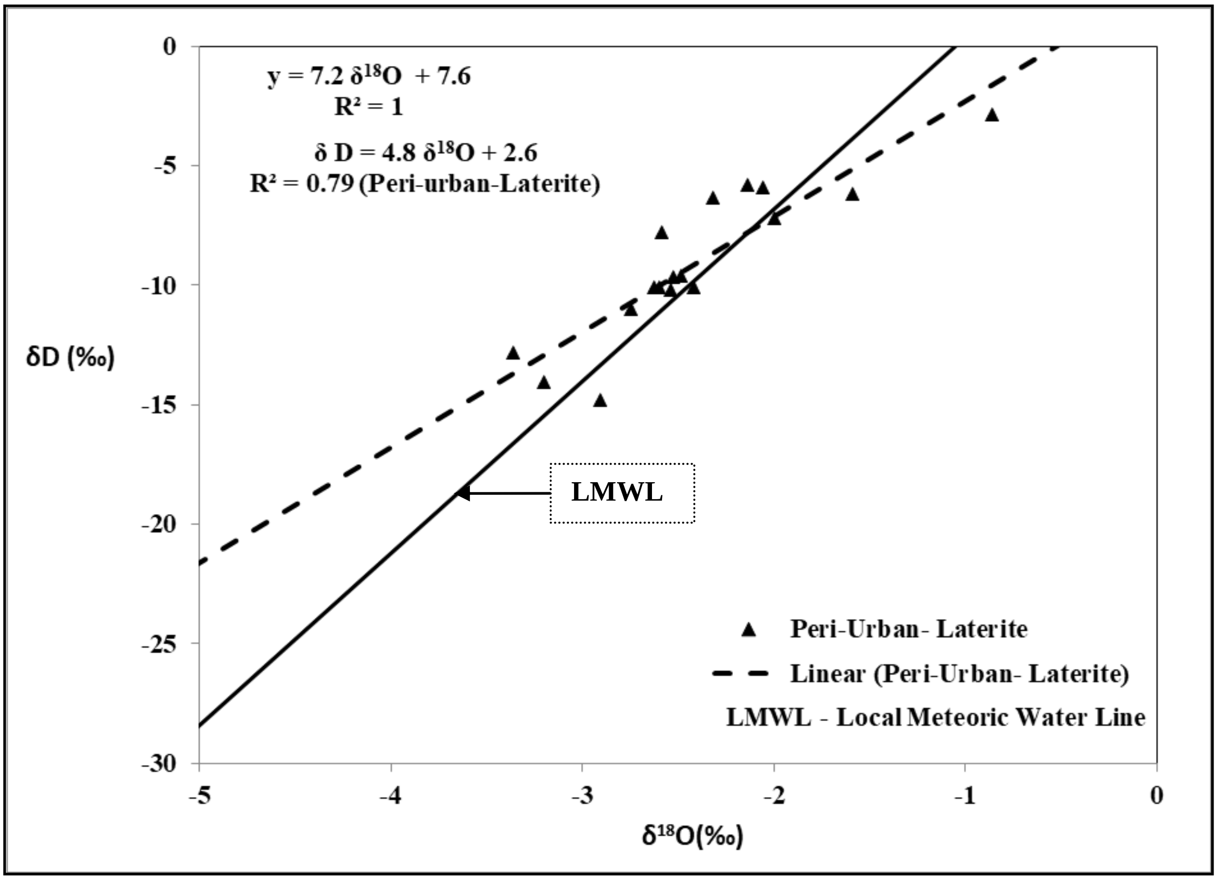


Figure 4.10. The relationship between $\delta^{18}O$ and δD of groundwater and rain water in the peri-urban (laterite) phreatic aquifer during pre-monsoon

The regression analysis of stable isotopic composition in groundwater and LMWL presented Table 4.4. The groundwater define a regression line with a slope similar to that of the Local Meteoric Water Line (LMWL). During pre-monsoon and post-monsoon period, the $\delta^{18}O$ and δD regression lines for urban alluvial and laterite groundwater samples had a slope value of 6.8 and 6.7 respectively (Table 4.4).

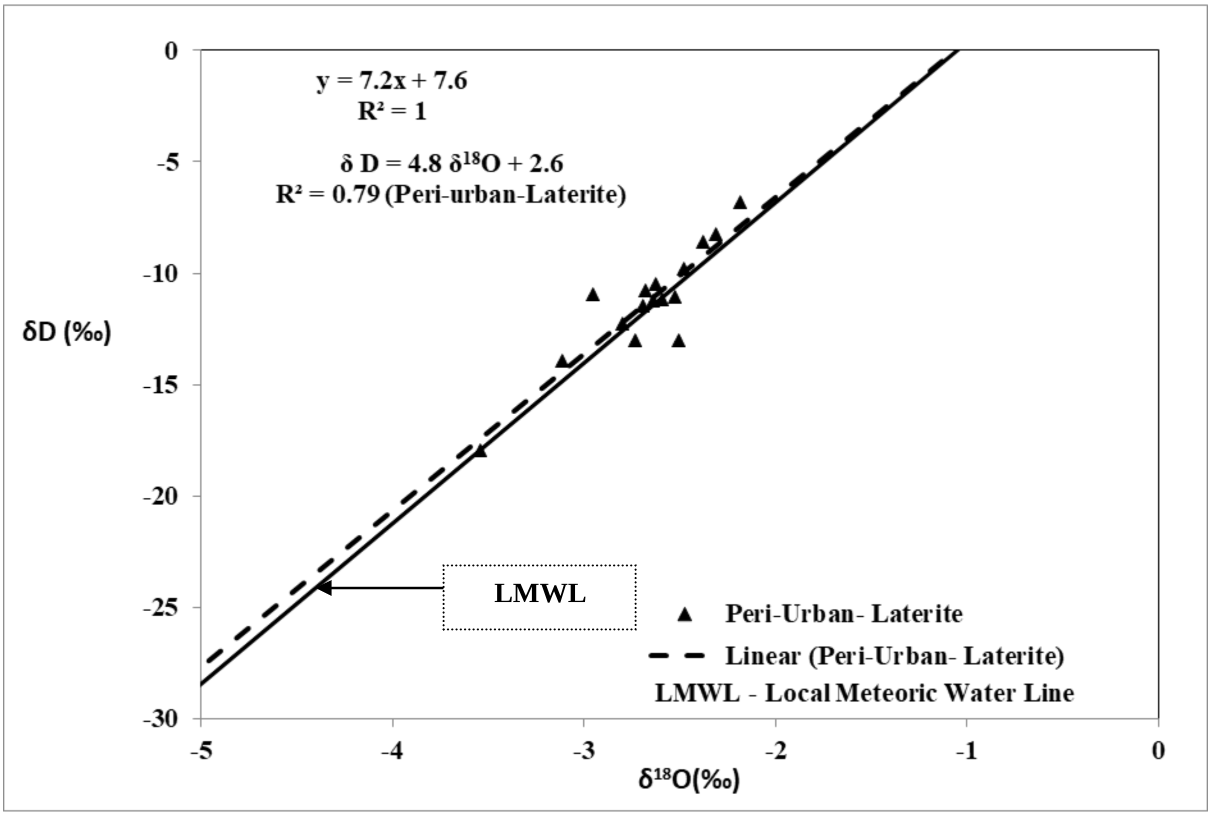


Figure 4.11. The relationship between $\delta^{18}O$ and δD of groundwater and rain water in the peri-urban (laterite) phreatic aquifer during post-monsoon

Table 4.4. Regression parameters of rainwater and groundwater in urban and peri-urban zones of the study area

	Slope		**Y-intercept**		**R2**	
	Pre-Monsoon	**Post-Monsoon**	**Pre-Monsoon**	**Post-Monsoon**	**Pre-Monsoon**	**Post-Monsoon**
LMWL	7.2		7.6		0.99	
Urban-Alluvium	6.8	6.8	6.4	6.4	0.97	0.97
Urban-laterite	6.7	6.7	7.2	7.2	0.91	0.91
Peri-urban-laterite	4.8	4.8	2.6	2.6	0.79	0.79

The $\delta^{18}O$ and δD regression lines for peri- urban laterite groundwater samples had a slope value of 4.8 during both pre-monsoon and post-monsoon period. The slope value of the regression line of urban and peri-urban phreatic groundwater samples during both seasons were less than that of LMWL (7.2) indicated the varying degree of evaporation on groundwater samples and it is further confirmed by study of Dindane et al. 2003.

4.6. Spatio-temporal variation in d-excess of groundwater

d-excess is a useful parameter to decipher the effect of evaporation in modifying the isotopic character of rainwater prior to groundwater recharge. When more than one moisture sources with different initial isotope compositions evolve along evaporation lines, as may presently be the case, it may be difficult to infer evaporation from the observed decrease in slopes of δD - $\delta^{18}O$ regression lines (Deshpande et al. 2003).

Local precipitation/regional precipitation shows that in the coastal zone the d-excess value is 10 ‰ and in the mid land region it is 12‰. d-excess in precipitation at Kozhikode have average value of 10‰. The range of d-excess value of precipitation for the entire study area indicated the presence of primary precipitation. The observed d-excess values were also concurred with observations of Deshpande et al. 2003. d-excess values of urban alluvial groundwater samples were varied from 6.1‰ to 11‰ in pre-monsoon and 7.3‰ to 11.9‰ in post-monsoon (Table 4.5). For urban laterite aquifers, d-excess values ranged from 8.7‰ to 12.9‰ in pre-monsoon and from 4.9‰ to 12.1‰ in post monsoon. For peri-urban laterite aquifers, d-excess values observed from 4‰ to 14‰ in pre-monsoon and from 7‰ to 12.7‰ in post monsoon. Average d-excess value of urban alluvial, urban laterite and peri-urban laterite aquifers during pre-monsoon are 9‰, 10.6‰ and 10.2‰ respectively. Average d-excess value of urban alluvial, urban laterite and peri-urban laterite aquifers during post-monsoon are 9.7‰, 9.2‰ and 10.1‰ respectively. Therefore, the range of d-excess values of groundwater in the entire study area were in same trend with that of rainwater.

Deshpande et al. 2003 studied the isotopic composition of shallow groundwater and surface water samples of west coast India(Kozhikode) and stated that if the range of d-excess values in precipitation is between 8‰ - 10‰, it is assumed to be representative of primary precipitation (rain water) in the entire study area. Coastal sample such as PU3, PU8, U9 & U16 having lower d-excess value (≤ 6‰) during pre-monsoon were indicated that significant evaporation of groundwater is leaving the residual groundwater with lower values of d-excess (Table 4.2 a &c). Regression lines for urban and peri-urban groundwater samples were showed a slope value of lower than LMWL that in the precipitation supported the same.

Table 4.5. Statistical analysis of d- excess value (‰) in both urban and peri- urban groundwater and surface water

	Average		Minimum		Maximum	
	Pre	**Post**	**Pre**	**Post**	**Pre**	**Post**
Urban-Alluvium	9	9.7	6.1	7.3	11	11.9
Urban-Laterite	10.6	9.2	8.7	4.9	12.9	12.1
Peri-urban-Laterite	10.2	10.1	4	7	14	12.7
Surface water	-0.15	9.36	-0.51	-8.84	0.4	23.4

4.7. Distribution of δD and δ^{18}O in the surface water of the study area

Surface water samples have been collected from five locations of three major rivers viz. chaliyar low land & midland, Korapuzha – low land & mid land and Kallai lowland. δ^{18}O and δD isotopic ratios of surface water samples were observed in the study area were given in Table 4.6. The δ^{18}O values vary from 0.6 ‰ to 1‰ during pre monsoon and -3.2‰ to -0.3‰

during post monsoon. The δD values vary from 4.6 ‰ to 7.6‰ during pre monsoon and-10.8‰ to 0.1‰ during post monsoon.

Table 4.6. Stable isotope composition of surface water samples during pre-monsoon and post –monsoon period

Sample code	River name	Pre-monsoon			Post-monsoon		
		$\delta^{18}O$	δD	D-Excess	$\delta^{18}O$	δD	D-Excess
JKR1	Chaliyar- Low land	0.7	5.8	0.4	-3.2	-2.3	23.4
JKR3	Chaliyar- Mid land	0.7	5.3	-0.5	-2.1	0.1	17.1
JKR2	Kallai –Low land	0.6	4.6	-0.3	-1.3	-7.4	3.2
JKR4	Korapuzha	1.0	7.6	-0.5	-0.3	-10.8	-8.8
JKR5	Korapuzha- Mid land	0.6	5.3	0.2	-2.6	-8.6	11.9

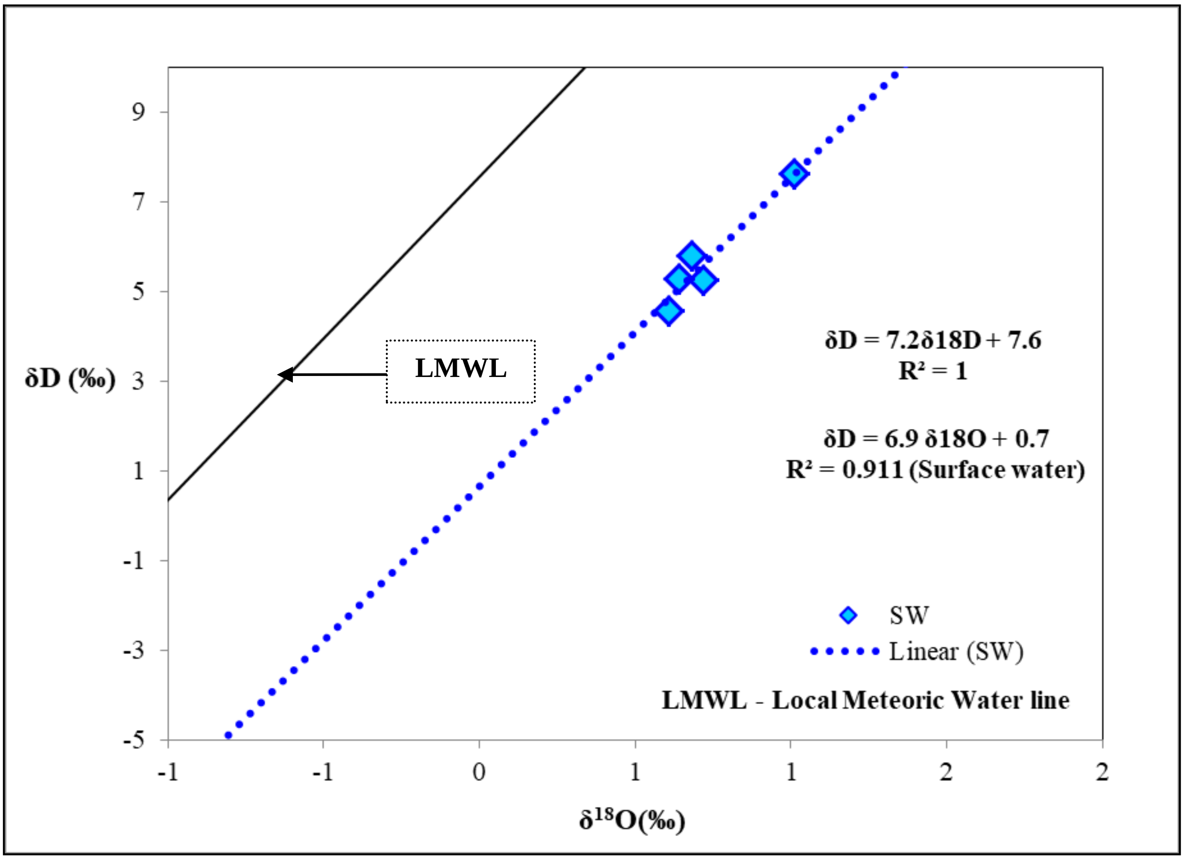


Figure 4.12. The relationship between $\delta^{18}O$ and δD of surface water and rain water in the study area during pre-monsoon

The plots of δD vs δ^{18}O for the surface water samples having a regression line slope value of 6.9 during pre monsoon (Figure 4.12) and -2.4 in post monsoon (Figure 4.13) season and which is much less than that of the LMWL value (7.2). Thus indicated evaporative enrichment of heavier isotopes in surface water. Figure (4.12 and 4.13) depicted that, the scatter is much larger for the post monsoon is due to spatially variable contribution of direct evaporation from flowing water and the NE winter rainfall. This is further confirmed by observations of Deshpande et al. 2003 on surface water samples of Kozhikode.

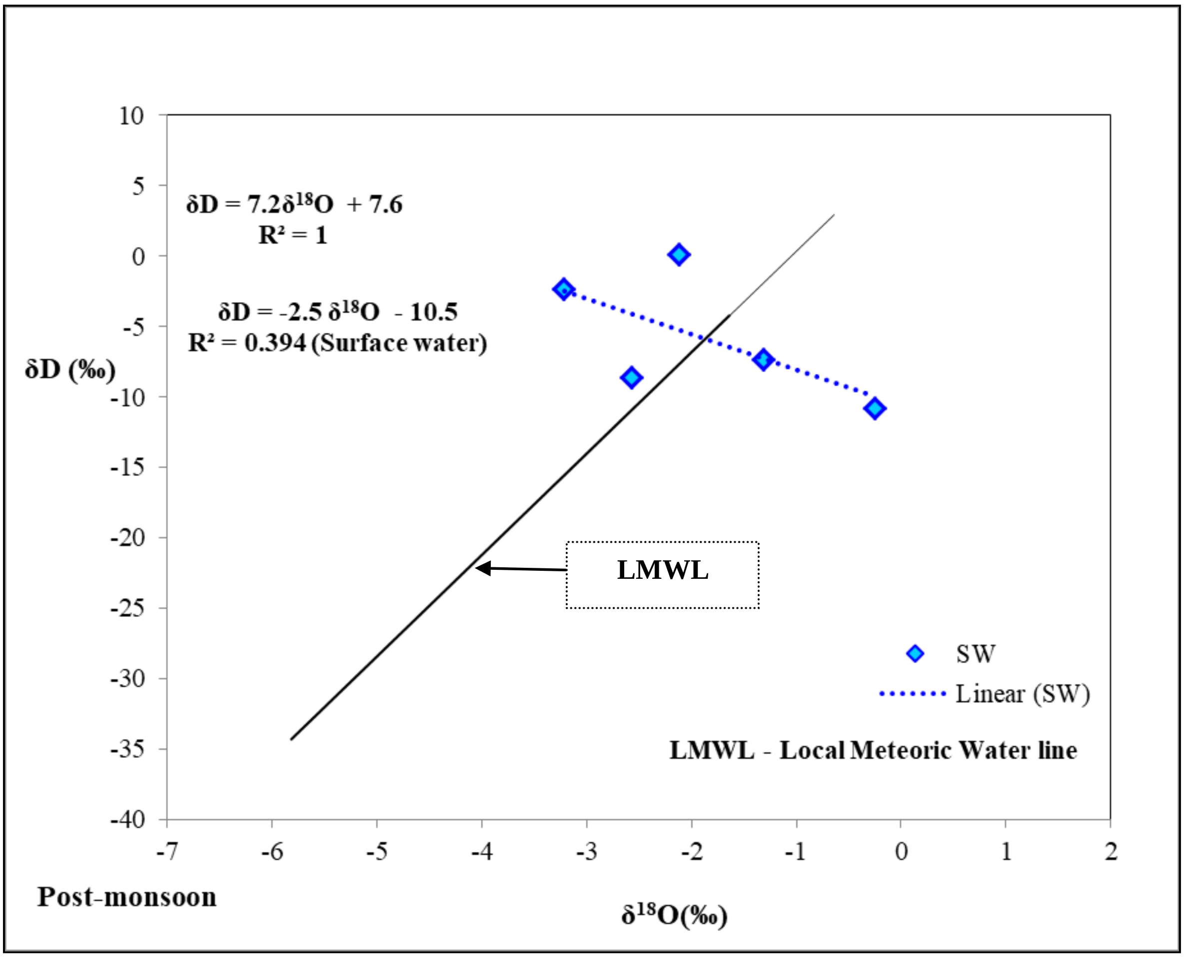


Figure 4.13. The relationship between δ^{18}O and δD of surface water and rainwater in the study area during post-monsoon

The d-excess values of surface water shown in Table 4.5, the low 'd-excess' values (≤ 6‰) seen in pre-monsoon would suggest that there is significant evaporation of rainwater leaving the residual surface water with lower d-excess values. While comparing the d-excess values and regression slope values of rain water, groundwater and surface water, it was concluded that the main recharging source for the groundwater in the urban and peri-urban phreatic aquifers of the study area is rain water and not surface water which drained in the study area.

4.8. Extent of salinization in groundwater and surface water

The extent of salinization in groundwater and surface water can be explained using variation of $\delta^{18}O$ and with chloride ion. The evaporation process also be underpinned with the study of $\delta^{18}O$ – Cl relationship. δD and $\delta^{18}O$ enrichment for surface water compared to groundwater in both seasons indicated the occurrence of evaporation process of the water body (Deshpande et al. 2003).

