Assessment of Ground Water Quality in the Vicinity of Sylhet City, Bangladesh:

A Multivariate Analysis

A Thesis

Submitted to the Department of Statistics, Shahjalal University of Science and Technology, Sylhet, in Partial Fulfillment of the Requirement for the Degree of Master of Science

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SYLHET- 3114, BANGLADESH

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Dedicated

To

My beloved parents

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I would like to express my deep and sincere gratitude to my thesis supervisor Professor Dr. Khalidur Rahman, Department of Statistics, SUST, for giving me the opportunity to do thesis and providing invaluable guidance through this work. His dynamism, vision, sincerity and motivation have deeply inspired me. He has taught me the methodology to carry out the research and to present the research works as clearly as possible. It was a great privilege and honor to work and study under his guidance. I would also like to him for his friendly behavior, empathy and great sense of humor.

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Mohammad Nayeem Hasan

ABSTRACT

Water is the most naturally abundant and the simplest molecule on the earth. Most of the residents of Sylhet city depend on the water supply provided by the Sylhet City Corporation (SCC). Hence, the quality of water distributed by SCC is vital for the health of the residents of the city. Although there are major concerns regarding the quality of water in this region, the number of researches on hydrochemical and water quality studies is very low here. This study has tried to conduct an assessment of the quality of groundwater resource and evaluate the present status of water quality in SCC area and to provide an overview of groundwater condition with respect to different water quality parameters.

Descriptive statistics were computed for each parameter and correlation coefficients were used to assess the degree of linear relationship between parameters. Hydrochemical assessment and multivariate statistical techniques were used to interpret the water quality of the selected pumps and to give meaningful results that were not possible while assessing the data at a glance.

It has been found that out of 20 water samples only 10 fulfill the acceptable requirement of $< 10\%$ errors in the balance between major cations and anions. Out of 66 pairs of water quality parameters, 11 pairs have been found significantly correlated. Principal component analysis (PCA) has extracted three significant PCs with eigenvalues > 1, which explain about 71% of the total variance in the data set of water quality parameters of the study area. PC1, PC2 and PC3 accounting for 36.8% , 18.72% and 15.4% of the total variance, respectively. CA has indicated five clusters or groups. Group A, Group B, Group C, Group D and Group E, respectively, consists of 10%, 20%, 15%, 25% and 30% of the total sample points.

The water in the study have been found good for irrigation. The predominant water type in the study area is the $MgHCO_3$ water, while some locations have $MgCl$ water type. All these results shed light on implementing the scientific remedial management measures for improving the existing groundwater quality of SSC area.

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CHAPTER I

INTRODUCTION

This chapter has a general introduction to the subject of the research and presents the layout of this thesis.

1.1 Background

Water, the most naturally abundant and the simplest molecule on the earth, is not only essential for the existence of human beings but also crucial for the existence of all flora and fauna on this planet (Letterman & American Water Works Association, 1999). It is an inevitable component of natural resources and plays an important role to serve as many purposes like drinking, irrigation, aquaculture and livestock usages. It is one of the most valuable natural resources needed for all living beings to survive. It maintains an ecological balance between various groups of living organisms and their physical and chemical environments (S. Gupta & Tiwari, 2005). In fact, after human resources, water is the most abundant resource in world as well as in Bangladesh (Gain, Giupponi, Gain, & Giupponi, 2014). Bangladesh comprises the third largest source of fresh water to discharge to the ocean (Ahmed, Kadir, & Hafez Ahmed, 2014). It is needless to say that without enough good water our survival will be threatened.

The demand for water has increased rapidly with the construction of power plant, development of industry, irrigated agriculture, urbanization, to improve in living standards and eco-environmental construction (Rahim, 2015). The total amount of water available on earth has been estimated at 1.4 billion cubic kilometers, which is enough to cover the planet with a layer of about 3-km deep (Begum, Harikrishna, & Khan, 2008). About 95% of the world's water is in the ocean, which is inadequate for human consumption and other uses due to its high salinity. Approximately 4% of the water is locked in polar ice caps and the remaining 1% constitutes all freshwater including groundwater. Only 0.1% is available as fresh water in the rivers, lakes, and streams, which are appropriate for human consumption. Because of this, it has been clearly proven that good quality water is extremely important (Bartram, 2003). Water with good quality and sufficient quantity from different resources is a backbone for socio-economic development of a country. Access to

safe drinking water is an essential element of health, fundamental human rights and effective policies for health protection (WHO, 2018).

Groundwater is defined as water that is found underneath the surface of the earth. Sources of groundwater include rain, snow, hail and sometimes surface water (e.g. rivers). The water infiltrates into the ground because of gravity, passes through the soil and rocks until it reaches a depth where the water can no longer infiltrate and is stored (Honachefsky, 2000). Groundwater is stored in an underground porous and permeable rock, called an aquifer, that enables the water to infiltrate and allows movement within the rock. Rapid increases in population and urbanization cause an increase in the demand for water and this, in turn, leads to over-pumping of groundwater (Lawrence, Gooddy, Kanatharana, Meesilp, & Ramnarong, 2000).

Groundwater plays a very significant role in the water cycle and in the supply of water for human activities (Akther, Ahmed, & Rasheed, 2009). The contribution of groundwater is more important than the water on the surface. More than two billion people rely directly on the groundwater for drinking (Morris et al., 2003). Groundwater provides about 50% of current drinking water, 40% of industrial water demand, and 20% of the water used for irrigation in the world (UNESCO, 2003). In Asia and the Pacific, about 32% of the population uses groundwater to drink (Morris et al., 2003). Due to deficiencies and contamination in surface water supplies, pressure on groundwater is increased. Over the next 25 years, pressure on groundwater in Asia will be increased as a result of the growth of population, agricultural practices and increasing water demand for every person, urban areas, industrial activities and energy demand (D. Hossain, Islam, Sultana, & Tusher, 2015).

Bangladesh, a small country, provides abundant water resources and is located in the basins of the Ganges, Meghna, Brahmaputra and Karnaphuli rivers. Bangladesh is also enriched with groundwater resources through numerous rivers. Since the last couple of decades groundwater has been widely using for drinking, irrigation and most other purposes, the level of groundwater is being reduced (Sumiya & Khatun, 2016). Now, 97% of the population relies on groundwater for potable supplies and it is also an important source for irrigation and industry. In the dry season, the groundwater level decreases, whereas the aquifers are completely filled during the rainy season

(Rahman, Hosono, Mazumder, & Jahan, 2018). Among the major cities, especially in Dhaka, where large-scale abstraction has led to a long-term drawdown of the water table.

Groundwater quality plays a vital role in domestic, irrigation and industrial sector (Bhuiyan, Ganyaglo, & Suzuki, 2015). Changing in the land-use pattern for urbanization and agricultural activities commonly results in the deterioration of water quality (Sharp, 2010). Consequently, groundwater quality issues like groundwater salinity is a major concern for water resources development projects (irrigation, floriculture) as well as for human health (drinking water supply). Furthermore, hydrogeological conditions and chemical compositions of groundwater are very important constraints and they play a vital role to have the type of materials used for water distribution systems, the quality of local ecological constructions and values (Carol, Kruse, & Mas-Pla, 2009). The groundwater chemistry can reveal the geological history of aquifers and important information on the fitness of groundwater for domestic, industrial and agricultural purposes (Aghazadeh & Mogaddam, 2010). Like many other natural resources, groundwater is being exploited at an increasing rate all over the world. As a source of potable water it is usually preferred to provide natural protection from pollutions in the developing world. It is commonly used for irrigation and to supply industrial and domestic needs. For effective management of underground resources, one should have a proper understanding of the underground water resources system (Hoque, Hoque, & Ahmed, 2007).

The main processes which determine groundwater chemical composition are water-rock interaction, recharge, and discharge (percolation and pumping), atmospheric inputs, inputs of chemicals by human activities, geological structure, mineralogy of aquifers and the geological processes within the aquifer. The interaction of all these factors leads to different types of water and provides an important reference to the geological history of the enclosing rocks (Hem, 1985; Jeong, 2001; Johnson & Meyer, 1975; Krishnaraj et al., 2012). The principal dissolved components of groundwater are six major ions Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^- and SO_4^- and they constitute 90% content of the total dissolved solids (TDS). The minor ions include K^+, Fe^-, NO_3^- and F^-. Due to human activities such as mining and irrigation, some of these minor ions are raised to higher levels and reaching concentrations equivalent to that of major ions (Hiscock, 2005). Groundwater composition is mostly influenced by the rocks and other materials which traverse through from

recharge to discharge. When it flows through the geological formation a number of processes occur which cause the exchange of soluble solids between the rocks and water. Consequently, the mineral composition of the rocks consequently plays a major role in the chemical constituents of groundwater (Elango & Kannan, 2007).

Groundwater chemical composition is directly connected to groundwater quality. Changes in the concentrations of ions in the water of an aquifer, from natural or anthropological activities can, change the suitability of the aquifer system. The acceptivility of quality of water depends on the purpose for what the water is going to be used and this directly translates to the procedures that can be used to determine the availability and presence of ion species in the water (Beamonte Córdoba, Casino Martínez, & Veres Ferrer, 2010). Consequently, in order to adequately manage this resource it is very important to understand the processes that control groundwater quality (Morán-Ramírez, Ledesma-Ruiz, Mahlknecht, & Ramos-Leal, 2016). One of the methods of assessing water quality is to conduct a geochemical study of the groundwater. Geochemical studies involve an in-depth evaluation of the chemical composition of groundwater in relation to the geology and therefore offer a better understanding of possible changes in quality. Such studies also promote sustainable development and effective management of groundwater. These studies have become very popular in determining the suitability of groundwater, mainly because of the rising need for clean water resources.

1.2 Problem Statement

Most of the residents of Sylhet city depend on the water supply provided by the Sylhet City Corporation (SCC). As most of the people depend on the supply of this water, the quality of water distributed by SCC in vital for the health of the residents of the city (Md. Munna, Islam, Hoque, Bhattacharya, & Nath, 2015). The water resources in the SCC are mostly based on groundwater, which is generally over-pumped. Despite the fact that there are major concerns regarding the quality of water in this region, research on hydrogeochemical and water quality studies is very low here. As a result, the hydrogeochemical processes (evolution), origins, mixing and quality of the water resource in SCC area are not well known. Moreover, the sources of concentration elements and sensibility of available water to pollution is not clear. This leads to great uncertainty in

understanding of the major hydrogeochemical processes, in the control of the evolution of water chemistry and complicates the planning and management of the water resources of the area.

Detailed studies of the groundwater quality in SCC are limited. However, the concept of water quality is complex because it depends on many factors. Water quality can be measured based on a set of physical and chemical variables. While measuring the sustainable development of a given area, water quality is one of the most important issues (Beamonte Córdoba et al., 2010). To the best of researcher's knowledge, no attempt has ever been made to identify these factor of groundwater quality in the area of SCC.

1.3 The Rationale of the Study

There is a need for a new tool for classifying water quality parameters and locations of the pump in an easy and understandable format. This tool would be a simple and inexpensive way to show and explain the existing quality in SCC area. Moreover, this study will show what factors can be controlled in improving water quality. This research is expected to bring new ideas in terms of the association between the quality of groundwater and concept to be implemented in the water quality evaluation in Bangladesh. Finally, this research project will allow the policymakers to notice the current status of the quality of water in the Sylhet city corporation area.

1.4 Objectives of the Study

The main objective of the study is to conduct an assessment of the quality of groundwater resource and evaluate the present status of water quality in SCC area and to provide an overview of groundwater condition with respect to different water quality parameters such as: pH, calcium, potassium, EC, alkalinity, sulfate, Chloride, TDS, nitrate using multivariate statistical analysis. This analysis will help in planning present water resource in the area as well as providing a baseline for future water quality evaluation studies.

This research focuses on providing all the audiences with a clear and comprehensive picture of the overall groundwater quality of SCC area. Thus, the specific objectives of this research are:
- To characterize the chemistry of groundwater.
- To evaluate the correlation and variability in groundwater quality parameters.

- To extract variables that are most relevant in the assessment of groundwater quality.
- Using multivariate statistical techniques, such as: Principal Component Analysis and Cluster Analysis, to determine the source of the existing chemical components present in the water.

1.5 Limitations of Study

Although this study was carefully prepared, the researche's was still aware of its limitations and shortcomings.

- First of all, the collected data from the related institutions was not as perfect as the researcher need. In addition, the parameters measured in these data sets were less than expected ambition.
- Secondly, there were a difficulties to reach to some data and resources for a limited budget.
- Thirdly, the overall quality of water in this research was evaluated based on the chosen physical and chemical parameters/variables. Biological parameters/parameters were not included.
-

1.6 Software Tools

This research required set of tools included:

1. ArcMap has been used to create maps for location of pumps of SCC authority, and the corresponding figures are placed in this report.
2. AqQA, AquaChem, Grapher, Easy_QUIM and PHREEQC Interactive have been used to interpret generated diagrams to determine geochemical characteristics of the groundwater samples.
3. R studio has been used for multivariate statistical analysis with the emphasis on cluster and grouping determination, and it determines the relation between groundwater quality and the geology of the study area.

1.7 Organization of the Thesis

Chapter 1: The current chapter contains the introduction of the research that includes the background, research problems, rationale of the study, objectives of the research and software tools.

Chapter 2: Deals with literature review related to definitions of water quality, the principle of hydrochemical analysis and multivariate analysis, and reviews previous works conducted in the study area.

Chapter 3: Presents a brief introduction to the study area description. It discusses the physiography, climate, vegetation, land-use, stratigraphy (geology), hydrogeological and hydrographic setting of the study area.

Chapter 5: This chapter provides a brief description of the methods used in the study. It mainly focuses on the methods such as hydrochemical analysis and multivariate analysis.

Chapter 6: This chapter presents the main findings of the study. Results and discussion include illustration and discussion of general hydrochemistry, principle component analysis (PCA), hierarchical cluster analysis (HCA), calculation results. Moreover, it discusses water uses for domestic and irrigation and its implication in pipelines and engineering works.

Chapter 7: The last chapter concludes by presenting the main issues discussed in this study as well as by providing recommendations for further improvement and researches.

CHAPTER II

LITERATURE REVIEW

The main purpose of the chapter is to present a resume of conceptual frame work relating to application of hydrochemical analysis and multivariate statistical analysis for water quality parameters of pumps in SCC area. Past studies gives way to future research endeavour. An acquaintance with earlier pertinent studies was felt necessary for better understanding of the research problem and to develop appropriate research methodology. The relevant studies and their findings are limited, which are related to SCC area. However, an attempt is made to orient much on the theoretical views of different authors/scientists on the subject and closely related results are reported. Keeping in view the subject of the study, the review of the available literature related to the study are presented under the following discusion.

Water is one of the most important natural resources, but it is not always in the right place, available at the right time or of the right quality. Improperly discarded chemical wastes, stormwater runoff, poorly maintained septic systems and many land-disturbing activities add to the problems of quality and quantity of our water supplies today. For this reason we have to know about quality of water (K. P. Singh, Malik, & Sinha, 2005).

The concept of ground water quality seems to be clear, but the way of how to study and evaluate it still remains tricky (Chenini & Khemiri, 2009). The definition of water quality is not objective, but is socially defined depending on the desired use of water. Different uses require different standards of water quality.

The concept of water quality is complex because so many factors influence in it. In particular, this concept is intrinsically tied to the different intended uses of the water; different uses require particular criteria. Water quality is one of the most important factors that must be considered when evaluating the sustainable development of a given region (Beamonte Córdoba et al., 2010).

According to Hounslow, (1995a), water quality is defined by the composition of physical, chemical and biological characteristics of a water sample. The chemical composition of

groundwater is the combined result of water composition that enters the groundwater reservoir and the reactions with the minerals present in the rocks (Iliopoulos, Stamatis, & Stournaras, 2011; Zhu & Anderson, 2002).

Water quality must be defined based on a set of physical and chemical variables that are closely related to the water's intended use. For each variable, acceptable and unacceptable values must be defined. Water whose variables meet the preestablished standards for a given use is considered suitable for that use. If the water fails to meet these standards, it must be treated before use (Beamonte Córdoba et al., 2010).Water quality is considered the main factor controlling health and the state of disease of both man and animals.

Water is vital to health, well-being, food security and socioeconomic development of mankind. Therefore, the presence of contaminants in natural freshwater continues to be one of the most important environmental issues in many areas of the world, particularly in developing countries, where several communities are far away from potable water supply. Low-income communities, which rely on untreated surface and groundwater supplies for domestic and agricultural uses are the most exposed to the impact of poor water quality. Unfortunately, they have no adequate infrastructure to monitor water quality regularly and implement control strategies (Ayoko, Singh, Balerea, & Kokot, 2007).

Kazi et al., (2009) reported that human activities are a major factor determining the quality of the surface and groundwater through atmospheric pollution, effluent discharges, use of agricultural chemicals, eroded soils and land use. Environmental pollution, mainly of water sources, has also become public concern. also The chemical composition of ground water is controlled by many factors that include the composition of precipitation, mineralogy of the watershed and aquifers, climate and topography. These factors should be combined to create diverse water types that change in composition spatially and temporally (Chenini & Khemiri, 2009).

The quality of water is affected by a wide range of natural and anthropogenic influences that change the concentration of chemical constituents in the water. This change in the quality of water occurs with depth and over geographic distances; this is because of several processes that affect

the water in the different environments. These factors mainly include the dissolution of ions in soils, sediments and rocks. Anthropogenic influences mainly include effluents generated by human, urban, agricultural, and industrial activities (Beamonte, Bermúdez, Casino, & Veres, 2007).

Potable or "drinking" water can be defined as the water delivered to the consumer that can be safely used for drinking, cooking, and washing purposes. This water must meet the physical, chemical, bacteriological, and radionuclide parameters when supplied by an approved source. Waters should be delivered to the consumer through a protected distribution system in sufficient quantity and pressure (Eljmassi, 2012).

Water quality is defined based on a set of physical and chemical variables that are closely related to the water's intended use. Beamonte Córdoba et al., (2010) defined a standard as a rule or principle considered by an authority. He continued to mention that, a proper standard for drinking water quality should therefore be a reference that will ensure that the water will not be harmful to human health. For each variable, acceptable and unacceptable values must, then be defined. If the water meets the pre-defined standards for a given use, it is considered suitable for that use. If the water fails to meet these standards, it must be treated before use.

In Guha, Mandal, & Dutta, (2011); Khatlwada, Takizawa, Tran, & Inoue, (2002); Mahmood, Muqbool, Mumtaz, & Ahmad, (2011); Simeonov, Massart, Andreev, & Tsakovski, (2000) used many descriptive statistics as a tool to make a comprehensive assessment of variability of groundwater quality.

Simeonov et al., (2000) conducted a study on assessment of metalic pollution in sediments from Black sea. Samples were collected from 39 sampling sites and each was analysed for 10 water quality parameters and reported that the descriptive statistics likes mean, maximum, minimum, standard deviation and standard error are useful and it gives the summary about the data.

Khatlwada et al., (2002) made a study on ground water contamination assessment. By using descriptive statistics of the water quality parameters, the parameters are grouped by comparing to the World Health organization (WHO) drinking water quality guidelines.

Mahmood et al., (2011) reported the descriptive statistics of the 16 parameters in the study and large standard deviation of most of the parameters revealed their randomly fluctuating concentration levels in the ground water. Correlation matrix was used to account for the degree of mutually shared variability between individual pairs of water quality variables.

Guha et al., (2011) conducted a study on evaluation of urban lentic water. The data was collected from 5 major water bodies. Each water body was sampled at least nine times during the study. The study included 21 parameters. The collected data was assessed by descriptive statistics and correlation analysis. The descriptive statistics gave the range of the parameters and the correlation matrix exhibited excellent positive correlation value between Na^+ and HCO_3^- and also high correlation between Na^+ and Cl^-, Mg^{2+} and Cl^-, Na^+ and SO_4^{2-}, Mg^{2+} and SO_4^{2-}, indicates that these soluble salts are predominant in the water samples.

Multivariate statistical methods have been widely used to facilitate the solution of environmental problems and suggest clues for the understanding of some natural processes (Sandow Mark Yidana, Banoeng-Yakubo, & Akabzaa, 2010). In recent times, multivariate statistical methods have been applied widely to investigate environmental phenomena (Sandow M Yidana, Ophori, & Banoeng-Yakubo, 2008). The multivariate statistical techniques are the appropriate tools for a meaningful data reduction and interpretation of multi-constituent chemical and physical measurements. Furthermore, the multivariate techniques have been widely used as unbiased methods for the analysis of water quality data to draw meaningful conclusions (Yilmaz, Buyukyildiz, & İhsan Marti, 2009). It is noted that multivariate statistical methods have been employed to extract significant information from hydrochemical data sets in compound systems (Chenini & Khemiri, 2009). The necessity and usefulness of multivariate statistical techniques have been evaluated and emphasized for large complex data sets with a view to get better information about the water quality and design of monitoring network for effective management of water resources.

The application of different multivariate statistical techniques, such as cluster analysis, principal component analysis , factor analysis and discriminate analysis, help in the interpretation of complex data matrices for a better understanding of water quality and ecological status of the study region. These techniques allow the identification of the possible sources that influence water systems and offers a valuable tool for reliable management of water resources as well as rapid solution for pollution problems (Kazi et al., 2009).

Statistical treatment of the data PCA and cluster analysis are unbiased methods which indicate associations between samples and/or variables. These associations, based on similar magnitudes and variations in chemical and physical constituents, may indicate the presence of seasonal or human influences. Hierarchical agglomerative cluster analysis indicates groupings of samples by linking inter-sample similarities and illustrates the overall similarity of variables within the data set (Menció & Mas-Pla, 2008).

In the recent years, in numerous studies multivariate statistical methods have been applied to characterize and evaluate surface and groundwater. In Bengraïne & Marhaba, (2003); Bu, Tan, Li, & Zhang, (2010); Love, Hallbauer, Amos, & Hranova, (2004); Omo-Irabor, Olobaniyi, Oduyemi, & Akunna, (2008); Palma et al., (2010); Razmkhah, Abrishamchi, & Torkian, (2010); Shirodkar et al., (2009); Sandow M. Yidana, Ophori, & Banoeng-Yakubo, (2008); Zhou, Liu, & Guo, (2007) the multivariate techniques as a tool to make a comprehensive assessment of groundwater quality.

Bengraïne & Marhaba, (2003) monitored, chemical, biological and physical data at 12 locations along the Passaic River, New Jersey, during the year 1998. In that study, principal component analysis (PCA) was used: (i) to extract the factors associated with the hydrochemistry variability; (ii) to obtain the spatial and temporal changes in the water quality. Solute content, temperature, nutrients and organics were the main patterns that extracted. The spatial analysis isolated two stations showing a possible point or non-point source of pollution. This study shows the importance of environmental monitoring associated with simple but powerful statistics to better understand a complex water system.

Omo-Irabor et al., (2008) subjected the chemical data set by Principal Component Analysis (PCA)/Factor Analysis (FA) and Hierarchic Cluster Analysis (HCA). The aim of this study was to determine the nature and spatial distribution of chemical pollutants in surface and groundwater in the western Niger Delta region.

Sandow M. Yidana et al., (2008), applied the multivariate techniques to surface water hydrochemical data of surface water of three different locations along the Ankobra Basin, Ghana, to extract principal factors corresponding to the different sources of variation in the hydrochemistry. The combined use of principal component analysis (PCA) and cluster analysis enabled the classification of water samples into distinct groups on the basis of their hydrochemical characteristics.

Zhou et al., (2007), demonstrated that the multivariate statistical methods are useful for interpreting complex data sets in the analysis of temporal and spatial variations in water quality and the optimization of regional water quality monitoring network.

Factor analysis, which includes PCA is a very powerful technique applied to reduce the dimensionality of a data set consisting of a large number of inter-related variables, while retaining as much as possible the variability present in data set (K. P. Singh et al., 2005).