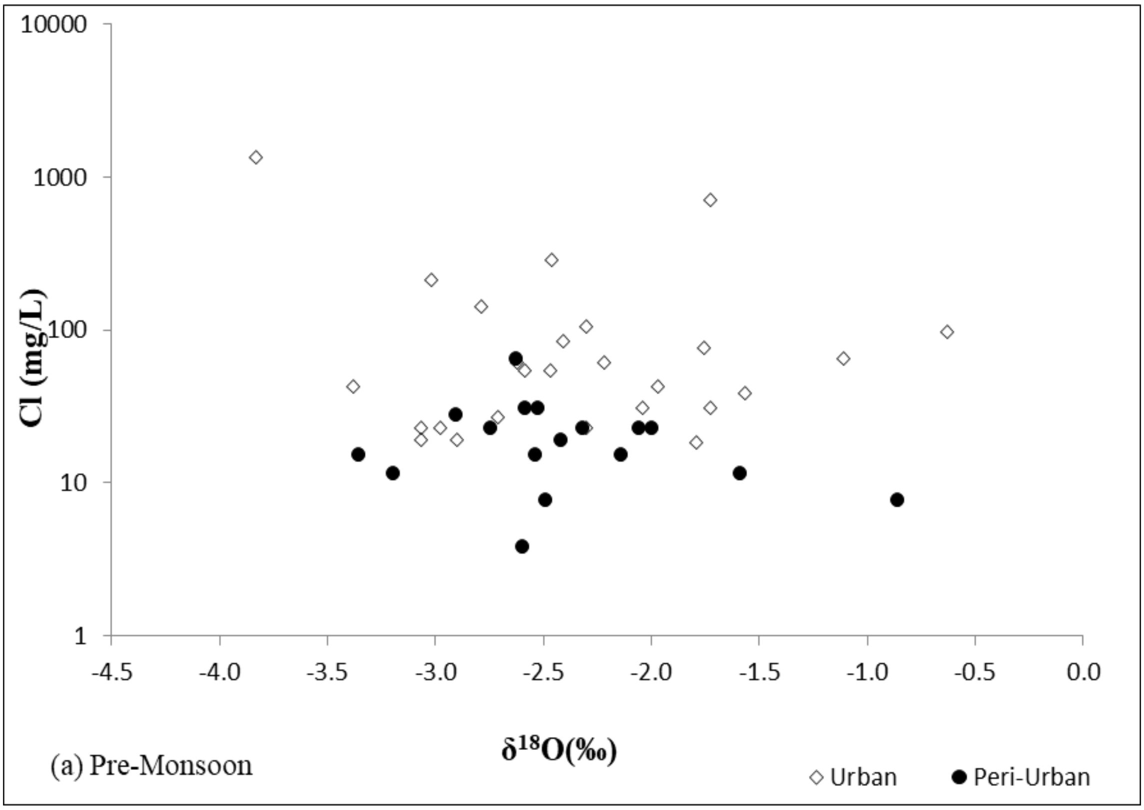


Figure 4.14 a. The relationship between $\delta^{18}O$ and Cl^- of urban and peri-urban groundwater during the pre–monsoon season

The scatter diagram of δ^{18}O and chloride concentration was plotted for urban and peri-urban groundwater in two seasons (Figure 4.14 a &b) used to find salinization mechanism as well as evaporation process. Here all urban and peri-urban samples have Cl$^-$ concentration below 1meq/L and δ^{18}O concentration of > -4‰ except some coastal urban samples, such as U14 and U15.

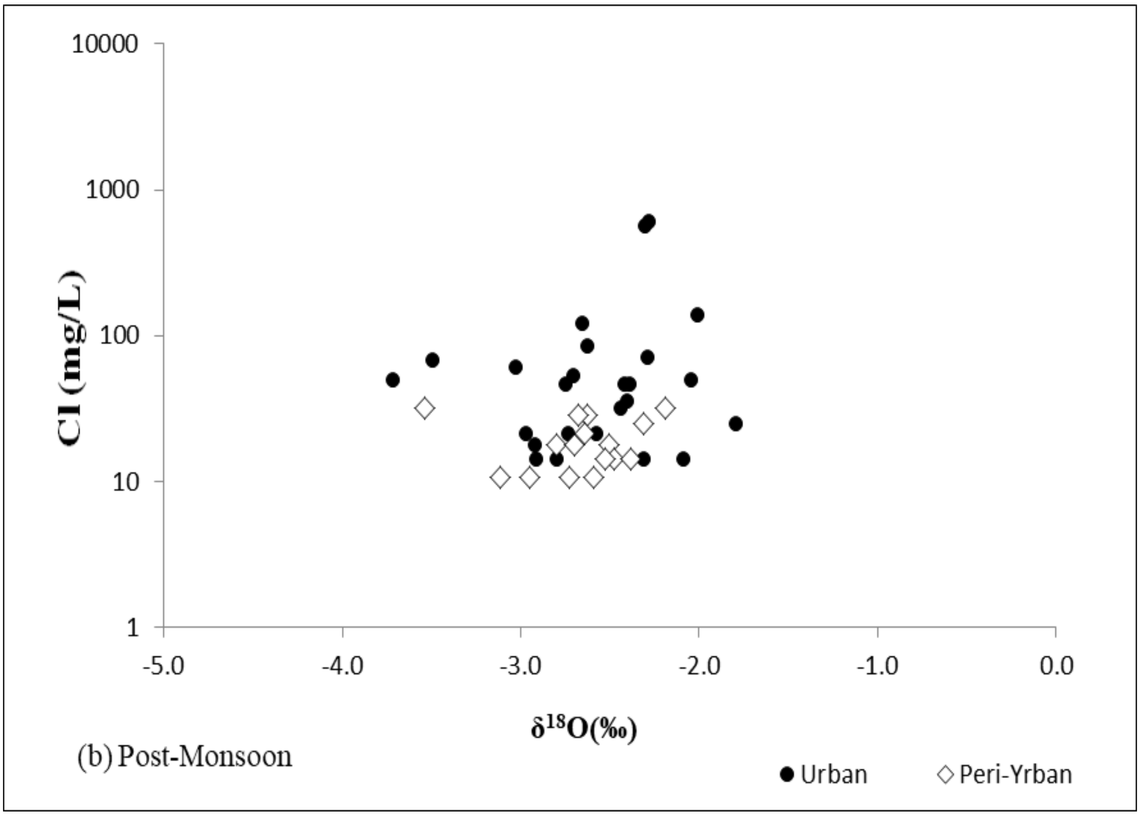


Figure 4.14 b. The relationship between δ^{18}O and Cl$^-$ of urban and peri-urban groundwater during the post-monsoon season

There is an increase in Cl$^-$ concentration in such urban samples from coastal phreatic aquifers along with enrichment in δ^{18}O indicated the evaporation process. As it can be seen from the Figure 4.14 a &b, Apart from the direct influence of the sea water, concentrations of ions by evaporation also contribute to the observed salinity in the area. Another possibility of samples U14 and U15 higher concentrations due to infiltration of sewage effluents.

4.9. Estimation of percentage contribution of rainwater to groundwater recharge

Analysis on relation between stable isotopic composition of rainwater and urban, peri-urban groundwater samples inferred that the groundwater of the area were close to the mean composition of precipitation. Monsoon-derived rainfall plays a vital role in the alluvial aquifer recharge (Warrier et al. 2010).Hydrogeological conditions of the study area favours the direct infiltration of rainwater to aquifer system. A two component (groundwater and rain water) mixing model has been used in this study to estimate the fraction of rain water in groundwater quantitatively. The prerequisite for such estimations is that there should be at least two isotopically different end members (Hameed et al. 2016). The distinct isotopic characteristics of rainwater contribution to groundwater recharge for urban and peri-urban region have shown in Table 4.7.

Let δ1 be the $\delta^{18}O$ of pre-monsoon groundwater end member which has no contribution from rainwater. δAM is $\delta^{18}O$ of groundwater from post-monsoon period and it is assumed that the admixture constitutes groundwater present in the aquifer prior to the monsoon season and infiltrated rain water. δ2 represents the average $\delta^{18}O$ of rain water. M1and M2 are the fractions of pre-monsoon groundwater and surface water in the admixture, respectively. The fraction of rain water in ground water was quantitatively estimated from the following isotope mass balance equation; from this percentage recharge contribution of rain water was calculated. As per the isotope mass balance equation:

$$\delta_1 M_1 + \delta_2 M_{2=} \delta_{AM}$$

$$M_1 + M_2 = 1$$

Where M_1 and M_2 are the fractions of pre-monsoon groundwater and rain water in the admixture, respectively. From the above equation, the percentage of rain water mixed with groundwater can evaluate from the following equation:

$$\text{Rain water contribution (\%)} = \left[\frac{(\delta AM-\delta 1)}{(\delta 2-\delta 1)}\right] X100 \ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

Using values of pre-monsoon and post-monsoon groundwater end member for the three zones, viz urban-alluvium, urban-lateritic and peri-urban aquifer zones, the rain water contribution to ground water in each zoneshasbeen estimated.The δ^{18} O values of pre-monsoon groundwater end-members (δ_1), δ_{18}O values of the post-monsoon groundwater end members (δ_{AM}), and δ^{18} O values of the rain water end members (δ_2) were given in Table 4.7 a, b & c.

Table 4.7 a . Estimated percentage contribution of rainwater to groundwater of urban alluvial aquifers during the post-monsoon season and the data selected for estimation

Urban-alluvium				
Sample Code	**Pre-monsoon(GW) δ^{18}O (δ_1 in ‰)**	**Post-monsoon (GW) δ^{18}O (δ_{AM} in ‰)**	**Rainwater δ^{18}O (δ_2 in ‰)**	**% of the contribution of rain water to groundwater**
U4	-0.63	-2.0	-3.8	44.3
U6	-1.76	-2.4		30.5
U8	-1.97	-3.0		57.0
U9	-1.97	-2.3		17.3
U10	-2.59	-2.8		12.9
U12	-2.22	-2.7		27.0
U16	-1.11	-2.6		55.8

Table 4.7 b . Estimated percentage contribution of rainwater to groundwater of urban laterite aquifers during the post-monsoon season and the data selected for estimation

Urban-Laterite				
Sample Code	**Pre-monsoon(GW) $\delta^{18}O$ (δ_1 in ‰)**	**Post-monsoon (GW) $\delta^{18}O$ (δ_{AM} in ‰)**	**Rainwater $\delta^{18}O$ (δ_2 in ‰)**	**% of the contribution of rain water to groundwater**
U21	-2.3	-3.5	-3.8	77.9
U19	-2.71	-2.9		18.4
U25	-1.57	-2.8		54.5
U29	-2.3	-2.6		18.2
U32	-2.04	-2.7		39.0
U36	-1.79	-2.3		25.7

Table 4.7 c. Estimated percentage contribution of rainwater to groundwater of peri-urban laterite aquifers during the post-monsoon season and the data selected for estimation

Peri-urban-Laterite				
Sample Code	**Pre-monsoon(GW) $\delta^{18}O$ (δ_1 in ‰)**	**Post-monsoon (GW) $\delta^{18}O$ (δ_{AM} in ‰)**	**Rainwater $\delta^{18}O$ (δ_2 in ‰)**	**% of the contribution of rain water to groundwater**
PU3	-0.9	-2.6	-3.7	61.6
PU8	-1.6	-2.3		33.9
PU4	-2.3	-2.6		19.2
PU11	-2.6	-2.8		18.6
PU13	-2.0	-2.5		29.2
PU28	-2.8	-3.5		81.0
PU40	-2.5	-3.1		48.5

The rainwater fraction ranged between 12% and 57% in the groundwater urban alluvial aquifers with an average of 35%.Where as in urban lateritel aquifers the rain water fraction ranges between 18% to 77% with an average value of 39%.In laterite aquifers which laid in the peri-urban zone, average rain water recharge is 42% with a range between 18% to 81%.

CHAPTER 5

GROUNDWATER SUITABILITY ZONATION USING GIS BASED MULTI-CRITERIA DECISION MAKING (MCDM) TECHNIQUE

Introduction

The GroundWater Quality Index (GWQI) is one of the most effective tools to assess the quality of water and can be used by policy makers to reassure concerned citizens (Lateef, 2011). It is a simple and concise method to express the hydrochemical data/ water quality variables which were evaluated with various standard methods into single number (Stambuck-Giljanovic, 1999; Stigter et al. 2006; Abtahi et al. 2015). The traditional approaches for assessing water quality are based on the comparison of experimentally determined parameters with local or international standards (Zagatto et al. 1998; Magesh and Chandrasekar, 2013). The present chapter was attempted to generate GWQI data of groundwater samples which were collected from urban and peri-urban phreatic aquifers of the Kozhikode district of the south-west coast of India and to evaluate the groundwater suitability zones of the area using Geographic Information System (GIS) and Multi-Criteria Decision Making (MCDM) techniques.

GIS provides the potential tool for handling complex spatial data and its integrated approaches with MCDM techniques lend a hand to deal with various groundwater resource investigations such as site suitability analyses. MCDM-GIS method will provide an effective platform for categorizing the water quality controlling criteria into suitable subclasses as per drinking water specifications and enable the pair-wise comparison process of such factors (Jesiya and Gopinath, 2019 a).

5.1. Establishment of Groundwater Quality Index

Groundwater Quality Index for suitability analysis was derived through three processes viz; reconnaissance survey & laboratory analysis, establishment of groundwater quality index and finally preparation of a groundwater suitability map of urban and peri-urban zones of the study area(Figure 2.2). Physico-chemical parameters of groundwater were evaluated after the reconnaissance survey and laboratory analysis (Table 2.2). Exploratory Data Analysis (EDA) were done using Geostatistical Wizard in ArcGIS and Normal Q-Q plots for all parameters shows that parameters except pH and sulphate have a slight asymmetry on its spatial distribution. Lognormal transformation were applied on parameters such as EC, TDS, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and CO_3+ HCO_3 and eliminated this asymmetry.

GWQI is a single dimensionless number used for assessing the quality of water based on specific criteria like drinking water suitability, agricultural purposes etc and for evaluating the influence of natural and anthropogenic activities based on several key parameters of groundwater chemistry (Jesiya and Gopinath, 2019 a). Generally GWQI were established based calculation developed by Brown et al. (1972), involves three steps, initially calculation of the weightage of the ith parameter. Second, the calculation of the individual quality rating of the water quality parameters. Finally, the summation of these sub-indices using the formula given below (Reza and Singh, 2010).

$$\mathrm{WQI} = \frac{\sum_{i=1}^{n} \mathrm{w_i} Q_i}{\sum_{i=1}^{n} \mathrm{w_i}} \text{……………………………} \quad (1)$$

Where Wi is the unit weight for the ith parameter, Qi is the quality rating as per international (WHO) and BIS standards. Therefore, the overall water quality index is the summing up of all sub-indices (Eq 1). According to Zahedi (2017), the major drawback of this calculation is if a water resource could possibly presented a higher WQI value just because of a considerably higher concentration in one chemical parameter which has a high weight and the same with lower concentration in that high-weigh parameter but higher values in other parameters might present a lower WQI. Studies revealed that the application of the classic WQI method would result in deterministic and rigid outcome (Lermontov et al. 2009). An integrated GIS based MCDM approach was adopted in the study in order to overcome these drawbacks. The concentration ranges of water quality parameters were converted to an index score to measure the influence of these parameters as shown in Table 5.1 and further transformed to a normallised weight for comparison on a common scale, i.e, saaty's scale preferences in the range of 1-9 (Saaty, 2005; Krishnan et al. 2016).

5.1.1. Deriving normallised weights using MCDM technique

Relative priority scales of absolute numbers from individual judgments were derived through AHP /ANP (an MCDM tool) methods (Saaty, 2005). The parameters selected for the GWQI estimation involved 11 criteria and 43 sub–criteria with different units (Table 5.1). Thematic layers had subclasses varying from two to six, indicating the relationships between these interrelated classes are complex. Each thematic layer of physico-chemical indicators and its sub-classes were categorized into 'highly suitable' suitable, moderately suitable and 'not suitable' / 'unsuitable' zones for drinking water and assigned weights based on their relative importance in the overall groundwater quality as per the WHO (2011) and BIS (2012) standards. A detailed involvement of expert's opinions which ensures the consideration of local environmental aspects on creating weights was incorporated. The water quality parameters under acceptable, desirable and permissible limits of BIS (2012) and WHO (2011) were classified as highly suitable, suitable and moderately suitable category, respectively. The parameter concentration exceeding permissible limit was considered as non–potable (Unsuitable) for drinking water.

The ANP, is an extension of AHP for decision making in which a problem is divided into various parameters (Figure 5.1) assembling them in a hierarchical structure, making judgments based on the relative importance of parameters and synthesizing the results (Saaty 1999). Figure 5.1, illustrated the ANP model where a problem (GWQI) divided into various water quality criteria and its sub classes. The 'cluster' of criteria which involves the 11 nodes of physico-chemical parameters of groundwater and the sub-criteria 'clusters' comprises of data intervals of each parameter in accordance with the standard drinking water specifications were arranged in hierarchical pattern.

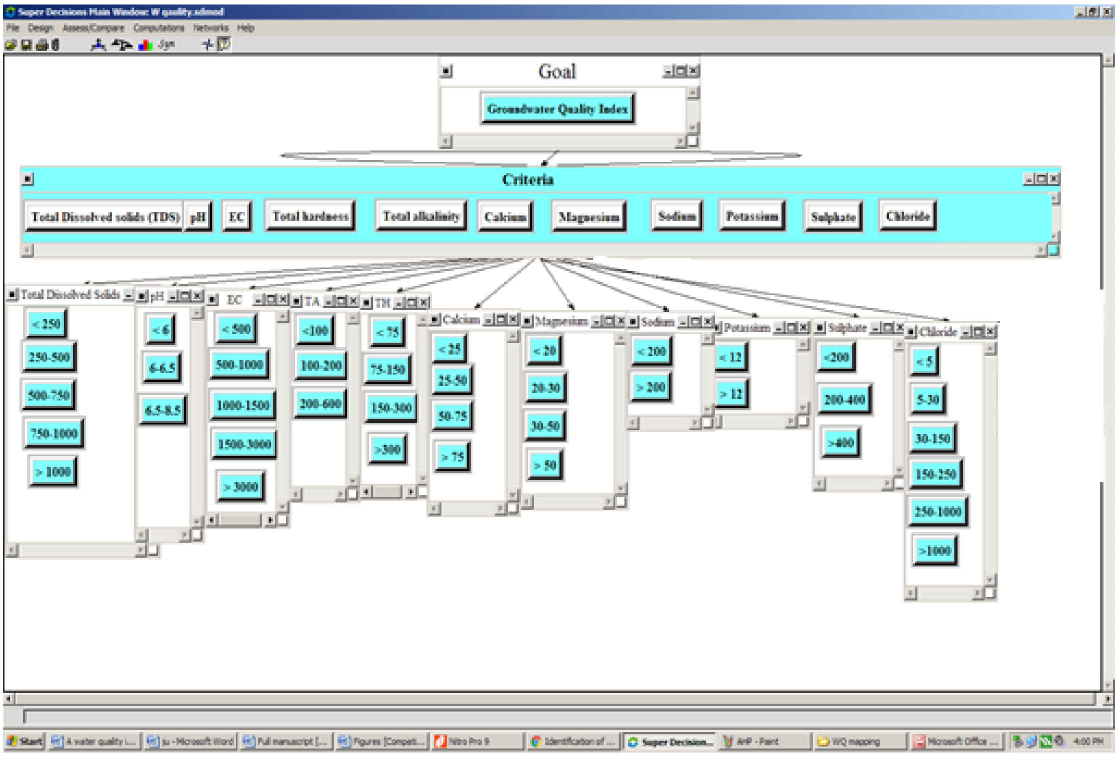
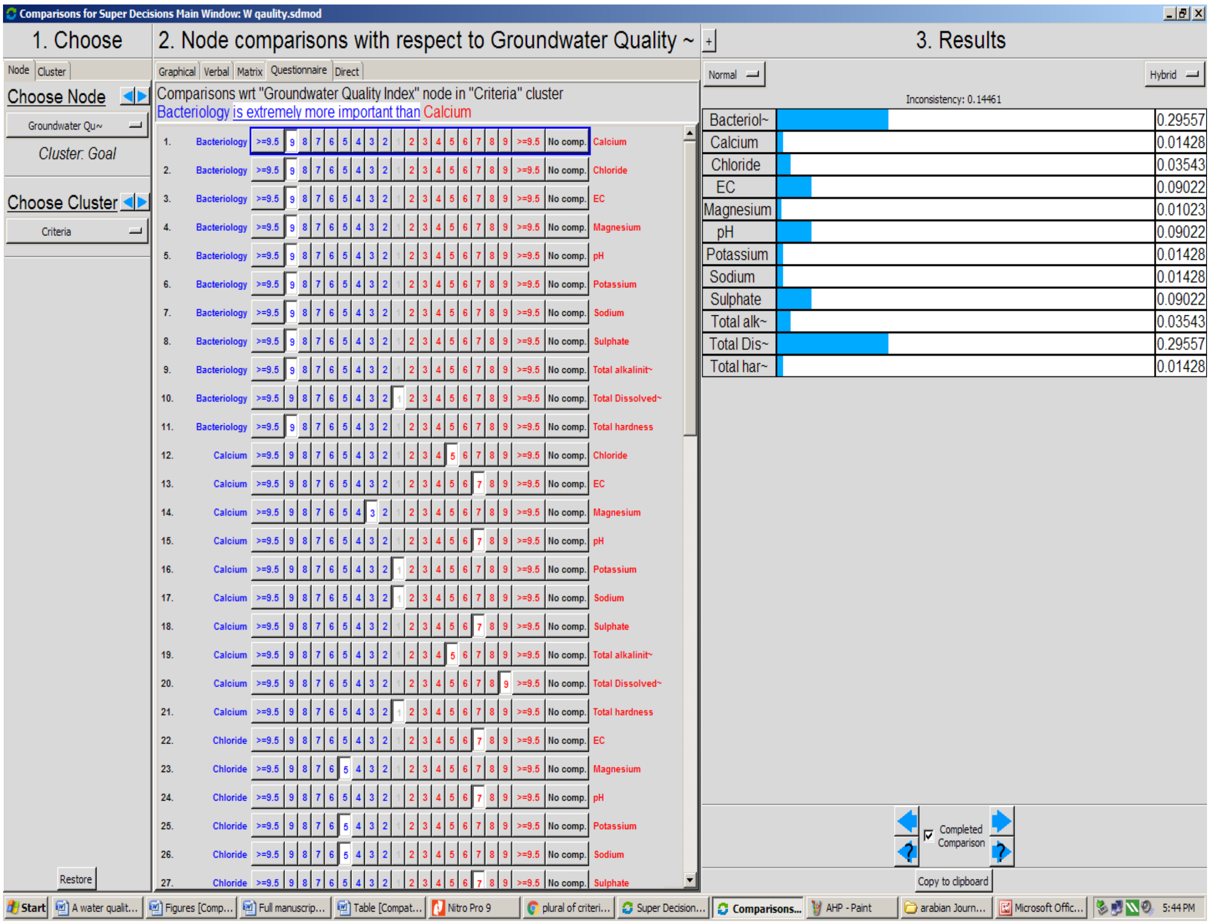


Figure 5.1. The ANP model for establishment of groundwater quality index

5.1.2.Pairwise comparisons and corresponding priorities

Pairwise comparisons of criteria and sub criteria using the pairwise-comparison matrix in ANP were provided a platform to combine the experts' judgment/information to a single value. Normalized weights (Wi) of main criteria were derived after pairwise comparisons of criteria among each other using pairwise comparison matrix in ANP (Figure 5.2). Followed by sub-criteria comparisons were derived ratings(Qi) for each sub criteria (Table 5.1). Consistency Ratio (CR) value were derived for all criteria and sub-criteria comparisons are less than 0.1. CR value < 0.1 verified the consistency of the comparison matrix and were recommended for the acceptance of pairwise comparisons.