According to Jolliffe & Cadima, (2016) The main purpose of FA is to reduce the contribution of less significant variables to simplify even more of the data structure coming from PCA. In Alkarkhi, Ahmad, Ismail, Easa, & Omar, (2009); Boyacioglu & Boyacioglu, (2008); Matejicek, (2006); Mazlum, Özer, & Mazlum, (1999); Papatheodorou, Lambrakis, & Panagopoulos, (2007); Praus, (2007); Sangam Shrestha, Kazama, & Nakamura, (2008); Yerel & Ankara, (2012) used the Factor/ Principle Component Analysis as a tool to identify probable source components for explaining the major components of that region.

Mazlum et al., (1999) reported that PCA/FA for the 12 physico-chemical components shows that the six components are sufficient to explain the monitoring area. These components explain more than 70% of the total variance of the original data set. Finally, the results show that small domestic waste discharge, industrial waste discharge, nitrification and seasonal effect are the main cause of variations in water quality in that region.

Praus, (2007) made a study on urban water quality evaluation. Samples were collected from city drinking water network on 18 water quality parameters. Factor analysis was performed using the Varimax rotation. Factor analysis confirmed the PCA results. 18 parameters of the drinking water quality characterization can be replaced by 6 factors explaining about 83% of the data variance and additionally, in the case of alkalinity showed relations between hardness and bicarbonate/carbonate concentration. The first two factors explained about 50% of the total variability present in the data.

Alkarkhi et al., (2009) have used factor analysis on ten variables to compare the compositional pattern between analyzed water samples and to identify the various factors that influence each of them. Two factors were extracted explaining more than 82% of the total variance in the data set. The factor 1 accounted for 59.29% of the total variance. This factor appears to be originated from the combined effect of anthropogenic activities accompanied with partial ecological recovery system of the river.

Sangam Shrestha et al., (2008) have reported that factor analysis helped to extract and identify the factor/sources responsible for variations in river water quality at different sampling sites. The results of PCA/FA while considering the only factors that explain the highest variance in most of the variations are explained by dissolved mineral salts along the whole Mekong River and in individual stations as well.

Matejicek, (2006) has used PCA and FA separately for six seasons (January, March, May, July, September and November). The selection is subordinated to the available data and to the expected differences in biological activities, which appears to be the dominant source of qualitative changes. In the case of factor analysis bi-plots, more than 50% of the variability is covered by two factors. The significant changes of factor analysis loadings are observed between the winter seasons and the summer seasons, which is also in correspondence with the original data.

Yerel & Ankara, (2012) made a study on assessment of water quality in Sakarya River in Turkey. In this study, surface water quality data were grouped using FA reported that four factors

explaining the 78.50% of the total variance in the surface water quality data set were determined. Based on this it may be concluded that of the four factors, it is the Factor 1 (Cl^-, Na^+, SO_4^{2-} and TDS) that best observed variances in the data. These results reveal that agriculture, anthropogenic and domestic pollution caused differences in terms of water quality in the downstream of the river.

In Love et al., (2004) study, two examples are presented. The first is of groundwater around a southern African iron ore mine and the second is of groundwater in the vicinity of a southern African municipal sewage disposal works. Groundwater samples were collected, their chemistry analysed and factor analysis was performed on each of the chemical datasets. In the first case study, factor analysis successfully separated signatures due to uncontaminated groundwater (calcium, magnesium and bicarbonate), agricultural activities (potassium and ammonium) and mining activities (sodium, chloride and sulphate). In the second case study, factor analysis did identify a chemical signature (nitrate and phosphate; minor iron) related to the sewage works—but since this signature involved parameters that were within regulated limits, the finding was of limited value for management purposes.

Cluster analysis is a group of multivariate techniques whose primary purpose is to assemble objects based on the characteristics they possess. . In Gholami & Srikantaswamy, (2009); I. Gupta, Dhage, & Kumar, (2009); Khatlwada et al., (2002); Yerel & Ankara, (2012) used the Cluster Analysis as a tool to make a study of variations in water quality.

Cluster analysis classifies objects, so that each object is similar to the others in the cluster with respect to a predetermined selection criterion. The resulting clusters of objects should then exhibit high internal (within-cluster) homogeneity and high external (between cluster) heterogeneity. Hierarchical agglomerative clustering is the most common approach, which provides intuitive similarity relationships between any one sample and the entire data set, and is typically illustrated by a dendrogram (tree diagram) (Jolliffe & Cadima, 2016) identified Cluster Analysis as "an efficient means to recognize groups of samples that have similar chemical and physical characteristics" (Shaban, Urban, El Saadi, & Faisal, 2010).

According to K. P. Singh et al., (2005), Cluster analysis is an unsupervised pattern recognition technique that uncovers intrinsic structure or underlying behavior of a data set without making a

priori assumption about the data, in order to classify the objects of the system into categories or clusters based on their nearness or similarity, Cluster analysis helps in grouping objects (cases) into classes (clusters) on the basis of similarities within a class and dissimilarities between different classes. The class characteristics are not known in advance but maybe determined from the analysis. The results of CA help in interpreting the data and indicate patterns.

Different types of cluster analysis have been employed to view water quality data for both surface and groundwaters Cluster Analysis seeks to classify homogeneous subgroups of cases in a population by minimizing the Within-group and maximizing Between-group variations.The Hierarchical Cluster Analysis (HCA) is an efficient means to recognize groups of samples that have similar chemical and physical characteristics (Shaban et al., 2010).

Simeonov et al., (2000) made a study on assessment of metal pollution in Black sea. The samples were collected from 4 different sampling sites. The hierarchical cluster analysis by using Ward's method reported four clusters which could be further divided into two bigger subgroups. The first contains heavily polluted sites, these sites are near to the coastal line and the waste inlets, big chemical cement plant and several sites from both coastal lakes located near to industrial source like glass and steel production factories. The second one indicates a moderately polluted buffer zone. In both big clusters two subgroups could be found. In the first one they represent the more severely polluted areas and the less contaminated lake. In the second it indicates the non-affected gulf parts.

Khatlwada et al., (2002) conducted a study on assessment of groundwater contamination. Samples are collected from 31 sampling sites covered both northzone (N) and south zone (S) and reported that clustering clearly showed a distinct pattern of three groups of the sampling sources. The wells in the north and south were put in the first group where as the shallow sources and the deep wells from the central zone made up the second and third group respectively. The pair had the shortest distance among all the cases and was combined at the first step. This suggests that the pair had most similar characteristics of the water quality parameters. A general trend on the clustering indicated that the water quality in private wells at the centre is well differentiated to the water quality at the north and south zones.

CHAPTER III

SITE DESCRIPTION AND ENVIRONMENTAL SETTING

People of Sylhet City Corporation (SCC) suffer from the availabilty of supply water in both quality and quantity, Groundwater is one of the most precious natural resources in our country as it is the only source of drinking water for the majority of the population, Nowadays There is a water crisis in the Sylhet City Corporation area, groundwater contamination has become a major concern in the recent years. Groundwater aquifer is considered the main and only water supply source for all kind of human usage in this area. Thus, this chapter presents a brief introduction to the study area description. It discusses the aquifer, topography,physiography,climate, land-use, stratigraphy (geology), hydrogeological and hydrographic setting of the study area.

3.1 Location

3.1.1 Sylhet District

The area now constitutes Sylhet zila was once a part of the Kingdom of Jaintia. It is situated on the bank of the river Surma. There are different opinions about the origin of the zila name. The general belief is that in the remote past a trading centre (locally known as hatta) of grinding stones (meaning Syl) was developed at the foot of hilly areas where the zila headquarters is located. In consequence, the zila came to be known as Srihatta. Subsequently, it was renamed as Sylhet. The zila is bounded on the north by India, on the east by India, on the south by Maulvibazar zila, and on the west by Sunamganj zila and Habiganj zila (Figure 3.1). The total area of the zila is 3452.07 sq. km. (1332.00 sq. miles). The zila lies between 24º 36' and 25º 11' north latitudes and between 91º 38' and 92º 30' east longitudes (Bangladesh Population and Housing Census, 2011).The region comprises about 1.02% of the total hilly areas (12%) of the country (Rahmatullah, Pk, Al-Imran, & Jahan, 2013).Sylhet zilla consists of 1 City Corporation, 12 upazilas, 101 unions, 1696 mauzas, 3206 villages, 27 City Wards, 242 City mahallas, 4 paurashavas, 36 wards and 111 mahallas with total population 34,34,188 (Bangladesh Population and Housing Census, 2011).
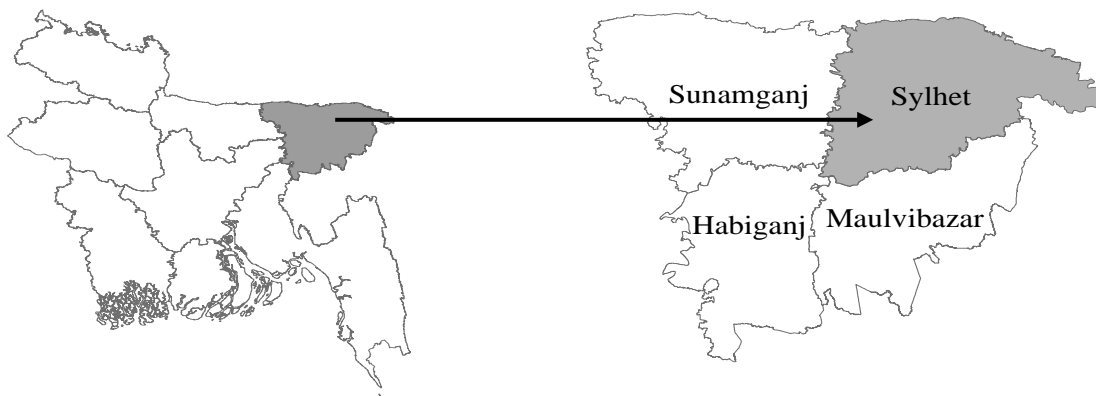
Figure 3.1a: Sylhet Division of Bangladesh   Figure 3.1b: District in Sylhet division

3.1.2 Sylhet Sadar

Sylhet Sadar is located at 24.8917°N 91.8833°E. It has 86074 households and total area 323.17 km².The city of Sylhet is located within central of Sylhet Sadar. It is bounded by companiganj, gowainghat and jaintiapur upazilas on the north, dakshin surma upazila on the south, Jaintiapur and golapganj upazilas on the east, chhatak and bishwanath upazilas on the west. At the 1991 Bangladesh census, Sylhet Sadar had a population of 554,412, of whom 287,304 were aged 18 or older. Males constituted 52.51% of the population, and females 47.49% (Figure 3.2).
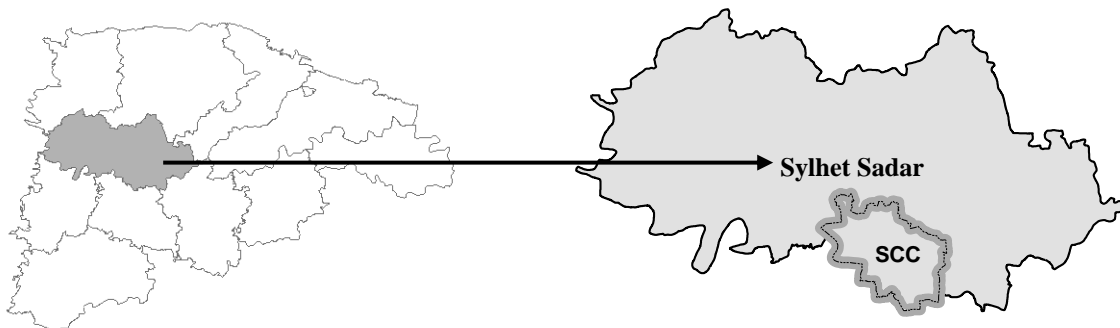
Figure 3.2a: Upazila in Sylhet District   Figure 3.2b: Sylhet Sadar and Sylhet City Corporation

3.2 Aquifer of Sylhet

To estimate the groundwater resources of an area it is essential to know the aquifer characteristics of the area. North East Minor Irrigation Project (NEMIP) conducted pumping tests to determine the aquifer parameters of greater Sylhet area. In the study area, there is limited information that is available or accessible in the aquifer systems. The main aquifer in the north-eastern region varies from semi-confined to confined types. A prospective aquifer in the north-eastern hills is the highly weathered alluvial sands of the Dupi Tila formation. These sands are fine to medium grained and crop out in small hillocks in Sylhet and Moulvibazar districts and in some parts of Habiganj district. However, the permeability of these sands is lower than that of the alluvial deposits. The young gravelly sands also form a potential aquifer, although they are poorly sorted and contain large amounts of gravel and pebbles, making it difficult to use low-cost drilling techniques (Khan, 1991).

3.3 Geological Setting

Understanding the geological setting of Bangladesh is important for foundation design as well as to assess the water quality.

3.3.1 Geology of the Study Area

To understand the regional geology it is important to understand the structural style of Bengal basin. Bangladesh occupies a large part of the Bengal basin which is lies tentatively between Latitude 20°43´ to 26°36´N and Longitude 88°30´ to 92°40´E and bounded by the peninsular shield area of Rajmahal Hills in the west, the Arakan-Yoma aniiclinorium and the Naga-Lushai orogenic belts in the east, the Shillong plateau and the Himalayan foredeep in the north and the Bay of Bengal in the south (Figure 3.3). The Bengal Basin occupies most of Banglaesh and West Bengal of India and part of the Bay of Bengal (Mahmood Alam, 1989).
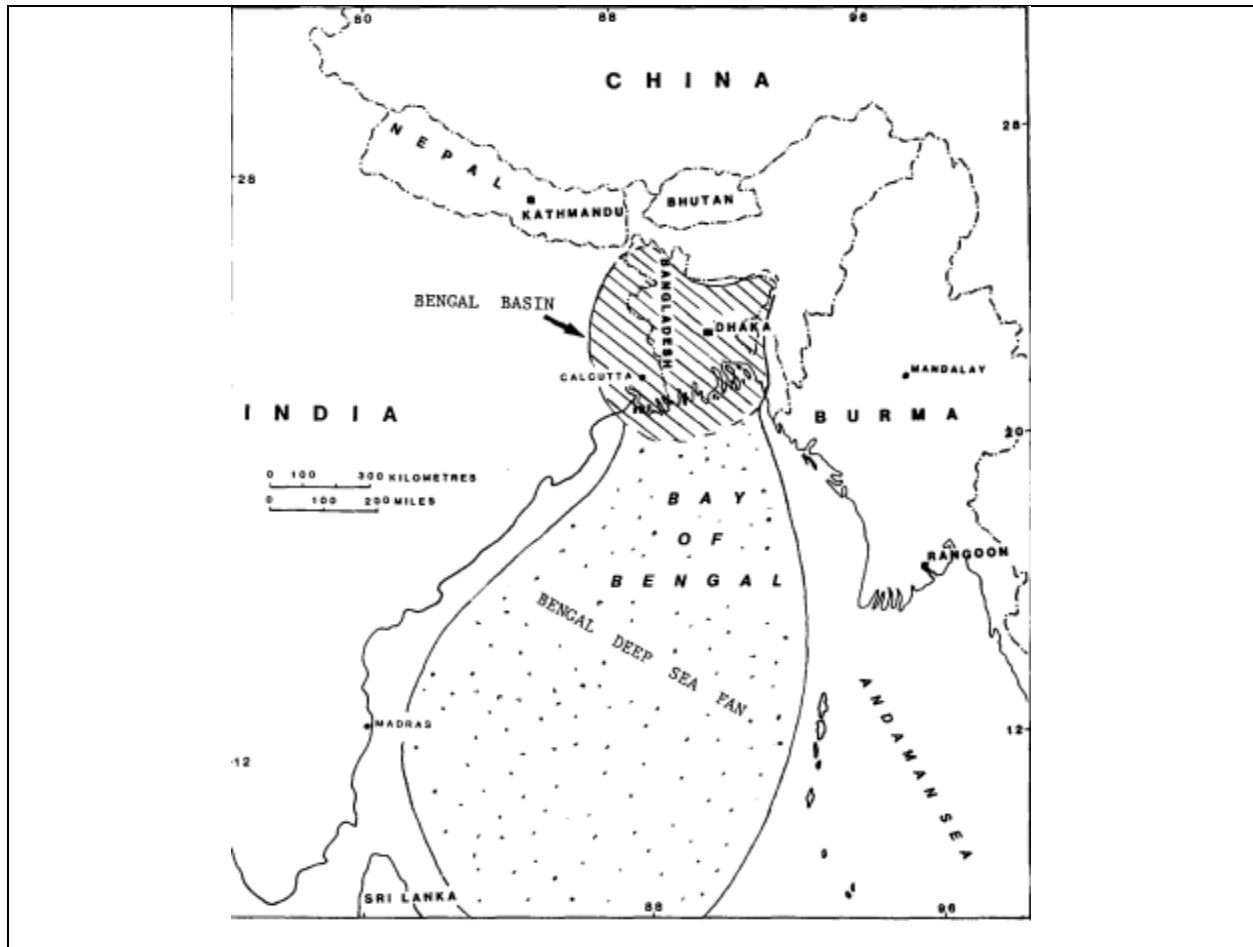
Figure 3.3: Index Map Showing the Indian Subcontinent and Bengal Geosyncline is Formed by the Bengal Besin of India and Bangladesh and the Bengal Deep sea Fan of the Bay of Bengal (Source: Mahmood Alam, 1989)

3.4 Geomorphology

Geomorphologically, the Bengal Basin of Bangladesh corresponds mainly to the low country of the Ganges-Brahmaputra plain (Schwartzberg & Ahmad, 2006). This plain terminates on the north at the Shillong Plateau and on the east in the Tripura and Chittagong hills. It includes one exceptional area, the southeast coastal region of Chittagong at the foot of the Chittagong hills. These hills are part of the frontal folded belt of the ArakanYoma, the principal youthful orogenic belt of western Burma. Around the head of the Bay of Bengal, the Ganges delta (Figure 3.4) forms the low, tidal-delta area of Sundarbans - - an area dissected by numerous tidal channels.
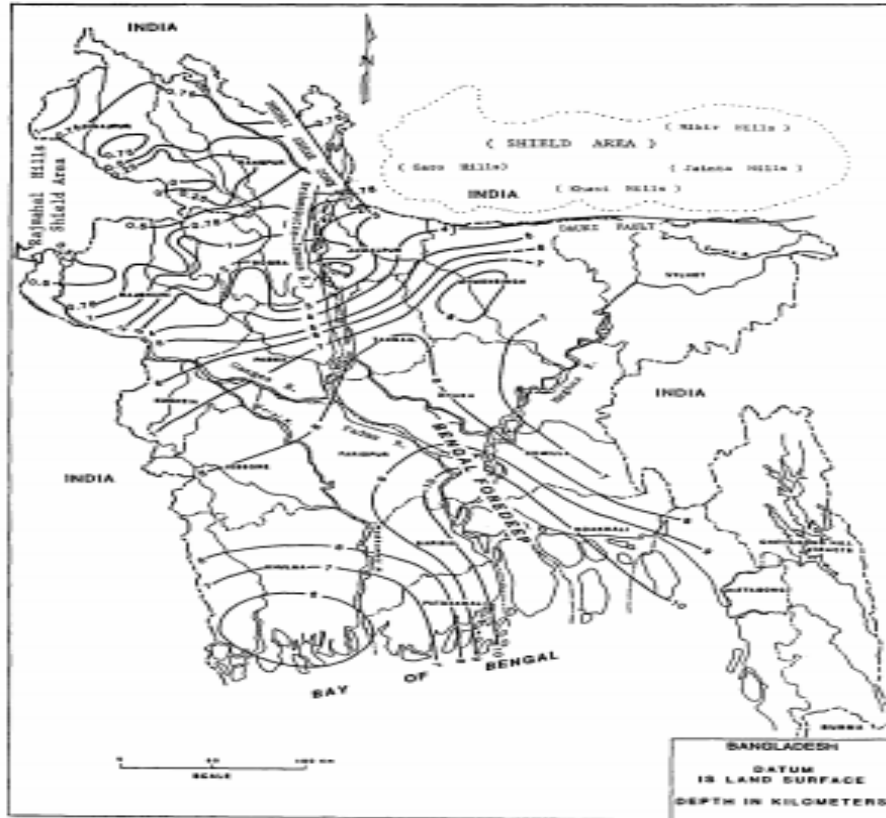
Figure 3.4: Depth to basement in the Bengal Basin of Bangladesh (data source: Aeromagnetic Survey, Overseas Development Administration London, 1980. Modified by Jones, 1985 and by the author).

Bangladesh can be divided into four (Ground Water Task Force, 2002) or five (Mahmood Alam, 1989) distinct regions each having distinguishing characters of its own.

1. The Holocene Floodplains - this is the broad area mainly north and east of the Ganges River, which includes the Sylhet basin, the Faridpur trough, and the piedmont alluvial plain of North Bengal. The soils are littleweathered gray silts and clays; locally there are near-surface peats.

2. The deltaic plain - this covers the area between the Ganges and the Bay of Bengal, passing southward into the Sundarbans - the low tidal area of Kulna and Patuakhali.

3. The Eastern and Northeastern Tertiary Hills Regions - these include the hills of Chittagong and the Chittagong Hill Tracts and some hills in Sylhet, all marked by deeply weathered lateritic red soils.

4. The Pleistocene Terrace or the Pleistocene Uplands - these include the Barind (North Bengal), the Madhupur Tract (Tangail and Dacca), the Lalmi Tract (Comilla), and some higher ground in Sylhet; these areas are also lateritic.

5. The southeast coastal plain - this is the coastal area extending from Noakhali to south of Cox's Bazar

The Flood plain and the Bengal Delta regions occupy seventy two (72) percent of the total land area of Bangladesh and the Pleistocene Terrace and the Tertiary Hills Regions cover rest 28%. The Ganges Delta, one of the largest deltas in the world, is located in the lower reaches of the Ganges and the Brahmaputra. Some important studies have been done of the landforms and Late Quaternary geology of this area (Umitsu, 1993). The Ganges delta lies at the junction of three tectonic plates: the Indian plate, the Eurasian plate, and the Burma plate. The rivers Ganges and Brahmaputra flow into the delta from the northwest and the north (Dola, Bahsar, Islam, & Sarker, 2018). Regional geological setting reveal that the land forming sediments were transported by the great river systems from the Himalayan Mountains and the Shilling Plateau to the north, Arakan Yoma Belt of Mayanmar to the east and Rajmal Hills of India to the west, The open southern portion of Bengal Basin served as a depositional center for the sediments (Reimann, 1993).

Bangladesh has been broadly divided into three major tectonic zones:
1. Stable Platform in the northwest including Bogra Shelf system and Paleocene-Eocene system.
2. Deep (Geosynclinal) Basin to the south east including Hatia tough system, Oligocene-Miocene system and Surma sub basin system.
3. A third unit, a narrow northeast-southwest trending zone called the 'Hinge Zone' separates the above two units almost through the middle of the country (Md Alam & Islam, 2009).