Comparisons wrt "Groundwater Quality Index" node in "Criteria" cluster
Bacteriology is extremely more important than Calcium

1.	Bacteriology	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Calcium
2.	Bacteriology	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Chloride
3.	Bacteriology	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	EC
4.	Bacteriology	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Magnesium
5.	Bacteriology	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	pH
6.	Bacteriology	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Potassium
7.	Bacteriology	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Sodium
8.	Bacteriology	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Sulphate
9.	Bacteriology	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Total alkalinit~
10.	Bacteriology	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Total Dissolved~
11.	Bacteriology	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Total hardness
12.	Calcium	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Chloride
13.	Calcium	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	EC
14.	Calcium	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Magnesium
15.	Calcium	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	pH
16.	Calcium	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Potassium
17.	Calcium	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Sodium
18.	Calcium	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Sulphate
19.	Calcium	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Total alkalinit~
20.	Calcium	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Total Dissolved~
21.	Calcium	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Total hardness
22.	Chloride	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	EC
23.	Chloride	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Magnesium
24.	Chloride	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	pH
25.	Chloride	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Potassium
26.	Chloride	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Sodium
27.	Chloride	>=9.5 9 8 7 6 5 4 3 2 1 2 3 4 5 6 7 8 9 >=9.5 No comp.	Sulphate

Inconsistency: 0.14461

Bacteriol~	0.29557
Calcium	0.01428
Chloride	0.03543
EC	0.09022
Magnesium	0.01023
pH	0.09022
Potassium	0.01428
Sodium	0.01428
Sulphate	0.09022
Total alk~	0.03543
Total Dis~	0.29557
Total har~	0.01428

Figure 5.2. Pairwise comparison matrix of AHP/ANP analysis

5.2. Integration of GIS & MCDM for groundwater suitability analysis

Normalized weights (Wi) and ratings (Qi) were used as an inputs for each raster data of the factors using reclassification method in ArcGIS and all these factors were integrated with weighted sum overlay analysis in the spatial analyst tool of Arc GIS 10.5.1. The resultant raster data i.e. Groundwater quality index value of the study area was divided into four classes such as highly suitable, suitable, moderately suitable and unsuitable zones according to the drinking water suitability (Figure 5.3). The groundwater suitability map of the study area were depicted that not only the site suitable for drinking water and but also the regions which need high priority in the sense of requiring more attention to make the groundwater fit for drinking purposes. Groundwater quality mapping proved as a useful tool to summarize and for the easy understanding of the status of groundwater quality of a particular area through the integration of various physico-chemical factors (Saraf et al. 1994, Rao and Jugran, 2003, Jesiya and Gopinath, 2019 a).

Table 5.1. Normallised weights and ratings derived after Analytical Network Process

Name of parameter	**Weight(ANP) (Wi)**	**Feature Class**	**Ratings (ANP) (Qi)**
Total Dissolved Solids	**0.296**	< 250	0.6383
		250-500	0.2151
		500-750	0.0826
		750-1000	0.0383
		> 1000	0.0257
Electrical conductivity	**0.090**	< 500	0.6383
		500-1000	0.2151
		1000-1500	0.0826
		1500-3000	0.0383
		> 3000	0.0257
pH	**0.090**	< 6	0.0598
		6-6.5	0.1399
		6.5-8.5	0.7405
		> 8.5	0.0598
Sodium	**0.014**	< 200	0.9
		> 200	0.1

Potassium	**0.014**	< 12	0.9
		> 12	0.1
Calcium	**0.014**	< 25	0.6669
		25-50	0.2072
		50-75	0.0792
		> 75	0.0467
Magnesium	**0.010**	< 20	0.6669
		20-30	0.2072
		30-50	0.0792
		> 50	0.0467
Chloride	**0.035**	< 5	0.5933
		5-30	0.2212
		30-150	0.0918
		150-250	0.0433
		250-1000	0.0252
		>1000	0.0252
Sulphate	**0.090**	<200	0.7662
		200-400	0.1579
		>400	0.0759
Total alkalinity	**0.035**	<100	0.6669
		100-200	0.2072
		200-600	0.0792
		> 600	0.0467
Total Hardness	**0.014**	< 75	0.7002
		75-150	0.2005
		150-300	0.0681
		>300	0.0312

The percentage of priority and weightage for each criterion (water quality parameters) concerning the quality index are given in Table 5.2. Highest weightages were assigned for total dissolved solids indicated its most significant role in the determination of the groundwater suitability zone. Whereas Mg^{2+} have the least and other parameters had in between significant role in the determination of the groundwater quality zone.

Table 5.2. Result of factor weight, priority and inconsistency index of water quality parameters for groundwater suitability zonation.

Sl.No	Criterion	Weight in %	Priority	Inconsistency Index
1	Total Dissolved Solid	29.6	1	0.14
2	Electrical conductivity	9.0	2	0.14
3	pH	9.0	2	0.13
4	Sulphate	9.0	2	0.13
5	Total alkalinity	3.5	3	0.13
6	Chloride	3.5	3	0.12
7	Sodium	1.4	4	0.02
8	Potassium	1.4	4	0.01
9	Calcium	1.4	4	0.14
10	Total hardness	1.4	4	0.13
11	Magnesium	1.0	5	0.13

Inconsistency index was calculated to check possible contradictions in different pairwise comparisons as given in Table 5.2. Here the inconsistency values for all comparisons are less than 0.15 for all parameters hence all comparisons were acceptable and suggested that no more improvements were required (Jesiya and Girish,2019 a). Based on the occurrence and influence of various water quality factors, about 312 km^2 (i.e., 60%) of the entire study area is characterized to be very good quality , suggesting that the groundwater is highly suitable for drinking purpose.

According to the BIS and WHO specifications, in the highly suitable drinking water zone the quality of groundwater is within the acceptable limit for drinking water. About 125 km^2(i.e., 24 %) of the total study area covers suitable zone, indicating that the groundwater quality in this zone is within the permissible range and as per the BIS standard that can use in the absence of an alternate source. 88 km^2 (i.e., 16 %) of the entire study area covers moderate to unsuitable water quality zone. The groundwater in the moderately suitable class can be used for drinking purpose only in the absence of alternate source.

While comparing the urban and peri-urban zone, 23.7% of urban and 84.1% of peri-urban zone were categorized as highly suitable drinking water zone (Table 5.3). Followed by 42% and 11% of urban and peri-urban zones were comes under suitable drinking water zone respectively. About 26.3% of total urban zone were categorized as moderately suitable zone for drinking purpose and some of the moderately suitable water samples in the urban phreatic zone stands on the brim of the maximum permissible limit and will go to the unsuitable category in future. The development trend (urbanization trend) of the Kozhikode district, is spreading from west to east direction, i.e towards midland region. Similarly water quality were also deteriorates along with the urbanization trend (Figure 5.3). In urban area, 8% of the total area were classified as unsuitable zone and majority of moderately to poor suitable of the urban zones were underlined by alluvial plain with gentle slope (i.e.0 - 15%).

Anthropogenic activities due to high density urban settlements occurred on the urban coastal zone were triggered the contamination process.

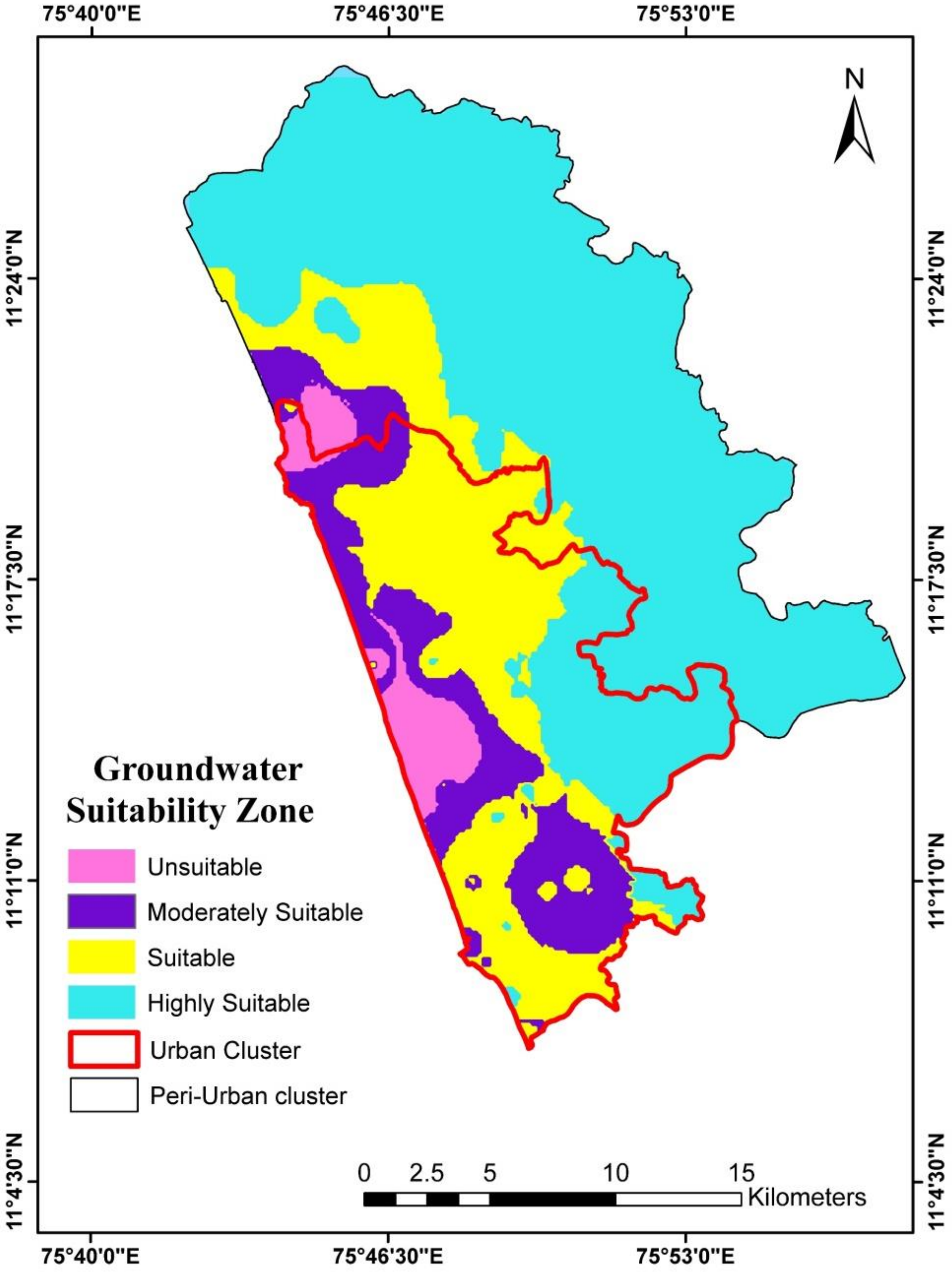


Figure 5.3. Groundwater suitability zone for drinking water purpose in the study area

Geospatial techniques were enabled to correlate the different landuse/land cover classes with the overall water quality status obtained in the study area and calculates the areal distribution of water quality zones under each landuse/ landcover classes except water bodies (Table 5.4). Geospatial correlation analysis were showed that the geologic formation (alluvium) along the coastal urban zone with dense population triggers the deterioration in water quality of phreatic aquifers.

Table 5.3. Areal distribution of groundwater suitability zones of the study area

Groundwater suitability zone	**Urban**		**Peri-urban**	
	Area (km^2)	**Area (%)**	**Area (km^2)**	**Area (%)**
Highly suitable	49.9	23.7	262.6	84.1
Suitable	89.3	42.1	35.8	11.5
Moderately suitable	55.7	26.3	8.9	2.9
Unsuitable	17.1	8	4.9	1.6

Presence of high count of coliforms and nitrate concentration (> 45 mg/L) were also visible in the poor groundwater quality/unsuitable zone. This is due to the high density of population, proximity of leach pits/septic tanks, lack of proper solid & liquid waste management system and presence of surface water bodies (Jesiya and Gopinath, 2019 a). Urbanization and thereby induced anthropogenic activities were led gradual decline of water quality in urban phreatic groundwater zones. The people in the coastal urban zone of the study area were forced to depends on the public water supply system for their drinking water requirements. In this context, best management practices were necessary in remediation of pollutant for the sustainable water sensitive urban development.

Table 5.4. Areal distribution of groundwater suitability zones within major landuse / landcover classes of the study area

Landuse/landcover classes	Urban			
	Highly Suitable (Km^2)	**Suitable (Km^2)**	**Moderately Suitable (Km^2)**	**Unsuitable (Km^2)**
Vegetation	30.3	41.51	17.44	2.04
Built-up area	13	29.8	40.73	13.93
Others	5.96	3.99	2.4	0.08
Peri-urban				
	Highly Suitable (Km^2)	**Suitable (Km^2)**	**Moderately Suitable (Km^2)**	**Unsuitable (Km^2)**
Vegetation	210	24.3	5.4	2.5
Built-up area	29..8	5	1.8	1.1
Others	0.12	0.01	-	-

5.3. Validation of groundwater quality suitability zonation

The outcome of overlay analysis will be contingent on the type of overlay analysis used, parameters selection, ratings, normalized weightages and cell size of raster data. Statistics of normalized and ideal weights derived through MCDM deal with ratings and weights facets associated with the influence of individual parameter on water quality assessment. Validation of the groundwater zonation map was carried out with avaerage TDS (mg/L) value of groundwater in the study area during post-monsoon period. The groundwater zonation was spatially joined with TDS values through spatial analyst tool by its spatial relationship. The analysis enables the updating of attributes of point feature (TDS (mg/L) of each location by the addition of attributes from the raster data (Groundwater suitability zonation). After spatial joining average TDS for each zone were calculated. Figure 5.4 were illustrated the relationship established between the four groundwater quality zone value and average TDS (mg/L) values in groundwater.

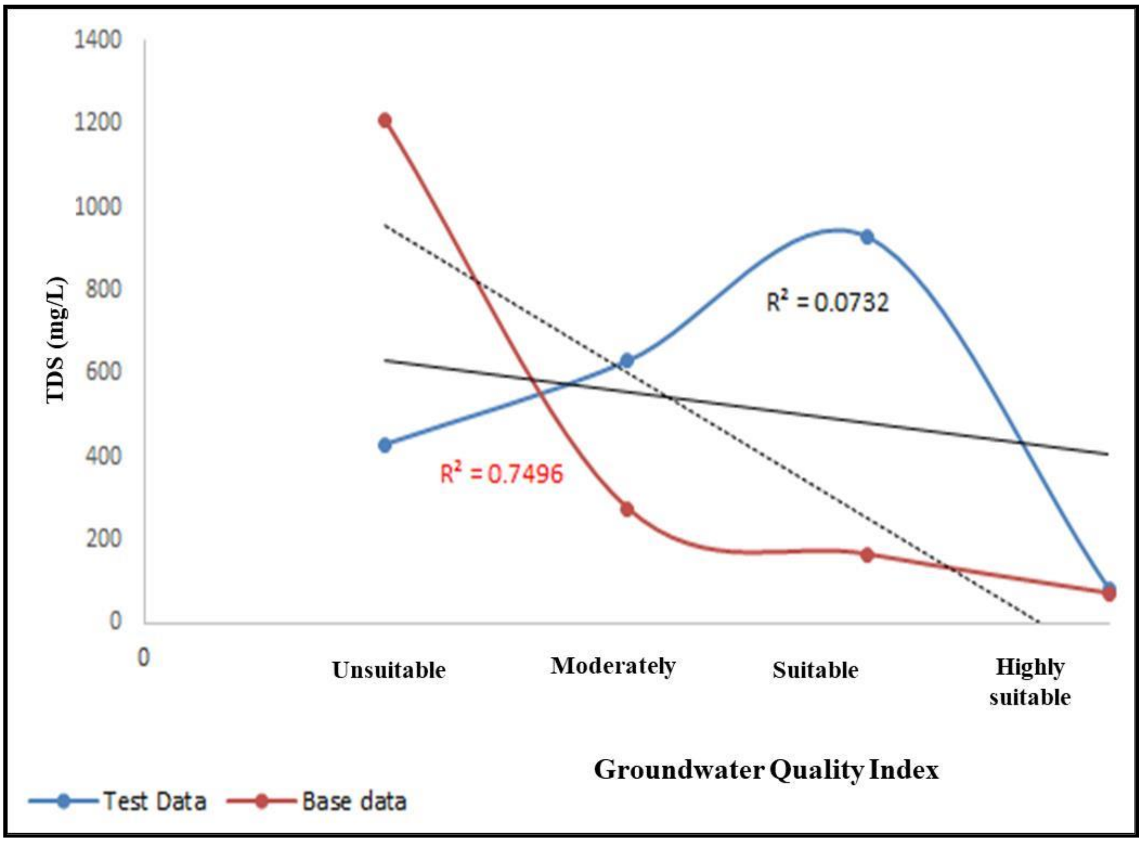


Figure 5.4. Illustration of relationship between groundwater quality zonation and TDS (mg/L)

The unsuitable quality zone having high average TDS value > 1200 ppm and with the increase in index value i.e. from moderate to highly suitable quality zone, average TDS value shows a decreasing trend. R^2 value with 0.749 indicates that there is a significant correlation `between groundwater quality index value and TDS concentration. MCDM analysis was indicated that TDS is the key parameters for deciding the quality status of groundwater.

Map removal method was carried out to check the sensitivity of the parameter towards the decision-making. For the above purpose, two type of water quality index dataset were used, viz. groundwater quality index with TDS (Base data) and groundwater quality index without TDS (Test data). Base data is the original GWQI data which was already discussed and Test data were derived in such a way that TDS data were exempted from the overlay analysis, and the groundwater quality zonation map was prepared. The resultant data (Test data) obtained from the map were correlated with average TDS values (Figure 5.4). R^2 value for correlation analysis of Test data vs TDS is 0.07, indicated less significant correlation. Map removal analysis thus proved that TDS were played vital role in groundwater suitability analysis and the analysis thus confirmed the validity of the quality zonation and significance of the parameters selected for the groundwater quality assessment.

CHAPTER 6

GEOSPATIAL ASSESSMENTS FOR GROUNDWATER MANAGEMENT

Introduction

The link between the changing urban and peri-urban hydrogeological characteristics and water quality parameters is an important dimension to monitor and plan an effective water sensitive urban development. Geospatial applications in groundwater studies in conjunction with field investigations will effectively exploit the expanding potential of remote sensing & GIS technologies and perfectly evolve standardize approaches in groundwater resource management (Jha et al. 2007). Remotely sensed images with its advantages of spatial, spectral and temporal availability of data provides quick and baseline information on the factors which controlling directly or indirectly the occurrence and movement of groundwater (Dinesh Kumar et al. 2007). Groundwater suitability analysis of urban and peri-urban phreatic ensemble (discussed in chapter 5) was confirmed that occurrence of contamination of groundwater resources was either from anthropogenic activities or from inherent aquifer material composition. This contamination in groundwater will reduces its supply, posing a threat to development and a challenge to such a groundwater dependent community (Navane and Sahoo, 2017). Groundwater vulnerability and groundwater potential zone assessments will act as an efficient groundwater management tool to deal such challenges (Saraf and Choudhury, 1998; Rahman, 2008; Iqbal et al. 2015). Geographic information system (GIS) offers sound tools to manage, process, analyze, map, and spatially organize the large volumes of data required for carrying out such analysis to facilitate groundwater management (Iqbal et al. 2015; Şener et al. 2018). Fuzzy-MCDM techniques have the capability to address the ambiguous uncertainties associated with groundwater vulnerability and potential assessments (Jesiya and Gopinath, 2019 b). Hence, a Fuzzy-AHP GIS based method were attempted in the present chapter for groundwater vulnerability (DRASTIC-L) and groundwater potential zone assessments in urban and peri-urban phreatic aquifers of the study area.