The deepest part of the basin east and southeast is characterized by several troughs within an oceanic crustal basement for example, Surma trough, Hatia trough and Faridpur trough. Surma and Faridpur troughs are separated by Modhupur- Tripura threshold and Faridpur and Hatia troughs are separated by Barisal gravity high (BRRL, 2017).
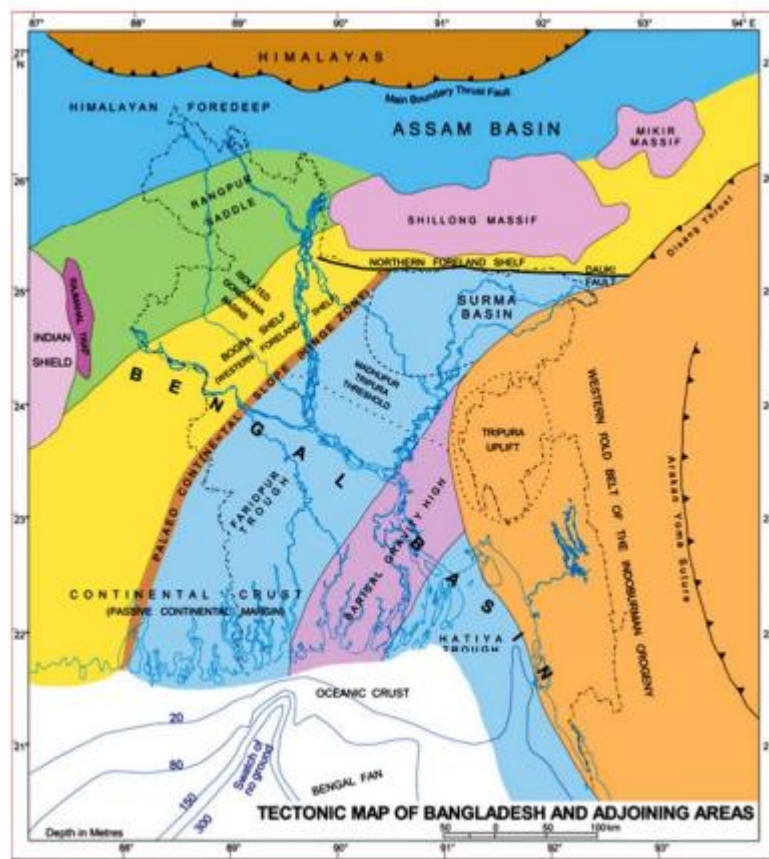
Figure 3.5: Tectonic Map of Bangladesh and Adjoining Areas (After Guha 1978, GSB 1990, Reimann 1993).

This three major tectonic zones are also classified by the Bengal Basin (ALAM, 1972; Mahmood Alam, 1989):

Bengal Basin

- Shield area
- Shelf
- Bengal foredeep
- Sub-Himalayan foredeep
- Mobile belt

Bengal foredeep:
- Faridpur trough
- Hatiya trough
- Sylhet trough
- Barisal high
- Madhupur high
- hinge zone
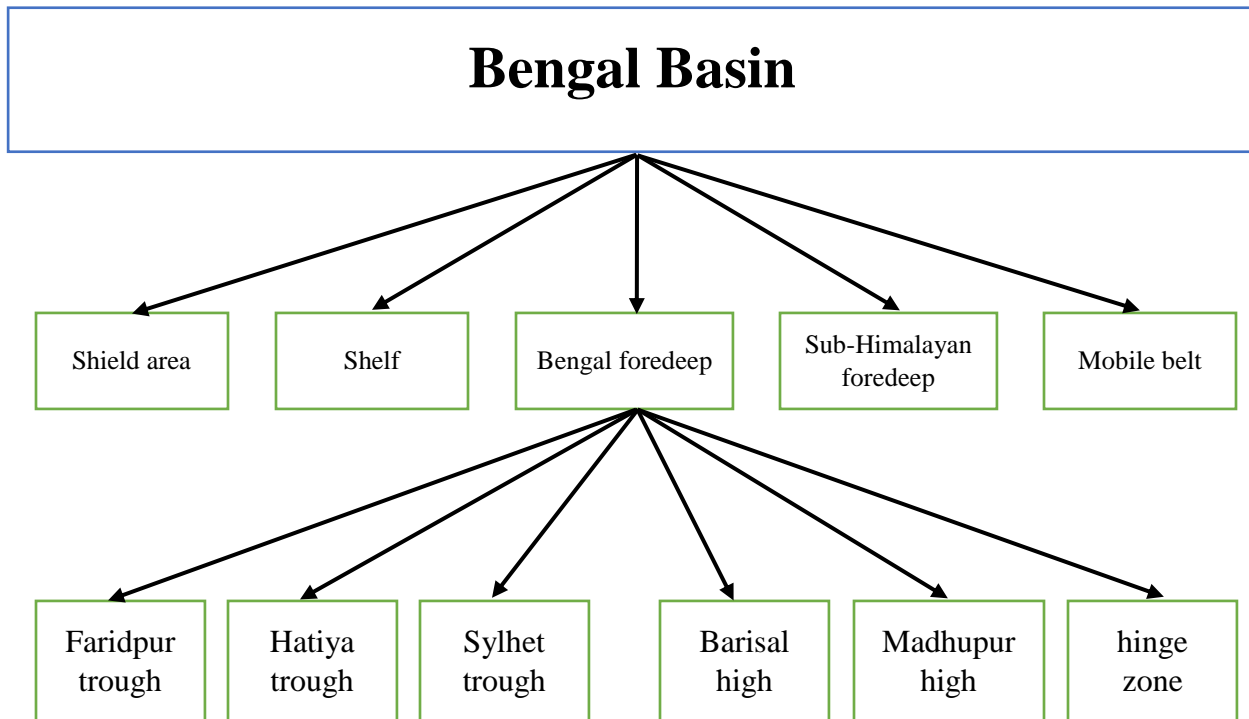
Sylhet district lies between 25˚04N to 25˚11 latitude & 92˚E to 92˚12E longitude. The investigated area lie within the Sylhet trough of Bengal foredeep. The Sylhet trough (Surma basin) is a sub-basin of the Bengal Basin in northeastern Bangladesh (Figure 3.8). The Sylhet trough has minimal topography (elevations of less than 5 to 20 m), is characterized by numerous lakes and swamps, and is actively subsiding. Estimates of the sediment thickness of the Sylhet trough range from about 13 to 17 km (Evans, 1964; Hiller & Elchi, 1984). The structure has discrete four way dip closure. The anticline is arcuate and slightly asymmetric; the asymmetry results in progressive shift of the crestal axis towards the southeast with increasing depth. The structure is influenced by several large faults recorded in seismic sections. These are reverse faults. The seismic section shows evidence of extentional collapse at the crest in shallower horizons and several normal faults can be traced (Akhtar, 2005). The eastern part of the Sylhet trough lies in the frontal zone of the IndoBurman ranges erogenic belt North-trending folds that are uplifted in the Tripura Chittagong fold belt plunge northward into the Sylhet trough subsurface (Figure 3.6). The folds decrease in amplitude westward and are not present west of about 91° (Lietz, 1982) where the Sylhet trough

merges with the main part of the Bengal Basin. The Sylhet trough is bounded to the north by the Shillong Plateau. The Shillong Plateau has an average elevation of about 1000 m and a maximum elevation of about 2000 m.
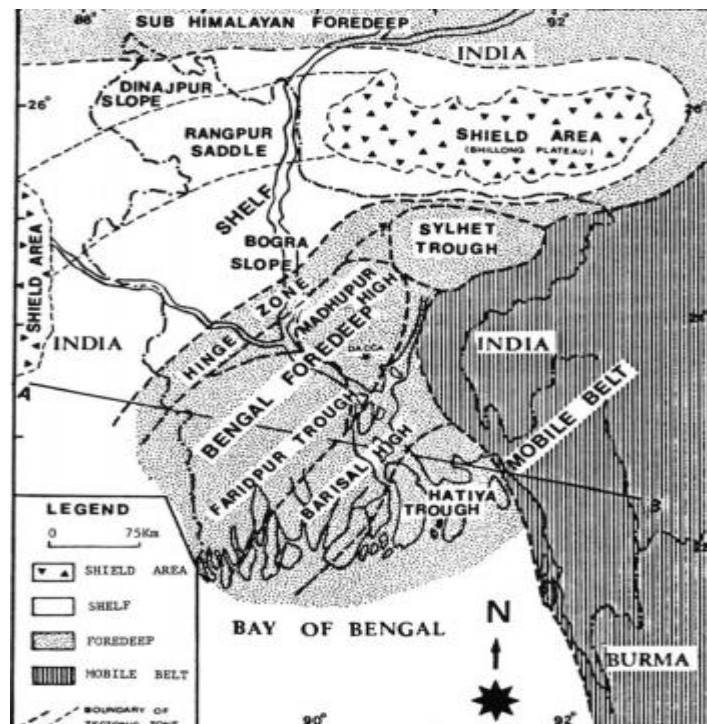
Figure 3.6: Sketch Map of the Structural Setting of the Bengal Basin Based on Bakhtine, 1966; Alam, 1972; Zaher and Rahman, 1980.

The northern limit of this subsiding trough is bounded by well-known Dauki fault. Dauki fault system is probably included in the same system of thrust faults, Disang and Naga of Assam. Faulting along the Shillong shelf zone coincided with rapid subsidence of Surma basin is during Miocene and later time.Thus, it has been postulated that there may be as much as 15-19 km of structural relief between the Shillong Plateau and the basement of the Sylhet trough (Hiller & Elchi, 1984). The Sylhet trough include the Atgram, Sylhet, Chattak, Kailas Tila, Beani Bazar, Patharia, Fenchuganj, Rasidpur and Habiganj (H. M. Z. Hossain, Roser, & Kimura, 2010).
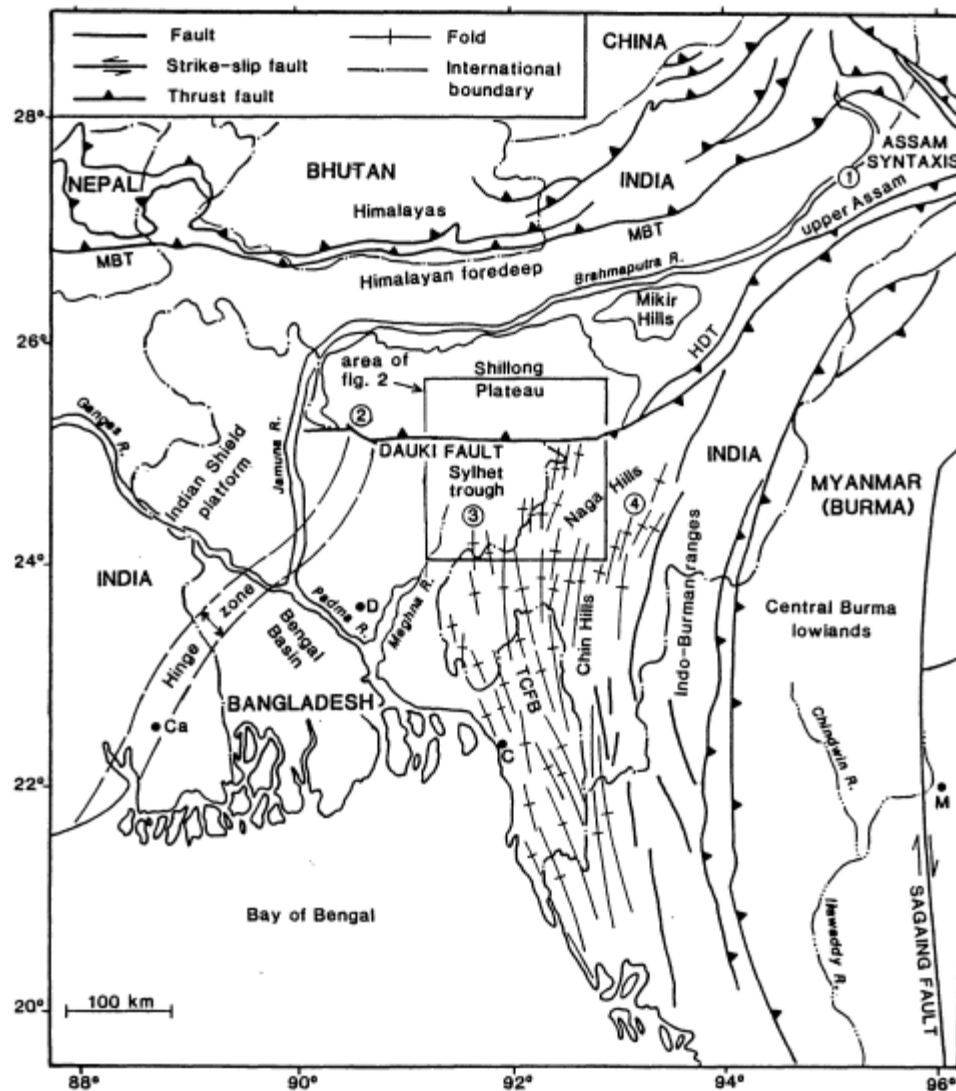
Figure 3.7: Schematic Map Showing the Location of the Sylhet Trough and Surrounding Tectonic Elements.

Tectonically, the structure of the Surma Basin and its adjoining areas are more active which is evidenced by the subsidence of the Surma Basin is about 30 to 40 ft within the last several hundred years. The Surma Basin is subsiding at present day at a rate of 21mm per year in central part and 1.5 to 2.5 mm per year in northern part. Theforced responsible for the development of the structure of the area are due to the under thrusting of the Indian plate towards NNE direction (A. Hossain, Hossain, & Abdullah, 2015)

3.5 Hydrogeological Setting

Geology, topography and climatic factors greatly influence the occurrence of groundwater in sylhet. By the same fact, geology and geological structures (faults, fractures and lithological contacts) play a great role in the movement and occurrence of groundwater in bengal basin area. The alluvial Holocene aquifers of the delta plain are prolific and found within shallow depth. Groundwater table levels in the Holocene aquifers are located close to the ground surface and fluctuate with the annual rainfall pattern. Locally, they are affected by heavy pumping and groundwater abstraction even though in most such places the system is fully recharged during the monsoon. The natural groundwater level amplitudes are in the order of 2-5 m over the year. As Bangladesh experiences a tropical monsoon climate with heavy rainfall during June to October the groundwater levels start to increase during May/June and decreases in September. The groundwater levels are lowest from January to March (BGS and DPHE 2000, Hasan et al. 2007). Several attempts have been made to describe the aquifers in the Bengal basin (UNDP 1982, EPC/MMP 1991, BGS and DPHE 2001, DPHE/DFID/JICA 2006, Mukherjee et al. 2008, 2007). Most aquifer models are based only on lithological description. EPC/MMP (1991) developed a four-layer model taking vertical head differences into account and assessing water balance. That model consisted of an upper aquitard, an upper shallow aquifer, a lower aquitard and a lower shallow aquifer. The alluvial aquifers of Bangladesh are commonly semi-confined to confined; their transmissivity, hydraulic conductivity and storage coefficients have been determined from a large number of pumping tests (BGS and DPHE 2000). Most aquifer tests have been analysed by classical methods and were based on partial penetration wells. Ravenscroft (2001) described three groundwater flow systems in Bangladesh, namely: i) a local system down to 10 m, this system is a product of local topography such as levees, local hills, terraces, haors and bils and rivers, ii) an intermediate flow system with flow-path down to a couple of 100 m driven by the 6 larger terraces, major rivers etc. and iii) a basin-scale flow system, down to a depth of several 1000 m. This system would include the whole Bengal Basin with its borders in the Tertiary Hills in the east, the Indian Shield in west, the Shillong Plateau in north and the Bay of Bengal in south. Groundwater flow patterns are affected because of heavy abstraction of groundwater for irrigation and drinking water purposes (Michael and Voss 2009a, b). Domestic drinking water wells in rural areas of Bangladesh are generally small diameter hand-pump wells. These wells can easily be installed to a depth down

to 100 m depending on local geological conditions. Based on population and per capita use, groundwater abstraction for domestic usage can be estimated. Approximately 50 l/day×person is used for industrial and domestic purposes in Bangladesh, in some areas of rural Bangladesh as much as 30 mm/yr can be abstracted for domestic purposes (Michael and Voss 2008). However groundwater abstraction for irrigation is about an order of magnitude higher in rural areas. In some areas of Bangladesh more than 600 mm groundwater/yr is used for irrigation purposes.

3.6 Sylhet City Corporation

Sylhet City Corporation area 27.36 sq km, located in between 24°51´ and 24°55´ north latitudes and in between 91°50´ and 91°54´ east longitudes. It is bounded by sylhet sadar upazila on the north, dakshin surma upazila on the south, Sylhet Sadar upazila on the east, Dakshin Surma and Sylhet Sadar upazilas on the west. It is consist of 27 Wards and 210 Mahallas with population 2,70,606. So, SCC represents one of the most densely populated areas and it is chalanging to SCC to fullfill the water demand of population in this area (Figure 3.8).
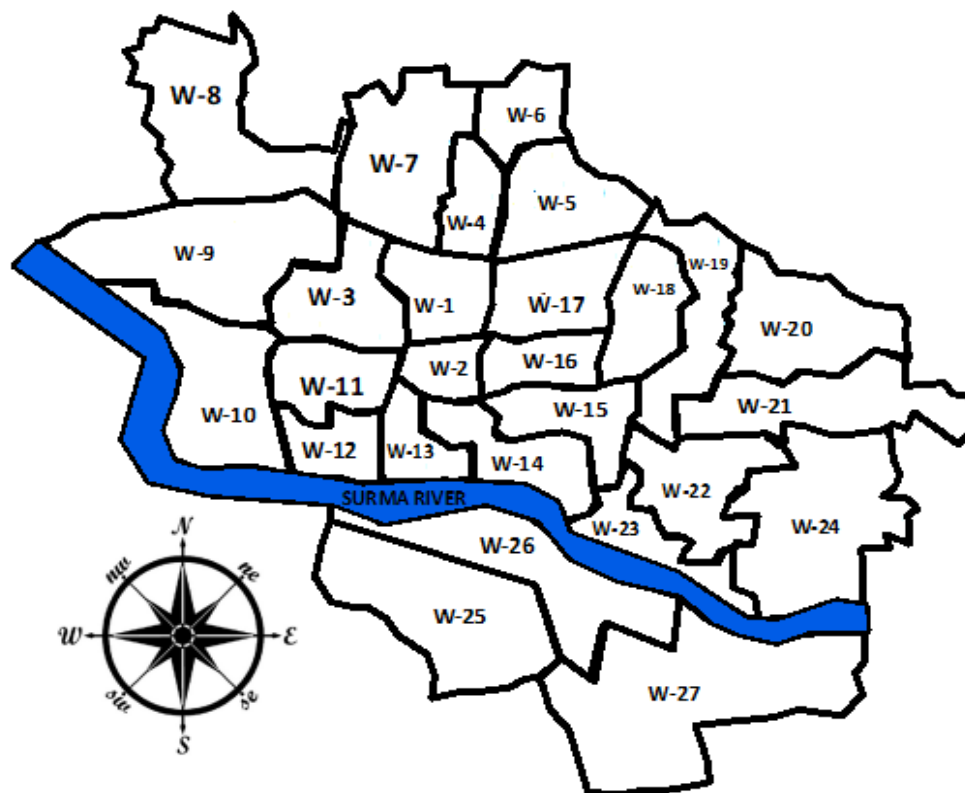
Figure 3.8: Administrative Wards of Sylhet City Corporation

3.7 Pump Location in SSC

At present Groundwater is considered as the most important source of water supply in Banglades. As a part of regular monitoring work by the Bangladesh Water Development Board (BWDB), the depths to groundwater are measured in piezometric observation wells situated in different parts of the study area. There are 20 observation pumps in the study area which are considered in this study in order to determine the groundwater quality (table 3.1). Also, the population density of Sylhet district is 990/ km^2 which indicates a tremendous pressure as it is the major freshwater source(Zafor et al., 2017).

Table 3.1 Geographic location of the groundwater sampling sites of SCC

ID	Ward	Pump Name	Latitude	Longitude
1	20	Raajpara Pump House	24.8768	91.8942
2	20	M. C. College (Near) Pump House	24.8837	91.8455
3	5	Baluchar New Pump House - 2	24.9088	91.8758
4	7	Nurani Bankola Para Pump House	24.9157	91.8654
5	8	Korer Para Pump House	24.9212	91.8444
6	9	Anser Camp Pump House	24.9073	91.8417
7	9	Akhalia Topoban Pump House	24.9085	91.8455
8	9	Baghbari Barnamala School Pump House	24.9060	91.8441
9	9	Khoshai Khana Pump House	24.9062	91.8399
10	1	Rikabi Bazar Pump House	24.8998	91.8632
11	6	Chowkidekhi Pump House	24.9196	91.8740
12	6	Badam Bagicha Pump House	24.9183	91.8723
13	1	Chowhotta Pump House	24.9013	91.8680
14	5	Darus salam Pump House	24.9094	91.8809
15	5	Hajaribagh Pump House	24.9086	91.8788
16	17	Kajitula Pump House	24.9035	91.8727
17	19	Shah Mijaji Mazar Pump House	24.9059	91.8869
18	19	Rai Nagar Mitali tila	24.9007	91.8864
19	14	Charar Par Pump House	24.8873	91.8781
20	18	Shonatula Pump House	24.9046	91.8832

The pumps used in this research in SCC are shown in (Figure 3.9) below and the name of location are shown in table x, 20 pumps through the area were used in this research.
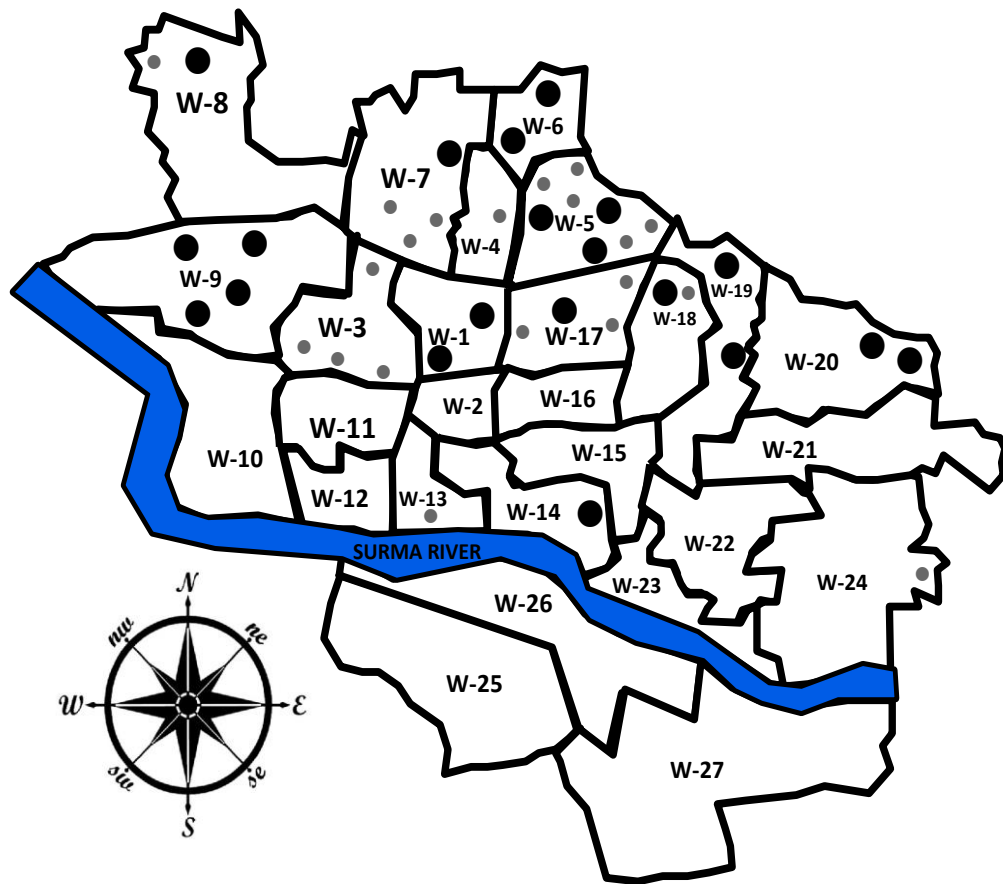
Figure 3.9: Groundwater Sampling Sites

CHAPTER IV

METHODOLOGY

In order to achieve the objectives of the research which aimed to conduct a holistic assessment of the quality of groundwater resource in SCC by using multivariate techniques. The following steps on the below show clearly the steps used to achieve the research objectives. Figure 4.1 shows the flowchart of the methods used in this research.

4.1 Data Collection and Processing

Water quality data was required to collect from different pumps that are operated by the authority of SCC.

The collected data is for the following parameters: Electrical conductivity (EC), Total dissolved solids (TDS), pH, Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Sodium (Na^+), Potassium (K^+), Chloride (Cl^-), ,Nitrate (NO_3^-), Sulphate (SO_4^{2-}), Carbonate (CO_3^{2-}) and Bi-Carbonate (HCO_3^-).