6.1. Groundwater vulnerability analysis

The DRASTIC-L method integrates simple qualitative indices and brings together key factors which are believed to influence the solute transport processes (Shirazi et al. 2012; Neshat and Pradhan, 2015). Parameters and its sub-criteria which have highest influence on contaminant transfer were assigned highest ratings, moderately influenced parameters were assigned moderate rating and parameters with least influence on contaminant transport were assigned with least ratings in this DRASTIC-L groundwater vulnerability assessment. By taking this aforesaid conditions in consideration the pairwise comparison matrices were prepared for eight DRASTIC-L parameters and its sub-criteria and are shown in Tables 6.1, 6.2 b, 6.3 b, 6.4 b, 6.5 b, 6.6 b, 6.7 b, 6.8 b and 6.9 along with its composite weightage (W).

6.1.1. Analysis of DRASTIC-L Parameters

6.1.1.1. Depth to Waterlevel

Depth to waterlevel (DWL) determines the depth of material through which the infiltrating water must travel before reaching the aquifer and also decided the amount of time during which contact with the surrounding media is maintained (Aller, 1985). Depth to waterlevel has a direct influence on the degree and extent, physical & chemical attenuation and degradation process of diffusing contaminant and sub-surface materials such as air, mineral and water (Rahman, 2008). Therefore DWL were given primary importance in vulnerability assessment as shown in Table 6.1.

Table 6.1. Comparison matrix and significant weighting values of modified DRASTIC-L parameters
(D- Depth to water level; R- Recharge; A-Aquifer media; S- Soil media; T- Topography; I- Impact of vadose zone; C- Hydraulic conductivity; L- Landuse/landcover; W- composite weightage)

	D	**R**	**A**	**S**	**T**	**I**	**C**	**L**	**W**
D	1	1, 3/2 ,2	3/2, 2, 5/2	2, 5/2 ,3	1	1	3/2, 2, 5/2	3/2, 2, 5/2	**0.224**
R	3/2, 2, 5/2	1	2, 5/2 3	3/2, 2, 5/2	3/2, 2, 5/2	1/2, 1/1.43, 1	2, 5/2 3	2, 5/2 3	**0.165**
A	2, 5/2, 3	1/2, 2/3, 1	1	1, 3/2, 2	2 ,5/2, 3	2/5, 1/2 ,1/1.67	1	1	**0.118**
S	(1/3, 2/5, 1/2)	2/5, 1/2 ,2/3	2/5, 1/2, 2/3	1	(1/2, 1,3/2)	1/3.33, 2/5, 1/2	2/5, 1/2, 2/3	2/5, 1/2,2/3	**0.087**
T	(2/7,1/3, 2/5)	1/3 2/5 1/2	1/3,2/5,1/2	(2/3, 1, 2)	1	1/3.45, 1/3.03, 2/5	1/3,2/5,1/2	1/3,2/5,1/2	**0.066**
I	3/2, 2, 5/2	1 1.43 2	3/2, 2, 5/2	2, 5/2, 3.33	3/2, 2 ,5/2	1	1/2, 2/3, 1	3/2, 2, 5/2	**0.224**
C	1/2 ,2/3, 1	1/2, 2/3, 1	1/2, 2/3, 1	1, 1.49, 2	1/2, 2/3 ,1	2/5, 1/2, 2/3	1	1/2, 2/3, 1	**0.119**
L	2, 5/2, 3	1/2, 2/3, 1	1	1, 3/2, 2	2 ,5/2, 3	2/5, 1/2 ,1/1.67	2, 5/2, 3	1	**0.118**

Ranges/intervals of DWL had been decided based on the intervals at which the significance of pollution potential changes and for the study area it varied from < 2 mbgl to > 12 mbgl. DWL Ranges were classified into shallow (< 2 mbgl), moderately shallow (2-4 mbgl), moderately deep (4-6 mbgl) and deep (6 - >12 mbgl) types which covered an area of 10 km^2, 141 Km^2, 232 km^2 and 142 km^2 respectively (Table 6.2 a).

Table 6.2 a. Ranges of depth to waterlevel and its corresponding areal distribution (in mbgl) of the study area

Depth to water level (mbgl)	Area(km^2)
< 2	10.0
2-4	141.1
4-6	232.1
6-8	110.2
8-10	29.2
10-12	2.0
> 12	0.5

Spatial distribution of DWL for urban and peri-urban phreatic aquifers were shown in Figure 6.1. Majority of the urban zone were occupied with 4-6 mbgl followed by 2-4 mbgl ranges of DWL. In the peri-urban zone, major DWL classes were occurred in 4-6 mbgl followed by 6-8 mbgl and 2 - 4 mbgl. Compared to peri-urban aquifers, urban aquifers were laid more in shallow water level conditions except two locations on eastern side. With the increase in depth to water level the chances of contamination gets decreases because it infers longer travel distances before contacting with groundwater. Shallow water level (< 2 mbgl) had highest chance of contamination and therefore assigned highest rating towards groundwater vulnerability. Moderately shallow (2 - 4 mbgl) and moderately deep wells (4-6 mbgl) were assigned consecutive moderate ratings (Table 6.2 b) because there is a moderate chance to transfer the contaminant into or through the aquifer due to the spatial continuity between overland and the aquifer Where as in deep well ranges (6 - > 12 mbgl) distance to travel before contacting with groundwater is more, therefore successive least weightages were assigned..

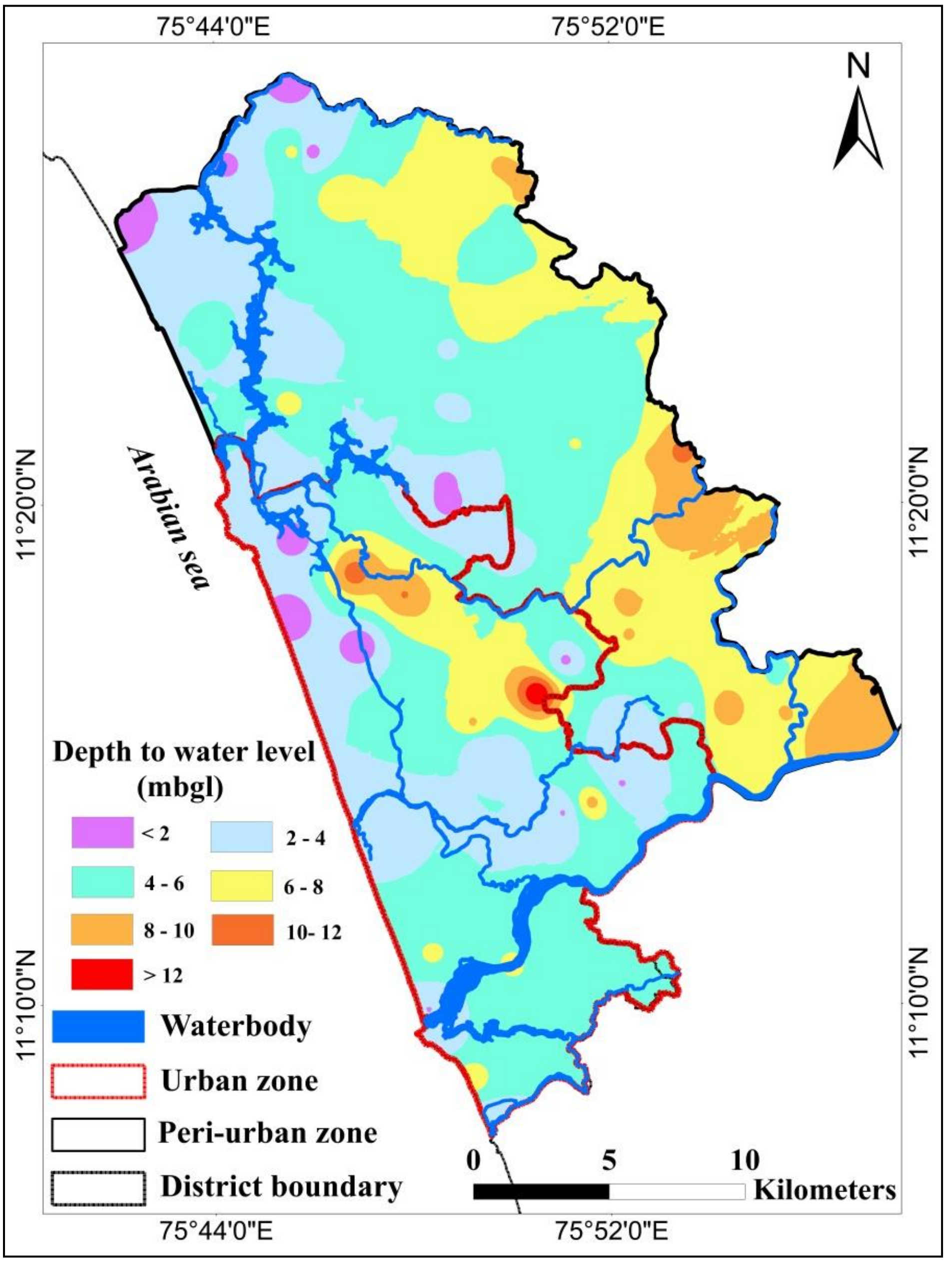


Figure 6.1.Spatial distribution of depth to the waterlevel

Table 6.2 b. Comparison matrix and significance weighting values of depth to water level (mbgl)

	> 2 mbgl	**2-4 mbgl**	**4-6 mbgl**	**6-8mbgl**	**8-10mbgl**	**10-12mbgl**	**>12mbgl**	**W**
<2 mbgl	1	1/2, 1, 3/2	1,3/2,2	3/2, 2, 5/2	2,5/2,3	5/2,3, 7/2	7/2,4/9/2	**0.243**
2-4 mbgl	2/3,1,2	1	1/2,1, 3/2	3/2,2,5/2	3/2,2,5/2	2,5/2,3	5/2,3,7/2	**0.201**
4-6 mbgl	1/2,2/3,1	2/3,1,2	1	1,3/2,2	1/2,1,3/2	3/2,2,5/2	5/2,3,7/2	**0.168**
6-8mbgl	2/5,1/2,2/3	1/2,2/3,1	1/2,2/3,1	1	2/3, 1,2	1,3/2,2	3/2,2,5/2	**0.122**
8-10mbgl	1/3,2/5,1/2	2/5,1/2,2/3	2/3,1,2	2/3,1,1/2	1	1/2,1,3/2	1/2, 1, 2	**0.110**
10-12mbgl	2/7,1/3,2/5	1/3,2/5,1/2	2/5,1/2,2/3	1/2,2/3,1	2/3,1,2	1	1,3/2,2	**0.089**
12mbgl	2/9,4,2/7	2/7,1/3,2/5	2/7,1/3,2/5	2/5,1/2,2/3	1/2,2/3,1	1/2,2/3,1	1	**0.063**

In urban zones of the study area, due to the inadequate and intermittent piped water supply people largely rely on groundwater sources like dug wells, shallow tube wells, stone spouts, etc, to meet daily water need and the situation became exacerbated by rapid population growth and urbanization. Shallow aquifers in urban zones are thereby prone to contamination by seepage from septic systems, effluents of untreated sewage systems and solid wastes (Jesiya and Gopinath,2019 b).

6.1.1.2. Net aquifer recharge

Amount of water per unit area of land which infiltrates to the ground surface and reaches the water table termed as 'net recharge' and forms the main vehicle to transport pollutants vertically into the groundwater zone and horizontally within aquifers (Aller, 1985). As per Rahman et al.(2008), it is the reporting agents for pollutants to the groundwater and recharge water is, therefore, a significant vehicle for percolating and transporting contaminants within the vadose zone to the saturated zone.

Rainfall recharge in the study area occurs mostly during the southwest monsoon period from June to September. Factors controlling the rate of aquifer recharge are precipitation, permeability of the rocks, depth to water table, soil type & moisture conditions, topography, vegetation, temperature, etc. (Belden, 1996). The net aquifer recharge index map for the study was derived through weighted sum overlay analysis of slope (%), rainfall and soil permeability data of the study area. Considering there influence on groundwater recharge, rating and weights for slope (%), rainfall and soil permeability were assigned using 1-5 saaty's scale of preference (Saaty, 2005). The equation applied for calculation of net recharge index value is as follows,

Net Recharge Index = Slope % + Rainfall + Soil permeability

The major advantage of the above said equation developed by Piscopo, 2001 is its ability to calculate the recharge index values for every unit of area (Al Adamat et al. 2003). The computation of recharge value in an aquifer is a complicated process which makes it harder to ascertain (Khan et al. 2003).

For the net recharge index calculation, slope (%) were derived from SRTM DEM(30m) and classified in to four slope classes such as < 5% , 5-10%, 10-15% and > 15%. According to Ground Water Resource Estimation Methodology - 1997, areas with gentle slope (< 5%) facilitate high recharge and assigned a rating of 5. The region characterized by steep slopes (> 15%) and where the runoff is expected to be very high assigned least rating of 2. Slope classes such as 5- 10% and 10-15% which laid in between these two classes were assigned with moderate ratings (Table 6.3 a)

Soil types of the entire study area composed of four categories, given in Table 6.4 and rating for soil types were done according to its degree of permeability. The factor ratings were ranging from 1-5 in such a way that highest rating were assigned for those soil types which having high soil permeability, and vice versa. Sandy loam to sandy clay loam soil types were excessive-drained and having moderately rapid to rapid permeability. Therefore assigned highest rating on aquifer recharge. Gravelly clay loam to gravelly clay soil type were characterized with moderate to moderately slow permeability, hence assigned moderate rating (Table 6.3 a) .Where as imperfectly-drained sandy loam to clay loam soil type with slow permeability were assigned least rating on net recharge index estimation.

Rainfall is a significant factor which transport leachate and other surface pollutants by infiltration (Voudouris et al. 2010) and the study area experiences similar rainfall pattern ranges from 3200-4000 mm with an average value of 3466mm. In the study area, there is no remarkable variation among the rainfall pattern. Therefore entire study were brings under a single rainfall class (3200-4000) and assigned a rating of 5. Finally Corresponding ratings were integrated to slope, rainfall and soil texture data using reclassification analysis and undergone weighted sum overlay analysis in ArcGIS environment.

Table 6.3 a. The rating for the calculation of net recharge index in urban and peri-urban aquifers of the study area

Slope		Soil permeability		Rainfall (mm)	
Slope (%)	**Rating**	**Type**	**Rating**	**Type**	**Rating**
< 5	5	Sandy loam to sandy clay loam	5	3200-4000	5
5 -10	4	Loam to clay	4		
10 - 15	3	Sandy loam to clay loam	1		
> 15	2	Gravelly clay loam to gravelly clay	2		

The resultant raster data derived after weighted sum overlay analysis is termed as net recharge index and the range of net recharge index were classified as < 15, 15-20, > 20. The areal distribution of the urban and peri-urban clusters of the study area based on net recharge index were given in Table 6.3 b.

Table 6.3 b. Areal distribution of net aquifer recharge index of the study area

Net Recharge Index	Area (km^2)
< 15	88.2
15-20	360.9
> 20	72.8

Spatial distribution of net recharge index for the study area were given in Figure 6.2. Western coastal tract of the study area characterized by gentle slope, coarse textural soil type, rapid soil permeability, and consequently high infiltration rate were comprised with a high recharge index of > 20. Coastal alluvium and flat terrain of the study area were enabled to infiltrates large quantity of rain and surface water into aquifer system compared to other lateritic terrain and therefore facilitates contaminant attenuation. Shallow depth of water level on these areas confirmed the vertical and horizontal movement of contaminants. Therefore zone with net recharge index value > 20 assigned as highest ratings towards groundwater vulnerability to contamination. The recharge water can carry contaminants vertically to the water table and horizontally within the aquifer; hence a large net recharge value corresponds to a high potential for groundwater pollution (Aller et al. 1987). Moreover, the area with net recharge index of 15-20 characterized with moderate recharge characteristics, therefore moderate ratings (Table 6.3 c). Urban cluster of the study area were characterized with a net recharge index of > 20 and 15-20 classes. Whereas majority of peri-urban cluster were characterized with < 15 and 15-20 net recharge index values except in western coastal area. The areas with deep slope and slow soil permeability were caused a low net recharge index of < 15. Least ratings were assigned to the net recharge index value of < 15.

Table 6.3 c. Comparison matrix and significance weighting values of net aquifer recharge index

	<15	**15-20**	**>20**	**W**
<15	1	1/2,1,/2	1,3/2,2	**0.292**
15-20	2/3,1,2	1	1/2,1, 3/2	**0.332**
>20	1/2,2/3,1	2/3,1,2	1	**0.371**

Amount of recharge due to rainfall in the study area was calculated using the GEC, 1997-Water table fluctuation method. Average water table fluctuations are 1.2 m and 1.4m for alluvial and lateritic zones of the study area respectively. And the recharge for the coastal alluvial zone is 11.65MCM, and that of the lateritic zone is 43.01MCM (Jesiya and Gopinath, 2019 b).

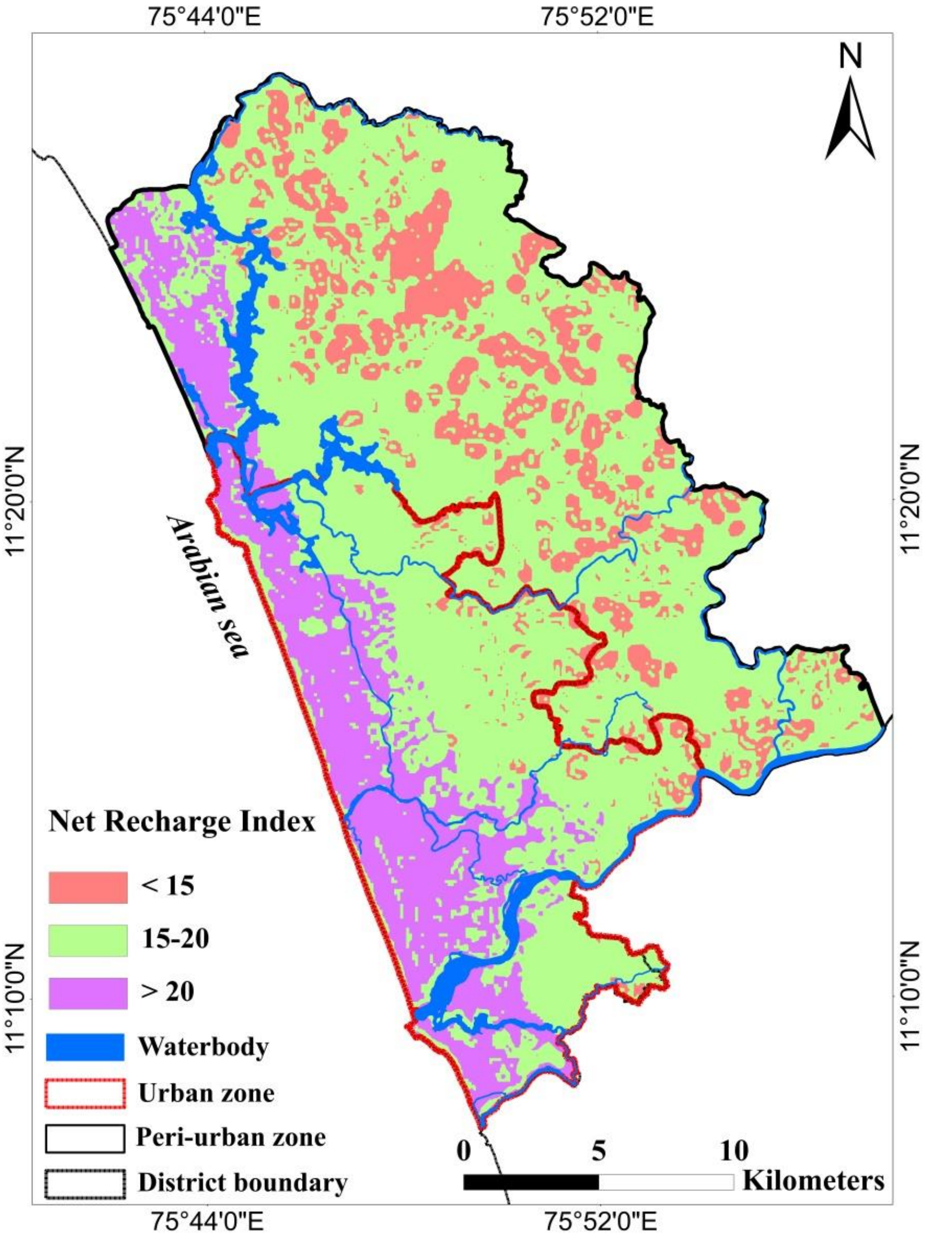


Figure 6.2. Spatial distribution of net recharge index in the study area

6.1.1.3. Aquifer media

The aquifer media component in DRASTIC-L refers to the consolidated or unconsolidated medium which serves as an aquifer and it has significant control over route and path length over a contaminant flow. The aquifer systems occupied in the study area are; coastal sandy formations, coastal sandy laterite aquifer, laterite aquifer, weathered rock formations - weathered rock aquifer and fractured rock aquifer. Coastal sandy formations, coastal sandy laterite aquifer area the dominant aquifer formations occupied in the study area. Quaternary deposits such as kadppuram formation, guruvayur formation, periyar formation and pebble bed constituted coastal sandy formations occupied an area of 115 km^2 (22 %) of the total study area (Table 6.4 a). Coastal sandy aquifers were consist of medium to fine sand with an admixture of shells. Periyar Formation is a fluvial deposit comprising of an admixture of sand, silt, and clay. Guruvayur formation is a strand line deposit of palaeo-marine origin and mostly comprises medium- to fine sand. Kadappuram Formation represents contemporary marine deposits, constituting the present and barrier beach. Sand formation occurred with 6-12m thickness in coastal sandy aquifers (Nazimuddin, 1993).