All tests were performed in the laboratory of Department of Civil & Environmental Engineering, SUST, Sylhet. The test results were analyzed and the maximum, minimum and average values were determined.

4.2 Statistical Methods

Water quality depends on variety of physico-chemical parameters and meaningful prediction or pattern recognition of the quality of water requires multivariate projection methods. For simultaneous and systematic interpretation, multivariate statistical techniques were used to interpret the water quality of the selected pumps and to give meaningful results that were not possible while assessing the data at a glance. The data have been analyzed by using RStudio software.

Assessment of Ground Water Quality in the Vicinity of Sylhet City, Bangladesh: A Multivariate Analysis

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┌─────────────┐
│ PRE-        │──────▶ Literature Review & Variable Selection ──────▶ Map Preparation
│ FIELDWORK   │
└─────────────┘

┌─────────────┐
│ FIELDWORK   │──────▶ Pump Selection ──────▶ Chemical Analysis
└─────────────┘

┌─────────────┐
│ DATA        │──────▶ Data Collections ──────▶ Validity Checking
│ COLLECTION  │
└─────────────┘

┌─────────────┐
│ DATA        │
│ ANALYSIS    │
└─────────────┘

        Hydrochemical Assessment          Statistical Analysis
                │                                 │
        Ground Water Quality Status       Univariate Statistics
                │                                 │
        Classification of Groundwater     Bivariate & Multiple correlation Analysis
                │                                 │
        Process Affecting Ground water    Factor Analysis
                │                                 │
        Environmental Impact              Cluster Analysis

┌─────────────┐
│ FINAL       │
│ ASSESSMENT  │
└─────────────┘
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Figure 4.1: General Structure of the Thesis

4.2.1 Descriptive Statistics

The descriptive statistics such as the Mean, Minimum value, Maximum value, Standard Deviation (SD) and Coefficient of Variation (CV) were computed for each parameter and used to study the variability of the water quality in all the pumps. Descriptive statistics gives the summary about the huge data. Through this we can observe the variation in parameters values from pump to pump and from year to year.

4.2.2 Assessment of Variability

An attempt was made to study the variability in water quality parameters, because the water quality parameters were varying from spot to spot, year to year and also pump to pump.

4.2.3 Correlation Coefficient Test

A correlation coefficient test were used to assess the degree of dependency of one cluster to another or how strong the relation is between two variables/parameters.

4.2.4 Pearson's Correlation Coefficient

In this study, Pearson's correlation analysis was utilized to calculate the correlation between two variables in order to characterize the relationship of the 12 water quality parameters for the 20 selected stations/pumps. For a correlation between variables x and y, the formula for calculating the sample Pearson's Correlation Coefficient is given by,

$$r = \frac{\sum_{i=1}^{n}(x_i - x)(y_i - y)}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}(y_i - \bar{y})^2}}$$

where x_i and y_i are the values of x and y for the ith individual.

4.2.5 Partial Correlation

Partial correlation is the measure of association between two variables, while controlling or adjusting the effect of one or more additional variables. Partial correlations can be used in many cases that assess for relationship, like whether or not the sale value of a particular commodity is

related to the expenditure on advertising when the effect of price is controlled. Formula for partial correlation coefficient for X and Y with controlling for Z

$$r_{yx.z} = \frac{r_{yx} - (r_{yz})(r_{xz})}{\sqrt{1 - r_{yz}^2}\sqrt{1 - r_{xz}^2}}$$

4.2.6 Data Standardization

Data standardization is essential in multivariate analysis; it increases the homogeneity of a dataset and enhances its normality, and therefore ensures that all parameters are close in terms of their variances (Sandow Mark Yidana et al., 2010). The data were therefore standardized to their corresponding z-scores as in Equation below, in order to achieve the objectives of normal distribution and homogeneity.

$$Z = \frac{X - \mu}{s}$$

Where, *x is the data,* μ *is the mean and s is the standard deviation of the datasets.*

4.3 Identify Different Factors

An attempt was made to identify the factors among the 12 water quality parameters which are contributing more to the total variability in the water quality.

4.3.1 Factor Analysis

Factor analysis (FA) is a multivariate statistical technique, which gives the general relationship between measured variables by showing multivariate patterns that may help to classify the original data. FA is designed to transform the original variables into new uncorrelated variables called factors, which are linear combinations of the original variables. It is a dimension reduction technique and suggests how many variables are important to explain the observed variances in the data.

Factor analysis was also applied to the data to determine and rank the sources of variation in the hydrochemistry. In the factor analysis, 'principal components' method was selected as the solution method. The total number of factors generated from a typical factor analysis indicates the total

number of possible sources of variation in the data. Factors are ranked in order of merit. The first factor or component has the highest eigen value and represents the most important source of variation in the data. The last factor is the least important process contributing to the chemical variation. Factor loadings are interpreted as correlation coefficients between the variables and the factors.

This treatment provides a small number of factors that usually account for approximately the same amount of information as the original set of observations. The observed variables are modeled as linear combinations of the potential factors including the error terms as follows:

$$Z_{ij} = a_1f_{1j} + a_2f_{2j} + ... + a_mf_{mj} + e_{ij}$$

Where

Z_{ij}= Measured variable, a_i= ith Factor loading, f_{ij}= Factor score, e_{ij}= Error term
i=1, 2, 3,...m, j=1, 2, 3,...p

4.3.2 Cluster Analysis

Cluster analysis is a multivariate technique first used by Tryon, (1958) which attempts to combine cases into groups when the group membership is not known prior to the analysis. That is, cluster analysis is a technique for grouping individuals or objects into unknown groups. These groups are relatively homogeneous within themselves and heterogeneous between each other, on the basis of a defined set of variables. These groups are called clusters.

In biology, cluster analysis has been used for decades in the area of taxonomy, where living things are classified into arbitrary groups on the basis of their characteristic groups. The classification proceeds from the most general to the most specific in steps. The most general classification was kingdom followed by phylum, subphylum, and class, etc. A similar approach has been successfully applied to the assessment of water quality (S. Shrestha & Kazama, 2007).

4.3.2.1 Clustering Methods

The commonly used methods of clustering fall into two general categories. (i) Hierarchical (ii) Non hierarchical. Hierarchical clustering is the most commonly used method of clustering; which

proceed by either a series of mergers or a series of successive divisions. In the initial stage no need to take decision regarding the number of clusters.

4.3.2.2 Hierarchical Clustering

Hierarchical Clustering is a method of cluster analysis, which needs to build a hierarchy of cluster. Strategies for hierarchical clustering generally fall into two types:

(a) Agglomeration: This is a "bottom up" approach in which each observation starts in its own cluster and pairs of clusters are merged as one moves up the hierarchy.

(b) Divisive: This is a "top down" approach in which all observations start in one cluster and splits one performed recursively as one moves down the hierarchy.

Hierarchical Cluster Analysis (HCA) is a multivariate statistical analysis and powerful classification method to divide water chemistry samples into similar groups and useful for data reduction and to check the overlap/continuity of clusters or similarities within the water chemistry data (Güler, Thyne, McCray, & Turner, 2002). Moreover, it is independent and quantitative method allowing groundwater classification into coherent groups that may be identified based on aquifer lithology, storage time or human impact and correlation with water quality parameters (Cloutier, Lefebvre, Therrien, & Savard, 2008). HCA provides complete analysis information in organized format and uses for interpretation of hydrogeochemical processes by formulating hypothesis (Geleta, 2012). However, the method does not provide cause-and-effect relationships of water chemistry (Güler et al., 2002). HCA is used to figure out the water chemistry evolution and to conduct geochemical modelling among different groups and subgroups (Lu, Tang, Chen, & Chen, 2015).

The main objective of this classification approach is to determine the chemical relationships and associated chemical processes between water samples. Moreover, samples with similar chemical behaviour can be define in terms of similar geologic, climate, resident time, infiltration, recharge area, flow and infiltration path and hydrogeochemical processes history (Geleta, 2012). In HCA classification, data log-transformation and standardization is required for equal weighting because

parameters with higher or smaller variance during their distribution affects the Euclidean distance calculation (Lu et al., 2015).

4.3.2.3 Euclidean Distance

Euclidean distance is the most commonly used measure of distance in two dimensions, one for the plot of observations in a scatter diagram, and another to measure the distances between the pairs of points. Generally, the following equation can be used as a distance measure:

$$d(x,y) = \Sigma_i\, (x_i - y_i)^2$$

It divides datasets into hierarchies based on similarity or dissimilarities in the field. In this study the Qmode HCA, groups pumps locations into clusters. The method is used for clustering is Squared Euclidean Distance which is the distance between two items, x and y, is the sum of the squared differences between the values for the items.

4.2.3.4 Dendrogram Presentation

The Dendrogram is a graphical representation of the results of hierarchical cluster analysis. This appears in the form of a tree like plot where, each step of hierarchical clustering is represented as a fusion of two branches of the tree resolving into a single one. The branches represent clusters obtained on each step of hierarchical clustering.

The HCA resulted in a dendrogram which is a presentation of the groundwater associations in the area. Samples with similar spatial characteristics and relationships are clustered together at low linkage distances, whilst dissimilar samples are linked at higher linkage distances.

4.4 Hydrochemical Data Reliability Check

The water quality variables data, which were collected from the different sources during the fieldwork and/or obtained from laboratory analysis, were checked for their accuracy using anion-cation balance. A solution must be electrically neutral i.e. the sum of cations in meq/l should equal the sum of the anions in meq/l (Hounslow, 1995b).Prior to the interpretation of geochemical data, it is instructive to carry out an initial check of the quality of the data. This was done based on the Charge Balance Error (CBE) by means of equation (1).

$$\text{CBE } (\%) = \frac{\sum \text{Cations} - \sum \text{Anions}}{\sum \text{Cations} + \sum \text{Anions}} * 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

which is based on the electroneutrality condition, where Σcations and Σanions represent the sum of the concentrations of major cations and major anions, respectively and are all expressed in milliequivalent units. The summation of all cations used to determine the charge balance error is presented in table 4.1. According to Hounslow, (1995b), if the electrical balance calculated is less than 5% then the analysis is assumed to be good and if it is greater than 5% the analysis is supposed to be poor, or some missed constituents are not include in the calculation or the water is very acidic. But sometimes up to 10% is acceptable in dilute and saline water due to some errors during measurement (Fetter, 2001). For the present study, the hydrogeochemical data from the laboratory analysis work were almost greater than 10%.

4.5 Graphical Methods

4.5.1 Stiff diagrams

Stiff diagrams show the composition of a single cluster, in terms of common cations and anions, with concentration represented in electrical equivalents. Stiff diagrams can be generated for each member of a cluster. In a Stiff diagram a polygonal shape is created from four parallel horizontal axes extending on either side of a vertical zero axis. For a water sample, cations are plotted in *milliequivalents* per liter on the left side of the zero axis, one to each horizontal axis. Similarly, for the same sample, anions are also plotted in *milliequivalents* per liter on the right side, one to each horizontal axis. Stiff patterns are useful in making a rapid visual comparison between water from different sources.

This diagram was created by the Grapher (graphing software for water analysis) version 13.

4.5.2 Collin's Bar Diagram

It is a vertical bar diagram. Each sample is represented by two bars, one for cations and the other for anions. The height of each bar is proportional to the total concentration of cations or anions in meq/l. As the sum of this cations should be equal to the sum of the anions, both concentration of cations and anions can be plotted either in absolute values or as the percentage of the total equivalent per million (epm) or milligram equivalents per litre (meq/l). By this diagram, it is

possible to see, by inspection, the fulfillment of the electroneutrality condition for each sample of water.

This diagram was created by the Rockware Aq.QA (The spreadsheet for water analysis) version 1.1.

4.5.3 Gibbs Diagram

Based on the data from the overall world (which produced a boomerang-shaped envelope of data), Gibbs concluded that three machanisms – atmospheric precipitation, rock dominance, and the evaporation-crystalization process – are the major factors controlling the composition of the dissolved salts (ions) of the world's waters. Other second-order factors, such as relief, vegetation, and composition of material in the basin dicate only minor deviations within the zones dominated by three prime factors.