Table 6.4 a. Areal distribution of aquifer media in the study area

Aquifer media	Area (km^2)
Guruvayur formation	74.29
Kadappuram formation (Marine)	12.06
Periyar formation (Fluvial)	8.86
Pebble bed	14.7
Hornblende-biotite Gneiss	107.06
Charnockite	305.2
Laterite	2.41

Pebble beds associated with grit and clay occurred on the coast and along banks of the Beypore river, and it is lateritised. It comprises well-rounded pebbles of quartz, granite, quartzite, and granulite. Sporadic laterite (0.4%) recorded from the charnockite country to the southwest. Lateritic aquifer zone composed of charnockite and horneblende-biotite gneiss composition occupied an area of 408 km^2 (78 %) of the urban and peri-urban cluster of the study area. Spatial distribution of geology of the urban and peri-urban phreatic aquifers were shown in Figure (1.3). The unconfined aquifers which composed of sandy alluvium, coastal sandy laterite formations are highly influenced the contaminants flow through discharge and recharge processes. Therefore coastal sandy formations were assigned with a high rating towards vulnerability to contamination. Lateritic zone composed of charnockite and horneblende-biotite gneiss composition were restricting the flow of contaminants from point and non-point sources and therefore assigned with moderate to least vulnerability index to contamination (Table 6.4 b) .

Table 6.4 b . Comparison matrix and significance weighting values of aquifer media

	Horneblende Biotite Gniess	**Pebble bed**	**Charnockite**	**Coastal sandy formation**	**Laterite**	**W**
Horneblende BiotiteGniess	1	2/7,1/3,2/5	1	2/7,1/3,2/5	1,3/2,2	**0.122**
Pebble bed	5/2,3,7/2	1	5/2,3,7/2	1	3/2,2,5/2	**0.301**
Charnockite	1	2/7,1/3,2/5	1	2/7,1/3.2/5	1,3/2,2	**0.118**
Coastal sandy formation	5/2,3,7/2	1	5/2,3,7/2	1	3/2,2,5/2	**0.347**
Laterite	1/2,2/3,1	2/5,1/2,2/3	1/2,2/3,1	2/5,1/2,2/3	1	**0.103**

6.1.1.4. Soil types

Soil media refers the upper weathered zone of the earth which has a significant impact on the amount of recharge which can infiltrate into ground and hence on the ability of a contaminant to move vertically into the vadose zone (Aller, 1985). Pollution potential of groundwater largely affected by grain size, type of clay, shrink/swell potential of the clay that controls the mobility of pollutants from the surface to the water table (Aller, 1985; Brindha and Elango, 2012 & 2015). Hydrogeologically, the study area consists of four distinct layers viz. topsoil, highly weathered rocks, moderately weathered rocks, and massive rock.

Table 6.5 a. Areal distribution of soil textures in the study area

Soil Texture	Area (km^2)
Sandy loam to sandy clay loam (Type I)	30.79
Loam to clay (Type II)	32.87
Sandy loam to clay loam (Type III)	26.50
Gravelly clay loam to gravelly clay (Type IV)	364.37

Compared to clay loam , sandy loam type was more potential to contaminants due to higher percentage of sand. Sandy clay loam to clay is the predominant texture. Sandy loam soils are also occurred. Light grey to very dark brown is the commoncolor of the soil in the area (Table 6.9). There are mainly four types of soil textures visible in the study area which are sandy loam to sandy clay loam (Type I), loam to clay (Type II), sandy loam to clay loam (Type III) and gravelly clay loam to gravelly clay (Type IV) (Table 6.5 a). Majority of the study area occupied with Type IV soil with an areal extent of 364.4 km^2 . Spatial distribution of soil types occurring in the urban and peri-urban zones of the study area (Figure 6.3) shown that western side of the urban and peri-urban zone occupied with Type I soil category. Type I consists of sandy loam to sandy clay loam texture having a thickness ranging from 150-175 cm. Sand content of Type I ranges from 80% and clay up to 15%. Even though these soils have a high water table, the water holding capacity is poor due to the predominance of sand. It is excessive- drained with moderately rapid to rapid permeability.

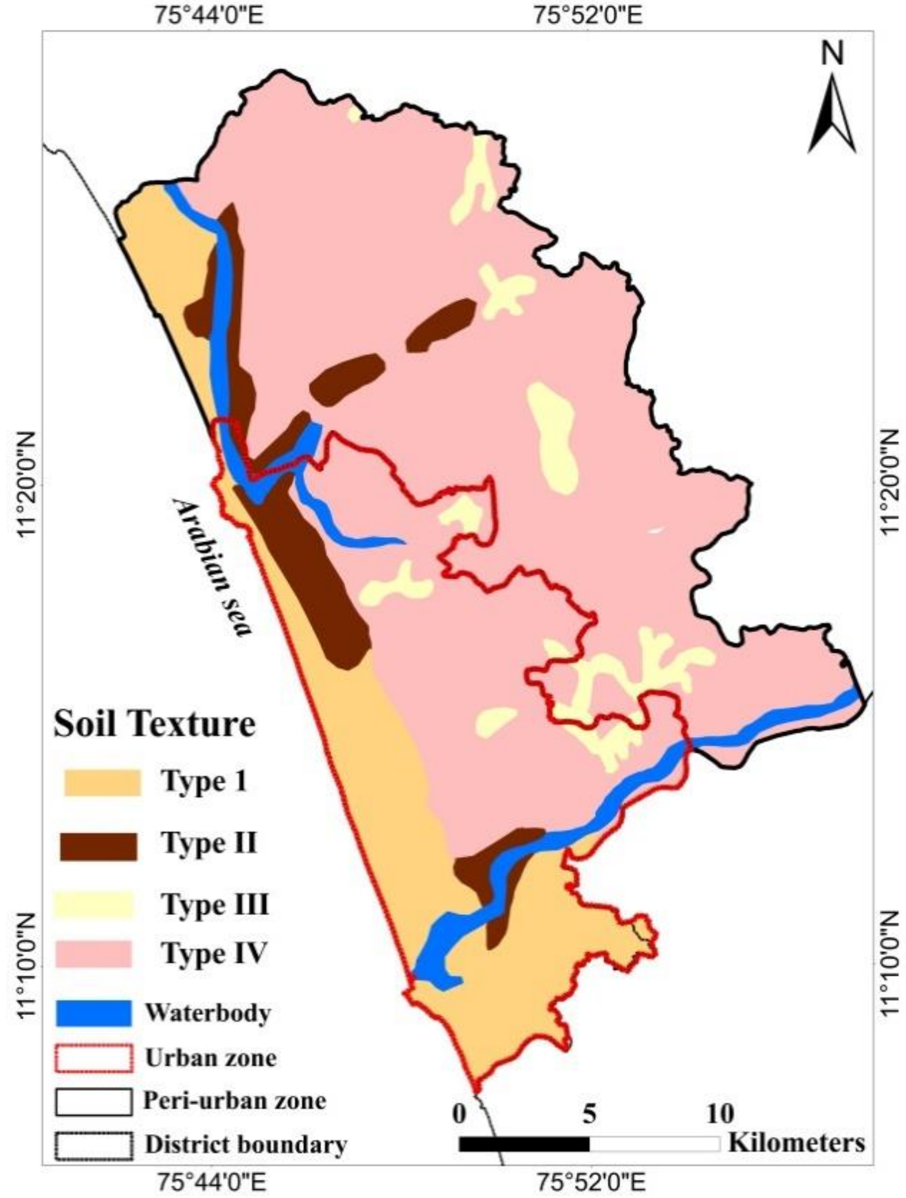


Figure 6.3. Spatial distribution of soil texture in the study area

This medium to coarse-textured soil occurred along the coastal line of the study area assigned with the highest ranking on vulnerability index assessment according to its higher potential for contaminant transfer (Table 6.5 b). Alluvium soil enriched with sand and silt occurred in urban cluster of Kozhikode and is more feasible to exchange of salt particles and contaminants (Salaj et al. 2018 b). The riverine alluvium and associated lowland areas are dominated with loam to clay soil (Type II) and are assigned with moderate vulnerability rating; where the presence of clay dominated sandy layer and its restrictive permeability limits the contaminants flow.Gravelly clay loam to gravelly clay textured soil (Type IV) is well-drained type with moderate to moderately slow permeability .

The gravel content of this type of soil is 15-40% and therefore assigned a moderate rating on DRASTIC-L analysis for urban and peri-urban phreatic aquifers. Pockets of sandy loam to clay loam textured soil type was occured in between gravelly clay loam to gravelly clay texture and formed in the riverine alluvium of very gently sloping terrain with a thickness of 140cm-160cm. It is imperfectly- drained with slow permeability, therefore assigned least rating on vulnerability assessment.

Table 6.5 b. Comparison matrix and significance weighting values of soil texture

	Type I	**Type II**	**Type III**	**Type IV**	**W**
Type I	1	5/2, 3,7/2	1,3/2,2	1	**0.354**
Type II	2/7,1/3,2/5	1	3/2,2,5/2	1,3/2, 2	**0.243**
Type III	2/5,1/2, 2/3	1,3/2,2	1	1/2,2/3,1	**0.201**
Type IV	1/2, 2/3, 1	2/5,1/2,2/3	1,3/2,2	1	**0.206**

6.1.1.5. Topography

Topography refers to the slope and slope variability of the land surface which determines the pollutant will run off or remain on the surface in one area long enough to infiltrate (Aller, 1985).

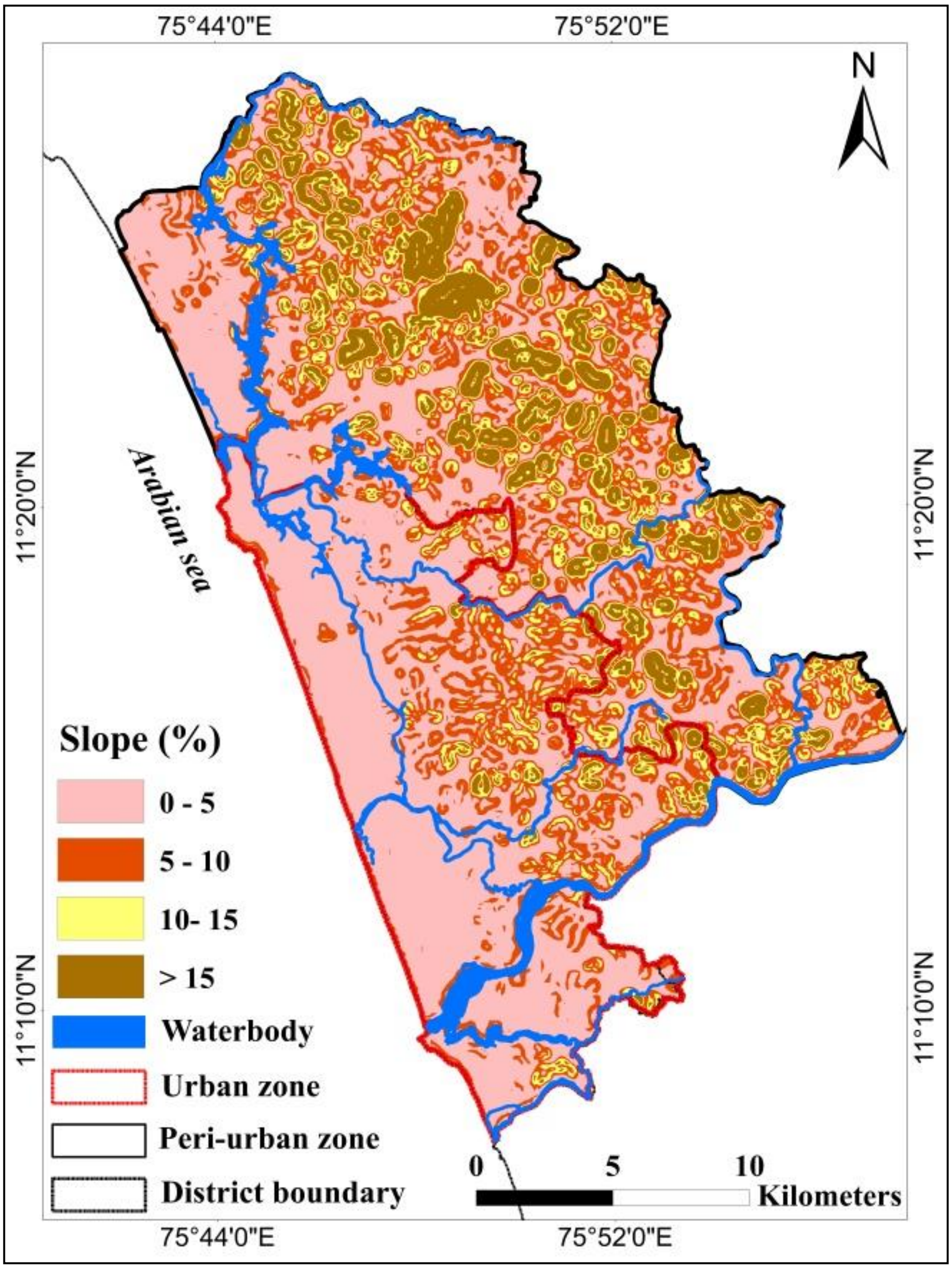


Figure 6.4. Spatial distribution of topography in the study area

The slope (in %) of the entire study area ranges from 0-55%. Majority of urban and peri-urban coastal zone came under very gentle slope terrain (< 5 %) (Figure 6.4) and which covers an area of 277.6 km^2 (53%) (Table 6.6 a). About 139 km^2 of the total study area were covered with a slope of 5-10 %. Spatial distribution of topography (Slope %) were shown in Figure 6.4. The < 5% slope terrain of with sandy textures were facilitated infiltration and consequently rapid transfer of contaminant into aquifers (Kaliraj et al. 2015).

Table 6.6 a. Areal distribution of slope (%) of the study area

Slope (%)	**Area(km^2)**
< 5	277.6
5-10	139.4
10-15	53.2
> 15	54.6

In this region (< 5% slope) neither the pollutant nor much precipitation was way out as runoff and hence assigned the highest ratings towards vulnerability (Table 6.6 b). The area occupied with 5-15% slope within the gently sloping terrain comes under moderate sloping category and contributes moderate vulnerability to contamination. Conversely, 10% of the area with > 15 % steep slope terrain consists of hillocks which facilitate a high runoff capacity and lesser probability of infiltration, therefore, assigned the least rating. Based on the slope value, the overall weightage of slope for the vulnerability index is ranging from highest to moderate range .

Table 6.6 b. Comparison matrix and significance weighting values of Topography

Topography	**< 5**	**5 - 10**	**10 - 15**	**> 15**	**W**
<5	1	1,3/2,2	3/2,2,5/2	5/2,3,7/2	**0.396**
5-10	1/2,2/3,1	1	1,3/2,2	3/2,2,5/2	**0.274**
10-15	2/5,1/2,2/	1/2,2/3,1	1	1,3/2,2	**0.195**
> 15	2/7,1/3,2/5	2/5,1/2,2/	1/2,2/,1	1	**0.134**

6.1.1.6. Impact of vadose zone

Vadose zone media was analysed the attenuation characteristics of the material below the typical soil horizon and above the water table (Aller, 1985). Influence of vadose zone on contaminant transfer is similar to that of soil cover and vadose media characteristics. Spatial extent of vadose zone in the urban and peri-urban aquifers of the study area was derived using lithology and hydrogeological maps of CGWB and Geological Survey of India. It mainly comprised of alluvium and laterite formations and alluvium formations including riverine & coastal formations which covered an area of 97 km^2 (Table 6.7 a).

Table 6.7 a. Areal distribution of vadose zone in the study area

Lithology	**Area (km^2)**
Alluvium	97.09
Laterite	427.89

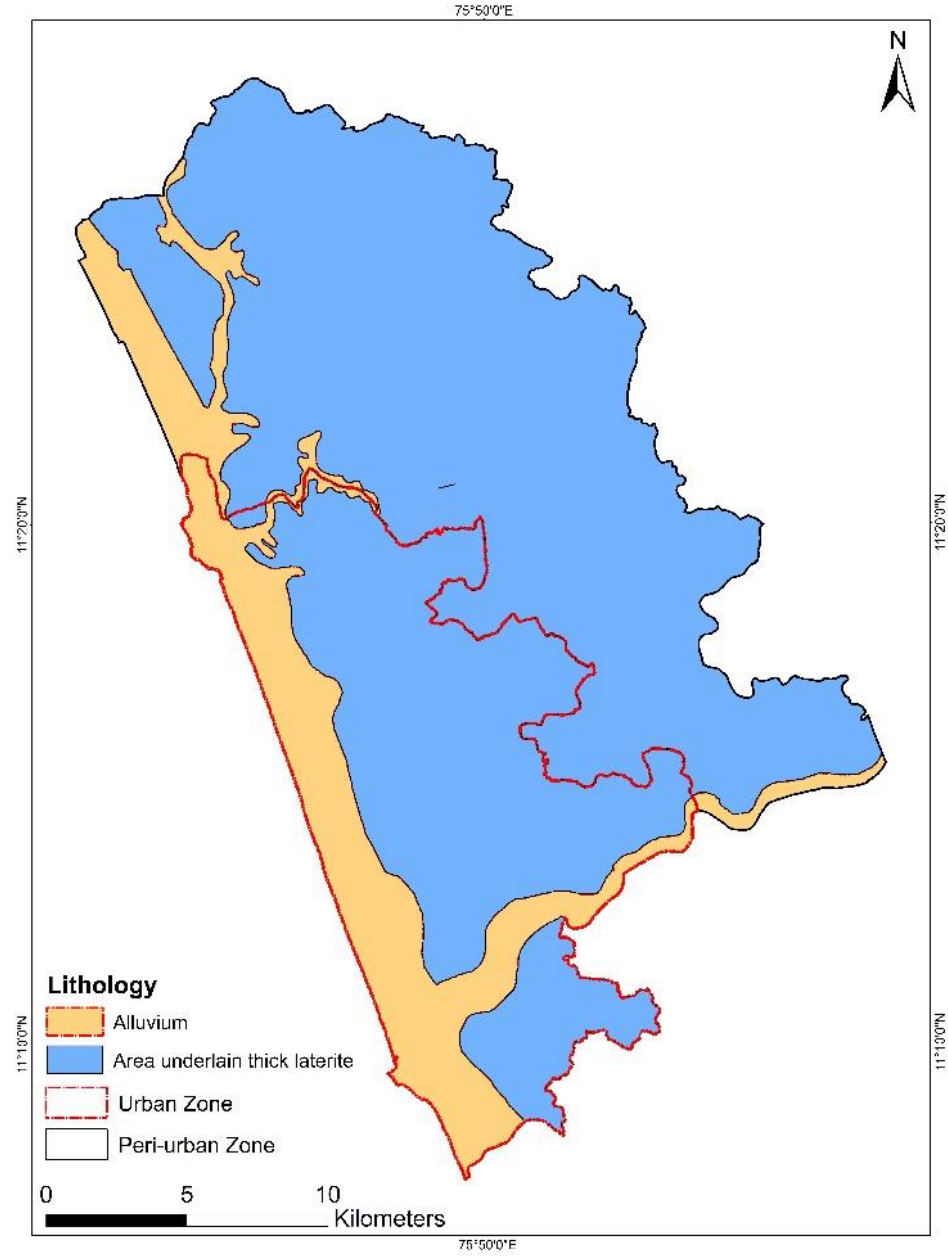


Figure 6.5. Spatial distribution of vadose zone in the study area

Coastal alluvium and riverine alluvium formations were observed in the western part and along river courses of the study area respectively. Coastal alluvium contain unconsolidated materials such as sand, silt, and clay having thickness varied between 2 and 8 m, and where the groundwater occurred under phreatic condition. The remaining part of the terrain (427.9 km^2) was covered by laterite with a thickness ranging from 3- 33.5m and was formed potential phreatic aquifers along with topographic lows and valleys. Vadose zone distribution of the urban and peri-urban aquifers of the total study area were showed in Figure 6.5. Unconsolidated mixtures of sand and gravel which contain an appreciable amount of fine material were affected pollution potential based on its clay concentration and grain size (Aller, 1985). Thus, the vadose zones such as coastal sand and alluvial deposits were characterized by high permeability thus facilitating the infiltration of contaminants as well as salt matters into the ground. The soil permeability of this zone is also high. Therefore, impact of vadose zone in coastal alluvium was attained highest rating (Table 6.7 b). A moderate rating were assigned to laterite formation in DRASTIC-L vulnerability assessment.

Table. 6.7 b Comparison matrix and significance weighting values of impact of vadose zone

	Coastal Sandy	**Coastal Alluvium**	**Laterite**	**W**
Coastal Sandy	1	1/2,1,3/2	3/2,2,5/2	**0.397**
Coastal Alluvium	2/3,1,2	1	1,3/2,2	**0.372**
Laterite	2/5,1/2,2/3	1/2,2/3,1	1	**0.225**

6.1.1.7. Hydraulic conductivity

The ability of the aquifer material to transmit water is termed as hydraulic conductivity. It determines the rate at which groundwater can flow and thereby the distance of transport of pollutants through the aquifer can be assessed. The conductivity at a given hydraulic gradient depends on the intrinsic permeability of the composed material and on the degree of saturation (Salaj et al. 2018 b).

Table 6.8 a. Areal distribution of hydraulic conductivity (m/d) in the study area

Lithology	Area (km^2)	Hydraulic conductivity
Alluvium	97.09	0.4 m/day - 5 m/day
Lateritic	427.89	2.4 m/day – 14.9 m/day

Hydraulic conductivity of coastal alluvial aquifers of the study area was 0.4-5 m/day and that of lateritic terrain was ranged from 2.4 m/day to 14.9 m /day (Table 6.8 a) . Higher conductivity increases contaminants flow within as well as around the aquifers thereby raising the groundwater vulnerability to contamination while the lower conductivity provides higher resistance against contamination transportation (Rahman, 2008). Coastal alluvial aquifers with higher hydraulic conductivity (< 5 m/day) were resulted in the rise in aquifer vulnerability, therefore, these areas were assigned with higher vulnerability rating (Table 6.8 b).

Basak and Nazimuddin , 1983; Salaj et al. 2018 b were confirmed that that lateral flow of groundwater through the coastal urban aquifers of the study area can transport contaminants within as well as around the aquifer systems. Therefore urban aquifers with these high hydraulic conductivity and lateral flow were enhanced the pollutant attenuation in the study area. A moderate rating were assigned to lateritic formation which composed of charnockite and horneblende-biotite gneiss composition and a hydraulic conductivity ranges from 2.4 m/day to 14.9 m/day. Figure 6.6 were showed the spatial distribution of hydraulic conductivity (m/day) of urban and peri-urban aquifers of the study area.

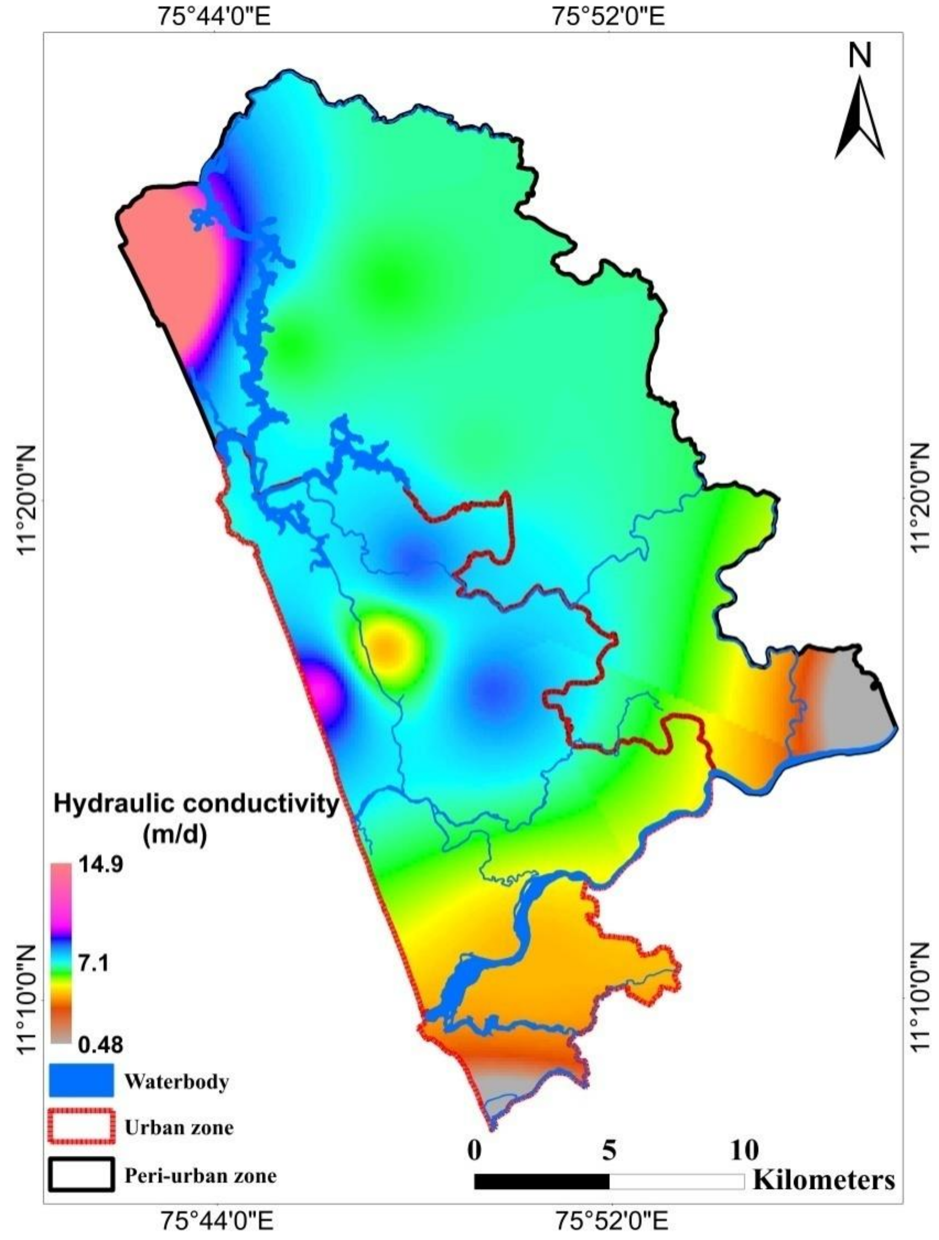


Figure 6.6. Spatial distribution of hydraulic conductivity in the study area

Table 6.8 b. Comparison matrix and significance weighting values of hydraulic conductivity

	Alluvial	Charnockite	Hornblende- biotite gniess	W
Alluvial	1	3/2,2,5/2	3/2,2,5/2	**0.495**
Charnockite	2/5,1/2,2/3	1	1	**0.250**
Hornblende-biotite gniess	2/5,1/2,2/3	1	1	**0.250**

6.1.1.8. Landuse/landcover classes

Landuse pattern of the study area were included with the DRASTIC-L parameters because the type of landuse pattern of the study area, have a remarkable influence on the urban hydrologic regime (Kaliraj et al. 2015, Jesiya and Gopinath, 2019). Areal distribution of major landuse classes such as built-up land, vegetation, water body, and others of the study area were given in Table 1.1 and spatial distribution of landuse classes for years 2005, 2010 and 2015 were given in Figure 1.4. In urban cluster of the study area, 48% increase in growth rate were observed for urban surfaces such as built-up area and settlements from the year 2010 to 2015 and simultaneous decline in vegetation zone which covers crop-land, mixed trees, agricultural plantations etc. Vegetation zone of urban cluster was showed 28% decline in areal distribution from 2010 to 2015. Similarly significant growth in built-up area and decline in vegetation zone were observed for peri-urban clusters also. Vegetation land in both urban and peri-urban clusters of the study area were encroached for built-up area and therefore will negatively affect groundwater table and recharge characteristics.

Table 6.9. Comparison matrix and significance weighting values of landuse/landcover classes

	Vegetation	**Built-up area**	**Others**	**W**
Vegetation	1	(2/7,1/3, 2/5)	(2/5, 1/2, 2/3)	**0.160**
Built-up area	(5/2, 3, 7/2)	1	(2, 5/2, 3)	**0.569**
Others	(3/2, 2, 5/2)	(1/3, 2/5, 1/2)	1	**0.272**

Impervious area increases with the increases in a built-up area and subsequently the rainfall recharge to ground reduces (Tam and Nga, 2018) and this expansion in impervious area were more visible in urban cluster. At the same time, frequency of contamination due to leakage from leach pits, waste water drainage system, etc were also increased. Both the situation adversely affects hydrogeology qualitatively and quantitatively. Residential/ commercial built-up classes in the study area were more confronted with aforesaid incidence than other landuse classes, hence highest weightages were assigned in groundwater vulnerability assessment (Table 6.9).

6.1.2. Groundwater vulnerability assessment

Groundwater vulnerability index data derived using Fuzzy-AHP rated DRASTIC-L assessment was classified the study area into four classes such as low, moderate, high and very high vulnerable zones based on their potential to groundwater vulnerability, as shown in Table 6.10. The site-specific groundwater vulnerability map was divided both urban and peri-urban zone into several hydrogeological sub-regions with different levels of vulnerability from the contamination point of view.

Of the urban cluster, 50.2% of the area were occupied with a very high vulnerable category which is characterised with near shore high-density urban settlements and vicinity of water bodies (Table 6.10). The aquifers underlying these vulnerable zones composed of coastal sand and alluvial sandy formations that are more sensitive to infiltrate contaminants. The expansion of impervious surface (settlements and built-ups) occurred in this highly vulnerable zone reducing net recharge and shallow groundwater table in the zone causing lateral diffusion of contaminants from intrinsic sources. Coastal line of the highly vulnerable zone is prone to erosion which leads removal of sediments from the shore eventually extending seawater flow towards inland area (Kaliraj et al. 2015; Salaj et al. 2018 a). These very high vulnerable zones are heavily confronted with contaminants due to sewage discharge, landfill leachate (solid waste dumping) and seawater intrusion. Highly permissible sandy alluvium and weathered laterite layers in the zone were triggered contaminants flow from surface water to groundwater sources.

Table 6.10. Areal distribution of aquifer vulnerability classes

Aquifer vulnerability classes	**Urban**	**Peri-Urban**
Low	**8.5 %** (17.9 Km^2)	**38.5 %** (120.3 Km^2)
Moderate	**20.7%** (44.1 Km^2)	**39.5 %** (123.4 Km^2)
High	**20.6%** (43.9 Km^2)	**12.7 %** (39.6 Km^2)
Very high	**50.2%** (106.9 Km^2)	**9.3 %** (28.9 Km^2)

About 21.9% of peri-urban zone was classified as high to very high vulnerable zone. Gentle slope, shallow aquifers underlying sandy and lateritic alluvial deposits, high recharge, and coarse sand aquifer media are together impart high to very high vulnerability to contamination. The area surrounded by high to very high vulnerable zones were categorized as moderate vulnerable zone and which comprised 20.7% and 39.5% of the urban and peri-urban zones of the study area respectively. Underlying lateritic unconfined formations, weathered charnockite rocks and other vulnerability influencing parameters occurred in these zones are moderately infiltrate runoff and contaminants into the aquifer. However, groundwater sources under moderately vulnerable zones are frequently influenced by attenuation of contaminants from the high to very high vulnerable zones. Urban growth showing a trend of expansion towards this moderately vulnerable zone and consequently increasing the risk of groundwater contamination by anthropogenic contaminants.

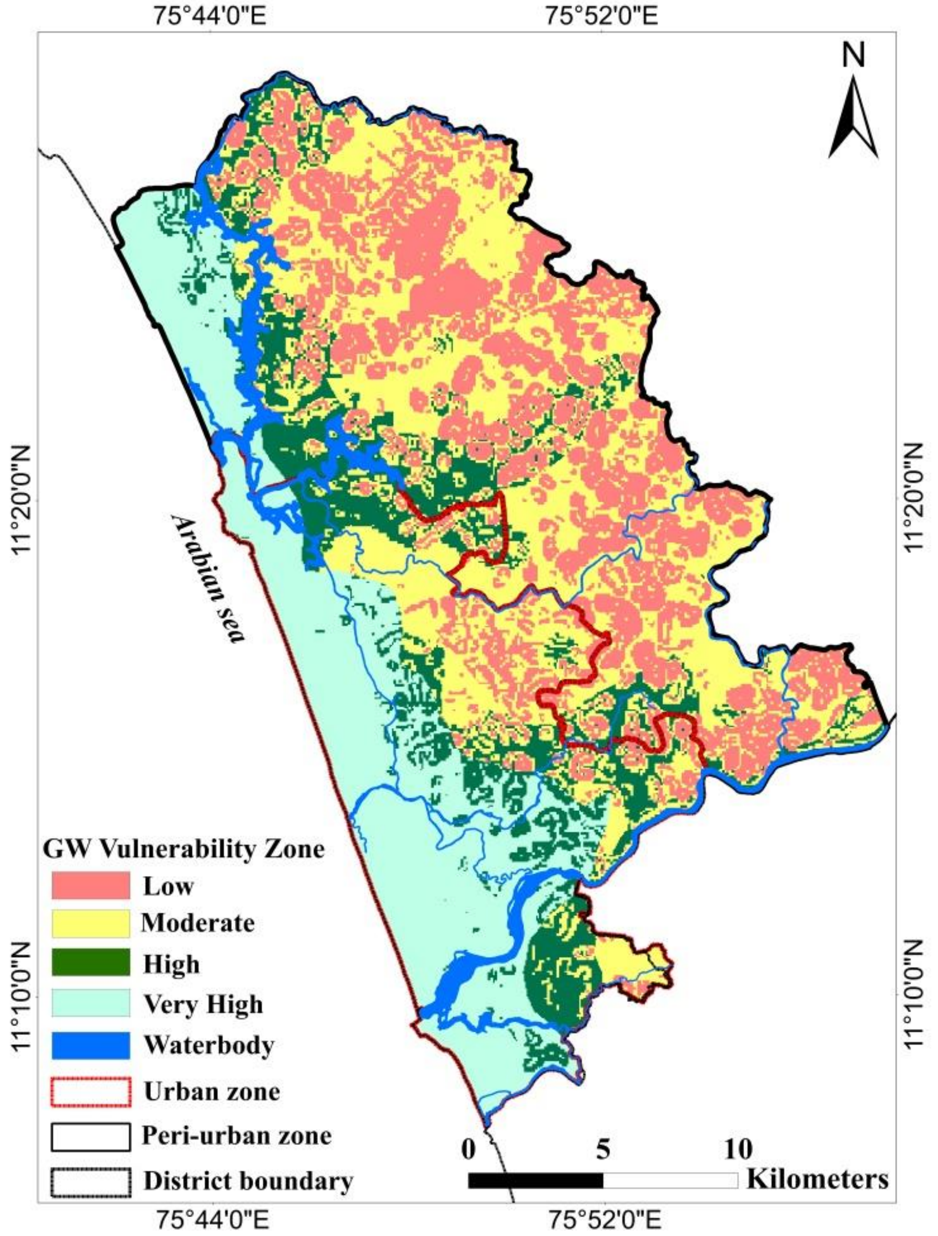


Figure 6.7. Groundwater vulnerability map for urban and peri-urban phreatic aquifers of the study area

Saturated sub-surface hydrogeological structures such as the thick consolidated lateritic cliffs, hard rocks were restricted recharge of surface runoff and thereby protecting aquifers from contaminant diffusion. Low vulnerable zone were covered 8.4% and 38.5% of urban and peri-urban zone respectively. Majority of peri-urban zone were falling under moderate to low vulnerable zone (Figure 6.7). Overall observations were revealed that urban conditions like drastic landuse/landcover change, high density settlement, and thereby induced contamination will severely effect hydrodynamics of the groundwater system. Therefore, diffusion of contaminants was deteriorated the groundwater quality to a level where it becomes unsuitable for drinking, domestic and development purposes in future.

6.1.3. Sensitivity analysis and validation

Impact of individual parameters towards aquifer vulnerability evaluated through the single-parameter sensitivity analysis.

Table 6.11. Sensitivity analysis of the FAHP- DRASTIC-L method

	Theoretical weight	Theoretical weight (%)	Effective weight (%)			
			Min	Max	Mean	SD
D	0.224	22.4	1.413	5.451	5.169	1.44
R	0.165	16.5	4.825	7.955	5.480	2.27
A	0.118	11.8	1.217	4.101	2.342	1.37
S	0.087	8.7	1.751	3.084	2.187	0.62
T	0.066	6.6	0.886	2.617	1.651	0.75
I	0.224	22.4	5.047	8.906	7.433	2.08
C	0.119	11.9	2.979	5.899	3.953	1.69
L	0.118	11.8	0.996	4.013	2.532	1.42

From the effective weight of each parameter, it is clear that vadose zone and DWL have the lead role in determining the sensitivity of the overall performance followed by net recharge index. Effective weight of both vadose zone and DWL are 7.4% with a theoretical weight in of 22.4% (Table 6.11) A slight fluctuation in these factors leads to variations in aquifer vulnerability of the study area.

The groundwater quality index values derived through the hydrochemical investigations were applied to validate the groundwater vulnerability analysis and depicted that there is very strong correlation occurred between the water quality index (WQI) data and groundwater vulnerability index (GWVI) data (Figure 6.8).

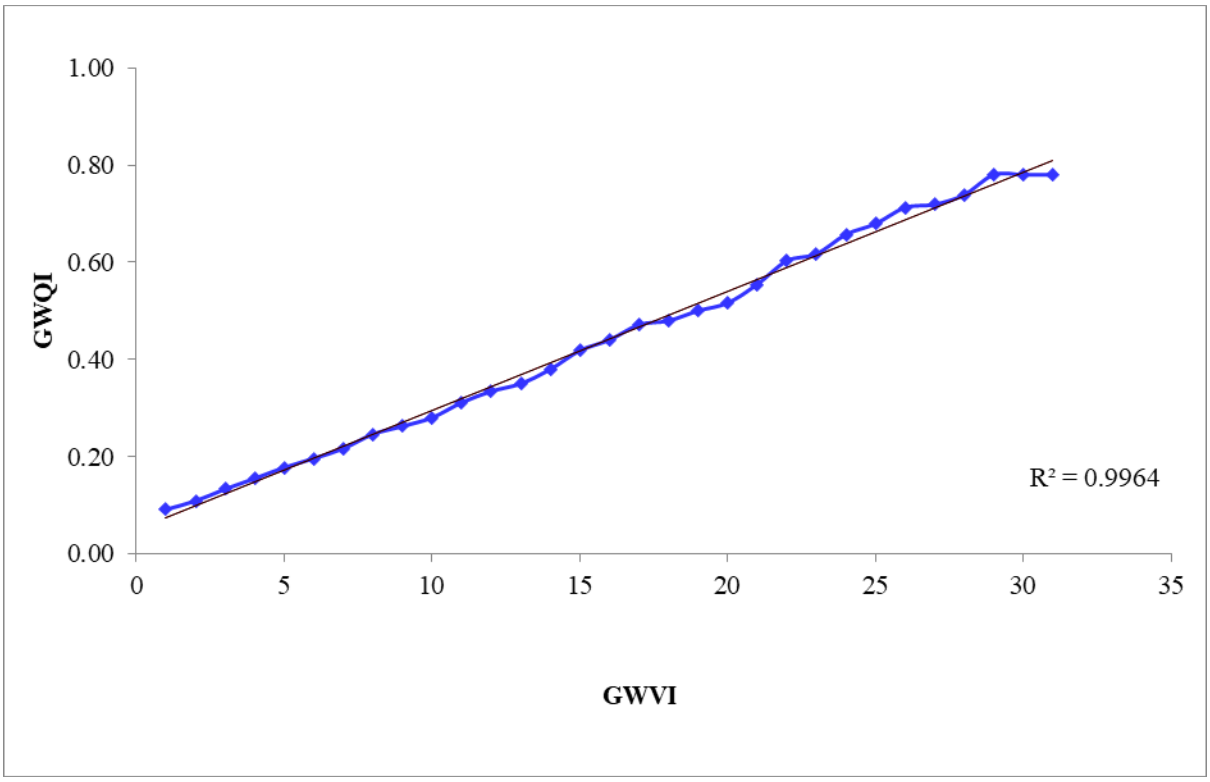


Figure 6.8.Validation analysis for Groundwater Vulnerability Index with Groundwater Quality Index

Statistical student's t-test was conducted for groundwater vulnerability index data (with DRASTIC-L parameters) against water quality index data and found that there is no significant difference between the means (P value > 0.05) i.e GWVI were in good agreement with GWQI. From the spatial and statistical analysis, it is clear that area with very high vulnerable to groundwater contamination were characterised with poor water quality status. Where as student’s t-test for groundwater vulnerability index data (DRASTC-L-without impact of vadose zone) against water quality index was indicated that there is a significant difference between the means (P value= 2.7 X $10^{-6} < 0.05$) (Table 6. 12) and this analysis was further substantiated the significance of impact of vadose zone in groundwater vulnerability assessment.

Table 6.12. Validation of GWVI against GWQI data

Index	**Minimum**	**Maximum**	**Average**	**Variance**	**t-statistics (P* -value)**
DRASTIC-L	0.0853	0.5636	0.3113	0.0200	0.08
DRASTC-L**	0.0592	0.3701	0.2056	0.0079	2.7 X 10^{-6}
WQI	0.0909	0.7805	0.4417	0.0499	

*** alpha value (P) at 0.05**
**** GWVI without I (Impact of vadose zone)**

6.2. Demarcation of groundwater potential zone

The exploitation of groundwater in the urban and peri-urban zone of the study area for their water needs confirms the necessity to predict the groundwater potential of the area. The groundwater potential mapping is one of the preliminary steps towards developing and managing the groundwater resources and it comprises an effective way to explore these invaluable natural resources (Dinesh kumar. et al. 2007; Machiwal et al. 2011; Manap et al. 2013). The occurrence of groundwater were influenced by its lithological properties, geomorphological structure, drainage characteristics, lineament density, porosity, landuse/ land cover, proximity to water bodies, etc. (Prasad et al. 2008; Chowdhury et al. 2009; Yeh et al. 2009; Rahmati et al. 2016). Groundwater Potential Index were derived through the Fuzzy-AHP approach where fuzzy numbers are used instead of the weight values to achieve realistic and the most accurate results. The influence of each factor on groundwater occurrence of the study area and criteria weights derived for each factor based on its influence were discussed below.

6.2.1. Description of factors influencing groundwater occurrence

6.2.1.1.Geomorphology

The study area is divided into two physiographic region viz. low land and midland terrain. The narrow stretch of low land/coastal plain were laid in north-south direction along the coast. The coastal plain with 0 to 5 % slope characterized as the very good potential zone of the study area covering an area of 77.6 km^2 (14.78%) Table 6.13. The midland terrain consists of low rolling terrain and moderately undulating terrain. Low rolling terrain consists of rolling laterite hills surrounded by valleys. The lateritic forms and valley fills were covered 304.09 km^2 (58%) and 79.85 km^2 (15.2%) study area respectively. Valley fills were contributed good groundwater potential zones where as lateritic terrain were assigned with moderate potential to groundwater. Good to very good potential of the valley fills are due to its topographical settings at the bottom of the hill and geological composition consisting of highly porous materials. The other landforms such as water bodies and Residual Hills covers an area of 22.41 km^2 (4.27%) and 10.33 km^2 (1.97%) respectively. Dinesh kumar et al (2007) were studied on groundwater potential of Muvattupuzha river basin, Kerala and explained that residual hills are poor in groundwater occurrence.

Therefore, residual hills were assigned with least rating. The spatial distribution of geomorphological features were given in Figure 6.9.

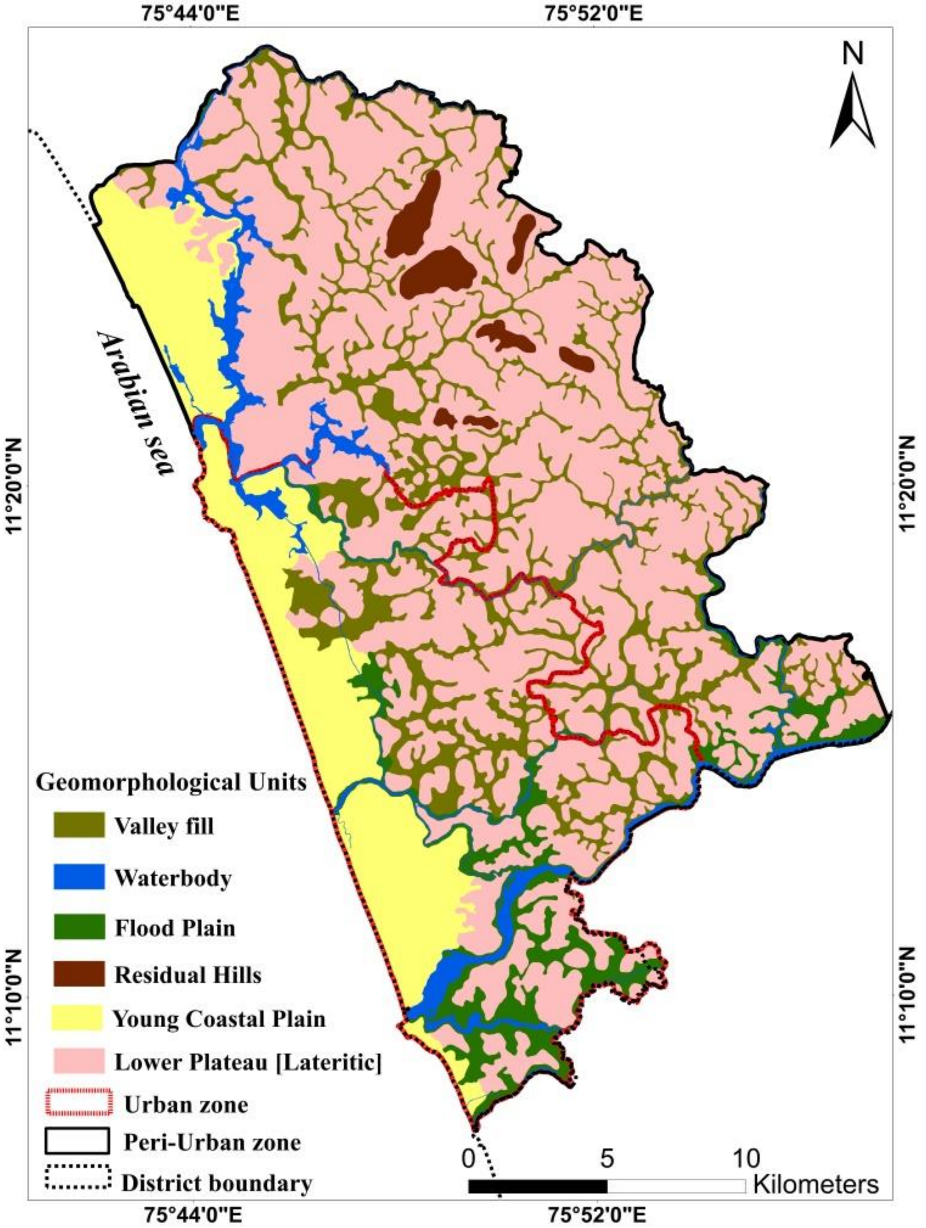


Figure 6.9. Geomorphology of urban and peri-urban zones in the study area

Table: 6.13. Rating and criteria weights evaluated after Fuzzy-AHP analysis

Criteria	Sub-criteria	Area		Weight	Rating	Total Weight
		Km^2	%			
Geomorphology	Waterbody	22.4	4.3	**0.2182**	0.2537	0.0554
	Young Coastal Plain	77.6	14.8		0.2132	0.0465
	Flood plain	30.9	5.9		0.1723	0.0376
	Valley fill	79.9	15.2		0.1687	0.0368
	Lower Plateau [Lateritic]	304.1	57.9		0.1100	0.0240
	Residual hills	10.3	2.0		0.0750	0.0164
Geology	Horneblende-Biotite Gniess	107.06	20.4	**0.1233**	0.1413	0.0174
	Charnockite	305.2	58.2		0.1877	0.0231
	Fluvial coastal alluvium	95.21	18.1		0.2233	0.0275
	Laterite	2.41	0.5		0.2157	0.0266
	Pebble bed	14.7	2.8		0.2413	0.0298
Drainage Density (km/ km^2)	< 1	92.2	17.6	**0.1588**	0.281	0.0446
	1-2	150.1	28.6		0.2477	0.0393
	2-3	52.4	10.0		0.1913	0.0304
	3-5	126.4	24.1		0.1542	0.0245

	>5	103.4	19.7		0.1238	0.0197
Lineament Density (km/ km^2)	0-0.5	395.8	75.4	**0.1588**	0.1310	0.0208
	0.5-1	42.27	8.1		0.1560	0.0248
	1-1.5	29.6	5.6		0.1925	0.0306
	1.5- 2	19.6	3.7		0.2375	0.0377
	>2	37.9	7.2		0.2827	0.0449
Slope (%)	0-5	14.2	2.7	**0.1758**	0.3160	0.0556
	5-15	112.2	21.4		0.2705	0.0476
	15-25	92.8	17.7		0.2228	0.0392
	> 25	306.0	58.3		0.1898	0.0334
Proximity to Surface water bodies (m)	< 50 m	56.3	10.7	**0.079**	0.4623	0.0365
	50-100 m	11.1	2.1		0.2807	0.0222
	> 100 m	457.1	87.2		0.2623	0.0207
Soil texture	Sandy clay loam	30.8	5.8	**0.0822**	0.354	0.0291
	Loam to clay	32.87	6.2		0.243	0.0200
	Sandy loam to clay loam	26.50	5.0		0.206	0.0169
	Gavelly clay loam to gravelly clay	364.37	69.0		0.201	0.0165

Landuse/landcover	Vegetation	330.9	63.0	**0.071**	0.273	0.0194
	Built-up area	140.3	26.7		0.198	0.0141
	Others	34.5	6.6		0.186	0.0132
	Waterbody	19.3	3.7		0.351	0.0249

6.2.1.2. Lithological properties

The predominant geological formations in the area are recent coastal alluvium, sub-recent laterite and archaean crystalline formations such as charnockite and Hornblende–biotite Gneiss. Charnockite is the dominant geological structure in the area, occupied an area of 305.2km^2 (58.2%). Laterite formations forms moderate to good potential phreatic aquifers along topographic lows and valleys (Table 6.13). Two types of alluvium viz. riverine and coastal consists of sand, silt and clay were covered an extent of 95.2 km^2 (18.1%). Coastal alluvium were occurred in the western part of the study area and the riverine alluvium occurs along river courses. The alluvium formation were contributed very good potential zone for groundwater occurrence under phreatic condition. The major water abstraction structures in the alluvial area is dug wells. Spatial distribution of geological units of the urban and peri-urban zone were shown in Figure 1.3.

6.2.1.3. Slope analysis

Urban and peri-urban zones of the study area classified in to four classes based on slope analysis, viz. 0-5%, 5-15 %, 15-25% and > 25% slope classes as shown in Table 6.13. The surface water runoff through the nearly flat to gentle slope terrain (0 to 5 %) is very slow which allow more residents time for rainwater to percolate and enhances rate of infiltration. Therefore those areas fall in very good category for groundwater storage (Table 6.13). These flat terrains were covered 14.19 km^2 (2.7%) of the total study area. The areas with 5-15% and

15-25% slope terrain were consist of rolling lateritic hills and valley fills (Figure 6.4). This slightly undulating topography allows some run-off and moderate infiltration rate in the terrain. The zone were together covered an area of 39% of the total area with a moderate ratings for groundwater storage. The slope zone of > 25 % category composed of steep slope terrain with less infiltration and enhance high surface run off, therefore poor potential to groundwater occurrence.

6.2.1.4. Soil texture

Urban and peri-urban aquifers of the study area consist of four major soil types viz. Sandy clay loam, loam to clay, Sandy loam to clay loam and gravelly clay loam to gravelly clay (Table 6.13). The coastal plain occupied with alluvial soil with sandy loam to sandy clay loam texture (Figure 6.3). Despite the soil type with poor water holding capacity (sand content- 80%), its excessive drained with moderately rapid to rapid permeability were enhanced high infiltration therefore very good for water potential. Riverine alluvium having loam to clay texture. The lateritic soil with gravelly clay loam to gravelly clay texture soil occupied in the majority of the area characterised with well drained, moderately slow permeability. Therefore degree of groundwater potential in this soil group is moderate to poor (Table 6.13).

6.2.1.5. Drainage density

Drainage density is an expression of the closeness of spacing of channels (Strahler, 1957) and it is expressed as length of stream within a square grid of the area in terms of km/km^2. Drainage density of the study area classified into five classes such as <1 km/km^2, 1-2 km/km^2, 2-3 km/km^2, 3-5 km/km and > 5 km/km^2 (Table 6.13). Spatial distribution of drainage density were shown in Figure 6.10. Groundwater recharge is directly related with drainage density. Swetha et al (2017) were studied the groundwater potential of kuttiyadi river basin and confirmed that areas having high density are not suitable for groundwater potential because of the greater surface runoff.

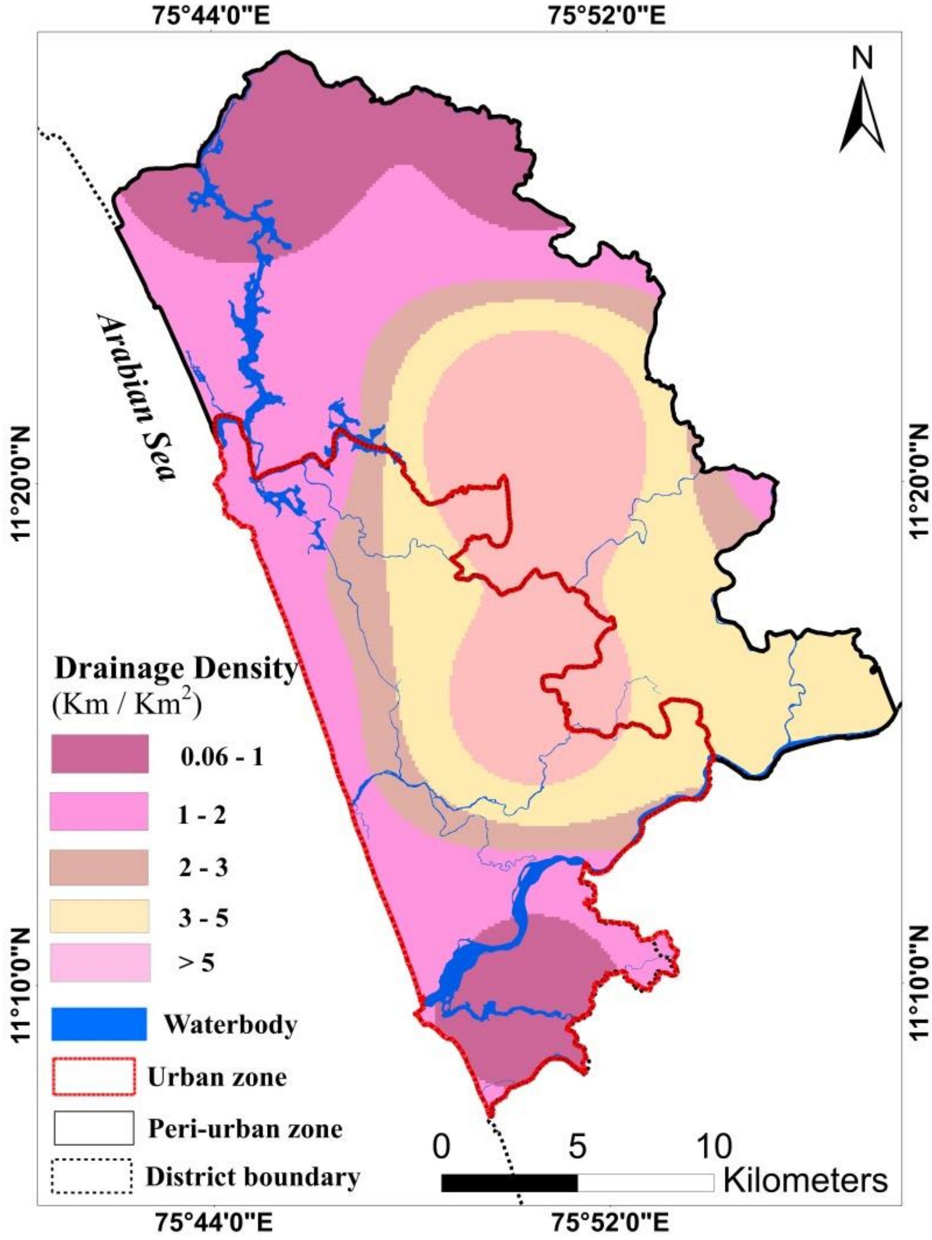


Figure 6.10. Drainage density of the study area

The study area with higher drainage density were assigned with least rating for groundwater potential assessment and vice versa. The region with low level of drainage density, i.e. 0.06-2 km/km^2 inhibits surface run off conversely enhance infiltration and thereby groundwater recharge. Therefore the drainage density class with 0.06-1 km/km^2

assigned with highest ratings towards groundwater recharge followed by 1-2 km/km^2, 2-3 km/km^2 classes with moderate ratings and > 5 km/km^2 assigned least ratings.

6.2.1.6. Lineament density

Lineament density map of an area can indirectly reveal the groundwater potential, since the presence of lineaments usually denotes a permeable zone.

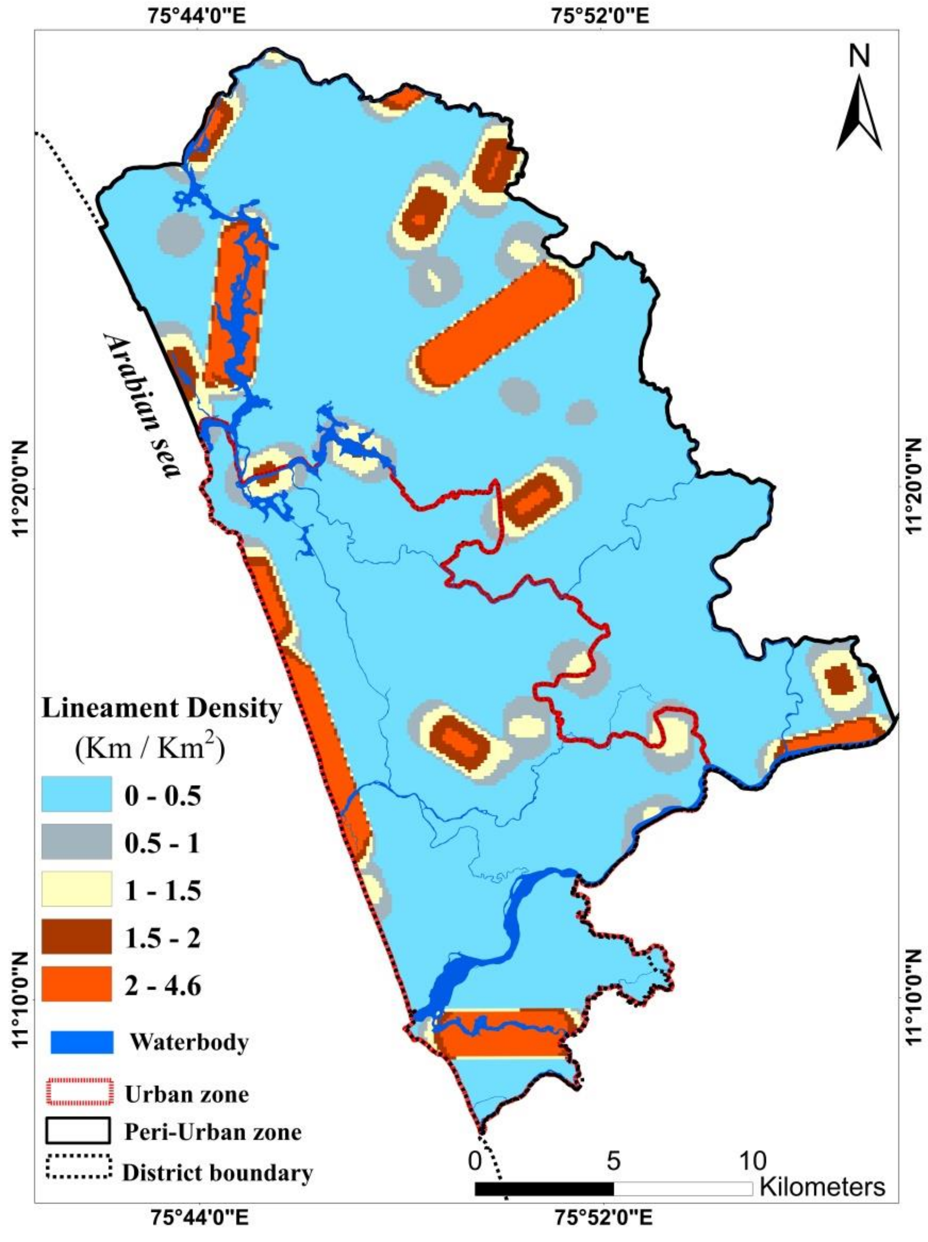


Figure 6.11. Lineament density of the study area

Areas with high lineament density are favourable for groundwater development. Intersection of lineaments and lineaments parallel to the drainage network areas are an evidence of movement and storage of groundwater (Rao et al. 2001). Therefore delineation and analysis of lineaments on a hydrogeological regime provides information on groundwater zones of that region. The prominent directions of the lineaments are NW and NE. Lineament density, cumulative length of lineaments per unit area classified into five classes (Table 6.13) which ranges from 0 to 4.6 km/km^2 (Figure 6.11).· Most of the study area with a lineament density range of 0-0.5 km/km^2 assigned least ratings in groundwater potential assessment (Table 6.13). Highest rating was assigned to lineament density class > 2 km/km^2, which was observed as isolated patches in the entire urban and peri-urban zones of the study area.

6.2.1.7. Landuse / landcover classification

Landuse changes have a direct influence on changes on soil properties including infiltration capability, (Dinesh Kumar et al. 2007), surface run off, evapotranspiration and groundwater recharge. The landuse/landcover classes of the urban and peri-urban cluster of the study area for the year 2015 was selected for groundwater potential assessment and it was mainly divided into vegetation, waterbody built up area and others (Figure 1.4). Vegetation class in the study are were included crop lands (coconut, rubber, and other crop), mixed trees and forest area which together covered an area of 330.9 km^2 (Table 6.13.).

Built up land including commercial/residential areas were occupied an area of 140 km^2 (7.43%). Fallow land, mining/ industrial waste land and barren rocky area were comes under ‘others’ landuse/landcover class and covered an area of 34.5 km^2. Water bodies and river channel were assigned with a highest rating where as built-up land, Fallow land and mining/ industrial waste land were assigned with least ratings in groundwater potential assessment (Table 6.13). Built-up land/urban zone were causes decrease in infiltration rate thereby adversely effects recharge of the groundwater regime therefore poor groundwater potential. Vegetation land were assigned with moderate rating in the study because the rate of infiltration is directly proportional vegetation cover, i.e. with the increase in vegetation cover the infiltration will be more and the runoff will be less.

6.2.1.8. Proximity to surface water bodies

Proximity to surface water bodies can be categorized into three classes such as (a) <50 m, (b) 50–100 m, and (c) >100m and were occupied 10.7%, 2.1% and 87.2% of the study area respectively (Table 6.13).

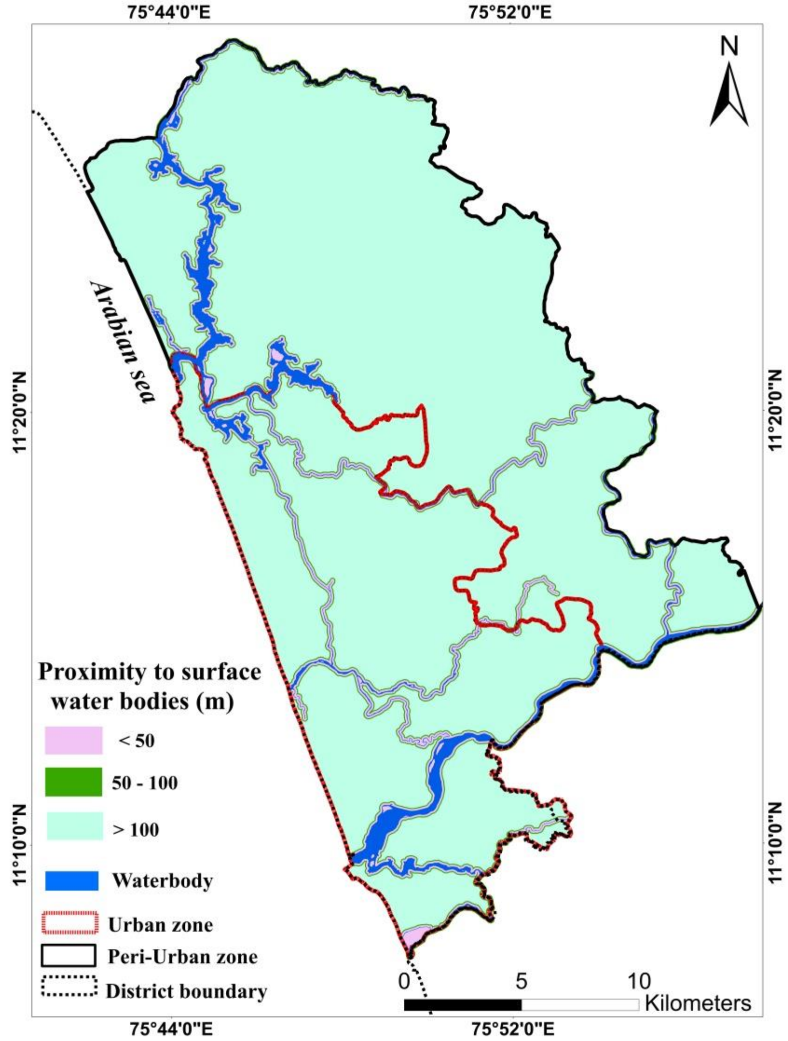


Figure. 6.12. Proximity to surface water bodies

Figure 6.12 was illustrated the spatial distribution of these classes in the study area. Groundwater potential of the area increases with increase in proximity to surface waterbodies. Therefore areas within <50m class assigned high ratings and with decrease in proximity to surface water bodies such as 50-100m and > 100m were assigned with moderate and east ratings in groundwater potential assessments.

6.2.2. Delineation of groundwater potential zones

The groundwater potential zones of the study area demarcated using GIS-based fuzzy AHP method. The thematic layers such as (a) geomorphology, (b) slope (c) geology, (d) landuse/land cover (e) Soil texture (f) Distance to surface water bodies, (g) Lineament Density, (h) Drainage density were integrated with one another according to their importance through overlay analysis in ArcGIS 10.5.1.

Table 6.14. Areal distribution of groundwater potential zones of the study area

Groundwater potential Zones	**Area**	
	Urban	**Peri-urban**
Poor	5.85 km^2 **(2.76 %)**	62.04 km^2 **(19.81%)**
Moderate	67.50 km^2 **(31.83%)**	158.32 km^2 **(50.56%)**
Good	65.76 km^2 **(31.01%)**	60.77 km^2 **(19.40%)**
Very Good	72.95 km^2 **(34.40%)**	32.03 km^2 **(10.23%)**

The very good potential zone occupied 34% and 10% of urban and peri-urban zones of the study area respectively (Table 6.14). The very high potential zone characterized with gentle slope terrain with coastal alluvium formation.

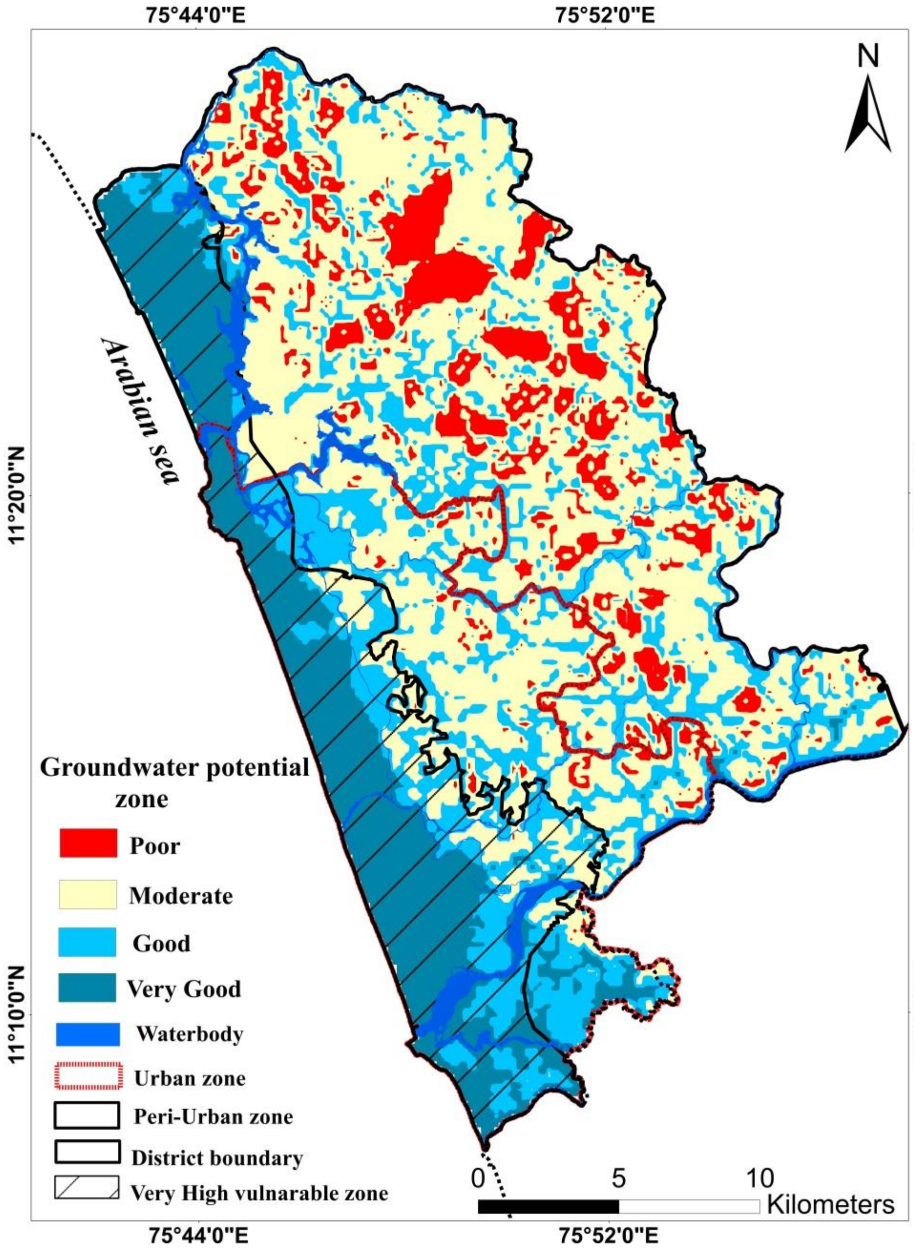


Figure 6.13. Groundwater potential map of the study area

Sandy loam to sandy clay texture soil type with moderate to rapid permeability favors very good potential to the aquifer in the zone. Open Dug wells are suitable for water collecting structures for the shallow very good potential zones. The factors such as geology, geomorphology, slope, soil texture, and drainage and lineament patterns in urban zone are characterised with moderate to very good potential to groundwater. Hydrogeologically, the urban zone occupied in coastal alluvium and the slope percentage for the area is gentle to moderate category. Moderate to steep sloping terrain along with lateritic plateau, patches of residual hills together contributes moderate groundwater potential in peri-urban zone (Figure 6.13). Integrating the aquifer vulnerability analysis using customised DRASTIC-L method which is discussed in previous section with groundwater potential analysis (Figure 6.13) were depicted that very good groundwater potential zones of the urban and peri-urban areas were vulnerable to contamination from water pollutants.

6.2.3. Validation of the groundwater potential zonation

Validation of the groundwater potential zonation can be performed using water level data collected from the field investigation (Swetha et al.2017).

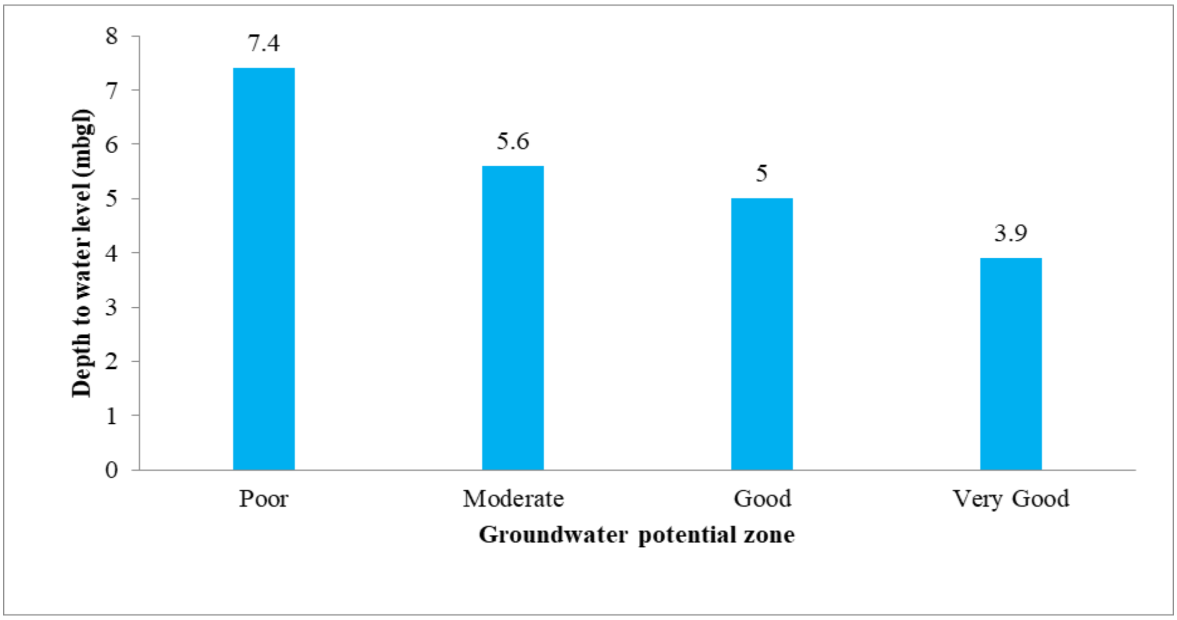


Figure 6.14. Validation of groundwater potential zones with depth to waterlevel data

In the present study, groundwater potential data were validated using average depth to water level (in mbgl) and Figure 6.14, illustrated validation analysis for each ground water potential class. The very good groundwater potential zone occupied with wells having average depth to water level of 3.9 mbgl and this shallow water level in the zone confirmed the high water yield. The corresponding average depth to water level of poor, moderate and good potential zones are 7.4, 5.6 and 5 mbgl respectively.

CHAPTER 7

SUMMARY AND CONCLUSIONS

Summary

Hydrogeochemical and isotopic characteristics of phreatic aquifers in the two differently urbanized environments viz. urban and peri-urban clusters of Kozhikode district, Kerala were investigated in the study. The urban and peri-urban boundaries were delineated as per the State urbanization report and Census-2011, in which peri-urban zones are areas surrounding the urban ensemble and showing the imprints of urban activities at a faster pace.

Spatio-temporal variations of hydrogeochemical factors which control the groundwater quality of phreatic aquifers and inherent hydrogeochemical processes of urban and peri-urban phreatic aquifers of the study area were evaluated using hydrogeochemical and multivariate statistical analyses. Evaluation of environmental stable isotopic composition (δD and $\delta^{18}O$) of rainwater, groundwater and surface water components of urban and peri-urban zones were carried out to reveal the origin and recharge mechanism of groundwater system of the study area. Spatial and temporal variation of stable isotope ratios of urban and peri-urban phreatic groundwater were identified and the percentage contribution of rainwater to groundwater was estimated in the urban- alluvial, laterite and peri-urban laterite phreatic aquifers using isotope mass balance model. Hydrogeochemical parameters of groundwater in urban and peri-urban phreatic aquifers evaluated in the study were successfully integrated using GIS and MCDM-ANP technique to evaluate the groundwater quality index and carried out groundwater suitability zonation using this index which is a concise numerical value of hydrochemical data/ water quality variables.

Groundwater vulnerability analysis was carried out in the study using customised Fuzzy-AHP-GIS-based DRASTIC-L model to associate various hydrogeological factors to groundwater vulnerability towards water pollutants and classified the study area into four zones based on the degree of groundwater vulnerability towards pollutants. Groundwater potential zones were evaluated using Fuzzy-AHP-GIS-based approach incorporated with groundwater vulnerability data derived from the study and generated a groundwater resource database for overall development on a sustainable basis, which can lend a hand to planners and decision makers for the sustainable policy decisions.

Conclusions from the present study are:-

- The acidic nature of the groundwater observed in urban and peri-urban phreatic aquifers can be caused by the addition of CO_2 through rainwater and wide distribution of lateritic soil.
- Based on TDS concentration, majority of groundwater in the study area can be classified as freshwater (TDS value < 1000 mg/L) and some samples from urban coastal alluvium as brackish, which can be due to the leaching of domestic sewage into the groundwater.
- Major ion concentration of groundwater revealed that majority of the urban and peri-urban groundwater were within the permissible limits of BIS (2012) and WHO (2011) drinking water standards except a few samples from urban alluvial phreatic aquifers. Incidence of high concentration of nitrates and faecal contamination were also observed in these coastal aquifers.
- The urban zone of the study area with severe space constraints have been facing difficulties in proper placement of leach pits from wells. The proximity of the sanitation facility to the drinking water source may have led to high nitrate and bacterial contamination.

- Aquifers in the urban and peri-urban zones having the depth to the water level of > 6 mbgl facilitated vertical percolation of water through longer soil columns resulting in the removal of microbial pollutants and thereby excluding bacteriological contaminants.
- Box-Whisker plots illustrated the spatial and seasonal variation of parameters both in urban and peri-urban phreatic aquifers and Mann-Whitney U test confirmed the significant spatial variation in ionic distribution among urban and peri-urban clusters whereas seasonal fluctuation was less significant.
- Seasonal change in groundwater composition was comparatively more visible in urban alluvial phreatic aquifers than in peri-urban lateritic aquifers due to its geological characetristics. During post-monsoon, dilution of groundwater by rainwater recharge took place and reduced the ionic concentration in the groundwater through the mixing of fresh infiltrated water with groundwater.
- The abundance of hydrogeochemical facies evaluated using Hill-Piper plots during pre-monsoon and post-monsoon period were

  In urban cluster - Ca-Mg-Cl-SO_4 > Na-K-Cl-SO_4 > Ca-Mg-HCO_3

  In peri-urban - Ca-Mg-Cl-SO_4 > Ca-Mg-HCO_3 > Na-K-Cl- SO_4
- Gibb’s analysis indicated that the groundwater chemistry of urban aquifers were mainly controlled by rock-water interaction and rainfall was more dominant in groundwater chemistry of peri-urban aquifers.
- Inter–ionic relationships and correlation analysis implied that dominant processes occurred in the groundwater are weathering of silicate minerals as well as the interaction between groundwater and aquifer matrix. Interaction with the aquifer matrix was confirmed through chloro-alkaline indices which indicated that majority of urban (60%) and peri-urban (66%) phreatic groundwater were undergoing direct ion-exchange processes.

- Strong correlations exist between electrical conductivity and Na^+, K^+, Ca^{2+}, Mg^{2+}, $Cl^–$, HCO_3^- +CO_3^- and SO_4^{2-} indicated that these ions are from the same source and play a vital role in the mineralization of groundwater in the study area through its continuous addition along the groundwater flow path.
- A local meteoric water line (LMWL) was established for the entire study area using stable isotopic ratios (δD and $\delta^{18}O$) of rainwater and found that the local trend of stable isotopic signatures of the study area almost follows the global trend. The southwest monsoon and the northeast monsoons show two distinct isotopic signatures.
- The regression analysis of isotopic ratios of hydrogen and oxygen of the rainwater and the groundwater of the study area showed that the major recharge source of groundwater is the meteoric waters.
- The isotope mass balance method was applied to find out the rainwater fraction in the phreatic aquifers of the study area. It was found that the average rainwater fraction in urban alluvial, urban laterite aquifers and peri-urban laterite aquifers were 35%, 39% and 42% respectively.
- About 66% of urban and 95% of peri-urban aquifers in thick lateritic mid-land terrain were categorized as highly suitable to suitable groundwater zone for drinking purpose. Moderate to poor groundwater suitability class covered 34% of the urban phreatic zone where high population density, indecorous groundwater use pattern and lack of protection measures trigger the quality deterioration. Groundwater quality of the entire study area showing deteriorating trend in accordance with the urbanization trend.
- The groundwater vulnerability assessment (DRASTIC-L) depicted that about 71% of urban and 21% of peri-urban zones of the study area, which are characterized by porous & permeable vadose media with shallow groundwater table, have a high to very high vulnerability index value.

- Of the total study area, 8% of urban and 39% of peri-urban aquifers with low vulnerability index value indicated that the groundwater in the zone is protected from contaminants leaching due to its inherent hydrogeology. Low porous vadose media and the presence of steep slope terrain favour this low vulnerability. Besides, the remaining 21% of urban and 40% of peri-urban areas showed moderate vulnerability to contamination.
- Validation analysis of groundwater vulnerability data using groundwater suitability data underpinned the fitness of vulnerability assessment in groundwater management studies.
- Groundwater resources potential assessment revealed that of the total urban area, 34%, 31%, 32% and 3% were comprised very good, good and moderate and poor groundwater potential zones respectively. In the peri-urban region, 10%, 19%, 51% and 20% were covered by very good, good, moderate and poor groundwater potential zones respectively.
- Integration of groundwater vulnerability data (DRASTIC-L) with groundwater potential analysis deduced that majority of the very high groundwater potential zones of the urban cluster were vulnerable to contamination from water pollutants.
- Validation of groundwater potential data with the depth to water level of the study area showed that the MCDM-GIS based integrated approach is a powerful decision-making tool for urban sensitive water management.
- The unfavourable zone in terms of quality and vulnerability to contamination occupied in the study area where the groundwater potential is very high.The groundwater potential is very high in unfavourable zone of urban area in terms of quality and vulnerability to contamination. Population and human activities were more in this zone and the major drinking/domestic water source is groundwater. Therefore the study recommended the requirement of best management practices for the study area to overcome this situation.

- Peri-urban aquifers can be developed for public drinking water supply schemes, and to meet the future requirement of the entire study area. Meanwhile, control in the further development of urban aquifers is essential.

Some prospective research fields suggested are:-

- The effect of urbanization-induced changes of the impervious areas on recharge characteristics of the phreatic hydrologic regime.
- Contaminant transport studies in the subsurface zone using ^{15}N isotope tracer.
- Mitigation measures for surface water pollution to ensure sustainable development of groundwater in the area.

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Annexure 1

LIST OF PUBLICATIONS AND ITS REPRINTS

1. **Jesiya, N. P**., & Gopinath, G. (2019). A Customized FuzzyAHP - GIS based DRASTIC-L model for intrinsic groundwater vulnerability assessment of urban and peri urban phreatic aquifer clusters. *Groundwater for Sustainable Development*, *8*, 654-666.
2. **Jesiya, N.P**., & Gopinath, G. (2019). Groundwater suitability zonation with synchronized GIS and MCDM approach for urban and peri-urban phreatic aquifer ensemble of southern India. *Urban Water J*, *15*(8), 801-811.
3. Bhadran, A., Vijesh, V. K., Gopinath, G., Girishbai, D., **Jesiya, N. P**., & Thrivikramji, K. P. (2018). Morpho-hypsometric evolution of the Karuvannur River Basin, a tropical river in central Kerala, southwestern peninsular India. *Arabian Journal of Geosciences*, *11*(15), 430.
4. Swetha, T. V., Girish Gopinath., Thrivikramji K. P., & **Jesiya, N. P.** (2017). Geospatial and MCDM tool mix for identification of potential groundwater prospects in a tropical river basin, Kerala. *Environmental Earth Sciences*, *76*(12), 428.
5. Girish, G., Ambili, G K., **Jesiya, N. P.,** & Lemoon, K. (2016). Hydro-hypsometric analysis of tropical river basins, Southwest Coast of India using geospatial technology. *Journal of Mountain Science*, *13*(5), 939-946.
6. **Jesiya, N. P.,** & Girish, G. (2015). Delineation of Groundwater Potential Zones in selected Urban and Peri-Urban Clusters of Kozhikode District, Kerala, India, *International Journal of Earth Sciences and Engineering (IJEE)*, *8* (02), 391-396.