Gibbs Diagram, therefore, assesses the controlling machanism(s) (i.e. the major factor(s)) of the water chemistry in terms of dissoleved ions present in water. The assessment is done by plotting hydrochemical data according to the variation in the ratios of $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ in meq/l as function of logarithmic value of TDS (Total dissolved salts) in mg/l. This is because the major cations that characterize the end-members of the worlds water are Ca for freshwater bodies and Na for high-saline water bodies. In addition, the three major machanisms – atmospheric precipitation, rock dominance, and the evaporation-crystallization process- that control world water chemistry is borne out by a consideration of the major anions of the worlds water: cloride (Cl^-) and bicarbonate (HCO_3^-). Thus, the Gibbs diagram is widely used to establish the relationship of water composition and aquifer lithological characteristics.

The use of Gibbs graphs for the identification of governing processes may yield limited information. The application of the diagram, for example, to groundwaters should be considered in the broader context of processes and hydrogeochemistry which differ significantly from surface water (based on which Gibbs developed the diagram) chemistry processes, due to longer residence times and more variable geochemical environments (e.g. redox conditions) of many groundwater systems. Overall, the use of interpretations linked to the original Gibbs diagram for defining groundwater geochemical processes may oversimplify the interpretation of aquifer systems and overlook important processes. Instead, other more sophisticated diagrams (e.g. Piper plot) and

analyses (e.g. isotope geochemistry) will lead to improve the understanding of hydrochemical processes.

4.5.4 Schoeller diagram

Schoeller diagrams represent the compositions of any number of clusters in diagrams. It can visually show the average of each clusters and also it help to decide which is the best number of clusters.when the compositions are near each other and cross each other, this mean that there is more needed clusters. When the compositions is far from each others, this mean that more clusters may be needed.

Schoeller diagram avoid some of the shortcomings of the ion-triangles and derivatives (Piper). The schoeller diagram is a histogram-type of diagram showing the log concentrations of solutes (the minors component in a solution, dissolved in the solvent) in meq/l from a number of samples and shows the effects of mixing of waters. It is a semi-logarithmic plot, in which on the abcissa (on arithmetic scale), the various cations and anions are arranged in the order. In a typical Schoeller diagram the concentrations of the main ionic constituents of each water sample (SO_4^{2-}, HCO_3^-, Cl^-, Mg^{2+}, Ca^{2+}, Na^+ /K^+) in meq/l are plotted on six equally spaced logarithmic scales, and points so plotted are then joined by straight lines. This diagram gives absolute concentration of different ions and not their relative concentration. Slopes of lines between constituents represent concentration ratios. Because of the use of logarithmic scale, if a straight line joining two points representing ionic concentrations in a water sample is parallel to another stratight line joining the other two points of the same two ions in another water sample, the ratio of those ions in both samples are equal. Finally, the Schoeller diagram can be so adapted that it may be utilized to determine the degree of saturation of calcium carbonate and calcium sulphate in groundwater. That is, this diagram is used to directly determine the saturation indices of groundwaters with respect to minerals such as calcite and gypsum.

Advantages:

- It is widely used for comparing water analysis.
- It can be adapted to determine the degree of saturation in water.
- It shows the concentration difference among various water analysis.
- A wide range of concentrations can be shown, because logarithmic values are used.

Disadvantages:

- It does not show the water type directly.

- Use only with continuous data.

- The number of samples that can be illustrated at one time is limited because of the lines.

This diagram was created by the Rockware Aq.QA (The spreadsheet for water analysis) version 1.1.

4.5.5 Wilcox's diagram

For judging the suitability of water quality for irrigation, Wilcox proposed a diagram with respect to a combination of EC and sodium percentage ($\%Na^+$). This combination classifies the diagram into five zones of excellent to good with EC values less than 700 micromhos/cm ($<700\mu S/cm$), good to permissible to doubtful, doubtful to unsuitable and unsuitable, with increasing salinity hazard and sodium hazard for irrigation.

The sodium percentage ($\%Na^+$) is calcualted in meq/l from $\frac{Na^+ + K^+}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} * 100$. Sodium is important in classifying irrigation water, because sodium reacts with soil, thereby reducing the permeability.

4.5.6 US Salinity Laboratory (USSL) diagram

Wilcox and staffs of US Salinity Laboratory proposed a diagram, which is called US Salinity Laboratory (USSL) Diagram, for evaluating the suitability of water for irrigation use. There is a significant relationship between sodium adsorption ratio (SAR) values for irrigation water and the extent to which sodium is absorbed by soils. If water used for irrigation is high in sodium and low in calcium, the cation exchange complex may become saturated with sodium, which can destroy the soil structure owing to dispersion of clay particles.

US Salinity Laboratory (USSL) proposed an important criterion based on salinity hazards. The total dissolved solids, measured in terms of specific electrical conductance (EC), gives the salinity hazard of irrigation water. Besides the salinity hazard, exclussive sodium content in water renders it unsuitable for soils containing exchangeable Ca^{2+} and Mg^{2+} ions. If the percentage of Na^+ to $Ca^{2+} + Mg^{2+} + Na^+$ is considerably above 50 in the irrigation water, soils containing exchangeable

calcium and magnesium take up sodium in exchange for calcium and magnesium causing deflocculation and impairment of the titlth and permeability of soils. The sodium hazard in irrigation water is evaluated by determining SAR, which is given as,

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

Where the concentration are expressed in meq/l.

The US Salinity Laboratory classification of irrigation water with respect to salinity and sodium hazard is shown in the above figures. US Salinity Laboratory diagram contains four classes of each salinity and alkalinity: low, medium, high and very high. Thus, a water sample may fall in any of the total sixteen classes based on the combination of salinity and alkalinity.

4.5.7 Mineral Saturation Index

Finally, we examined the mineral saturation index (SI) of the brine samples, as this parameter characterizes the state of the groundwater and minerals and ultimately allows determination of the saturation level of the dissolved minerals within the groundwater. More specifically, when the SI is > 0, the mineral is in a supersaturated state and will precipitate out, while, when SI is < 0, the mineral is in an unsaturated state. An SI of 0 indicates that the minerals are in equilibrium. In the case of halite, a high solubility was observed, and the multicomponent halite-containing brine exhibited a high degree of salinity and was easily precipitated, thereby indicating that a continuous salt-in/salt-out process took place during the brine extraction process. Indexes of saturation in calcite, gypsum, anhydrite, sylvite and thenardite were calculated by using PHREEQC hydrochemical simulation software.

4.6 Parameters Used

The Parameters used is the common physiochemical parameters which often is measured by the literature stated above. The used parameters are presented below and little description about it.

1. **Total Dissolved Solids (TDS):** TDS comprise inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulfates) and small amounts of organic matter that are dissolved in water. TDS in drinking-water originate from natural sources, sewage, urban runoff and industrial wastewater.

   TDS is calculated by adding the mass of ions plus SiO_2

TDS = sum of ions + SiO_2

2. **Electrical Conductivity (EC):** Conductivity is a measure of the ability of water to pass an electrical current. Conductivity in water is affected by the presence of inorganic dissolved solids such as chloride, nitrate, sulfate, and phosphate anions (ions that carry a negative charge) or sodium, magnesium, calcium, iron, and aluminum cations (ions that carry a positive charge).

   Conductivity, which is also called electrical conductivity (EC) is a reciprocal of the resistance in Ohms between the opposite faces of a 1 - cm cube of an aqueous solution at specified temperature (usually 25^0C). It is temperature dependent and the international it is Siemens/m that is numerically equivalent to the Mhos/m (Hounslow, 1995a; Mazor, 1991).

   Conductivity is a good estimator of TDS because TDS in mg/l is proportional to the conductivity in micromhos.
   TDS (mg/l) = A * conductivity (μMhos/cm), where A = 0.54 -0.96 usually (0.55-0.76)
   Conductivity may also be estimated from the sum of cation expressed in meq/l.
   Conductivity (μMhos/cm) = sum cations (meq/l) * 100

3. **Potential of Hydrogen (pH):** pH is a measure of how acidic/basic water is. The range goes from 0 - 14, with 7 being neutral. pHs of less than 7 indicate acidity, whereas a pH of greater than 7 indicates a base. pH is really a measure of the relative amount of free hydrogen and hydroxyl ions in the water. Water that has more free hydrogen ions is acidic, whereas water that has more free hydroxyl ions is basic. Since pH can be affected by chemicals in the water. The pH of a solution indicates effective concentration of the hydrogen ion $H+$.

   The units of pH are the negative logarithm of hydrogen ion concentration, expressed in moles per litter.

$$pH = -\log(H^+)$$

4. **Calcium (Ca^{2+}):** The presence of calcium in water supplies results from passage over deposits of limestone, dolomite, gypsum, and gypsiferous shale. Calcium contributes to the total hardness of water.

5. **Magnesium (Mg^{2+}):** Magnesium occurs commonly in the minerals magnesite and dolomite. Magnesium is Important contributor to the hardness of a water, magnesium salts break down when heated, forming scale in boilers.

6. **Sodium (Na^+):** Sodium salts (e.g., sodium chloride) are found in virtually all food (the main source of daily exposure) and drinking-water. It should be noted that some water softeners can add significantly to the sodium content of drinking-water.

7. **Chloride (Cl^-):** Chloride in drinking-water originates from natural sources, sewage and industrial effluents, urban runoff containing de-icing salt and saline intrusion. Excessive chloride concentrations increase rates of corrosion of metals in the distribution system, depending on the alkalinity of the water. This can lead to increased concentrations of metals in the supply.

8. **Nitrate (NO_3^-):** Nitrate can reach both surface water and groundwater as a consequence of agricultural activity (including excess application of inorganic nitrogenous fertilizers and manures), from wastewater disposal and from oxidation of nitrogenous waste products in human and animal excreta, including septic tanks. Some groundwater may also have nitrate contamination as a consequence of leaching from natural vegetation.

9. **Sulfate (SO_4^{2-}):** Sulfates occur naturally in numerous minerals and are used commercially, principally in the chemical industry. They are discharged into water in industrial wastes and through atmospheric deposition; however, the highest levels usually occur in groundwater and are from natural sources.

10. **Potassium (K^+):** Potassium is an essential element in both plant and human nutrition, and occurs in groundwaters as a result of mineral dissolution, from decomposing plant material, and from agricultural runoff.

11. **Alkalinity:** Alkalinity of water may be due to the presence of one or more of a number of ions. These include hydroxides, carbonates and bicarbonates.

12. **Sodium Adsorption ratio (SAR):** SAR measures the amount to which sodium in irrigation water replaces the adsorbed ($Ca^{2+} + Mg^{t+}$) in the soil clays, and can damage the soil structure (Hounslow, 1995a).

$$SAR = \frac{Na}{\sqrt{(Ca + Mg)/2}}$$

13. **Saturation index (SI):** When a mineral is dissolved in water, the cations and anions of which it is composed will attain a specific concentration. Their sum essentially equals the solubility of that mineral and it used to evaluate departure from equilibrium.

$$\text{Saturation index (SI)} = \log K_{sat}$$

where IAP is ion activity product and K_{sat} is solubility product t.

4.7 Software Used

In this study many software programs were used besides the MS EXCEL.

ArcMap: ArcMap is the main component of Esri's ArcGIS suite of geospatial processing programs, and is used primarily to view, edit, create, and analyze geospatial data. It is an extensive and integrated software platform technology for building operational GIS. ArcGIS comprises four key software parts: a geographic information model for modeling aspects of the real world; components for storing and managing geographic information in files and databases; a set of out-of-the-box applications for creating, editing, manipulating, mapping, analyzing and disseminating geographic information; and a collection of web services that provide content and capabilities to networked software clients. ArcMap allows the user to explore data within a data set, symbolize features accordingly, and create maps(Shekhar, Xiong, & Zhou, 2013). ArcGIS has very wide

ranging functionality packaged up into a generic set of menu driven GIS applications that implement key geographic workflows. The applications deal with geographic data creation, import and editing, data integration and management, data manipulation and organization, and data analysis, mapping and reporting (Shekhar et al., 2013).

The geographic information that is loaded into ArcMap can be viewed in two ways: data view and layout view.In data view, the user can interact with the geographic information presented, and the map elements are hidden from view. Most projects begin in this view, and continue to the layout view for final editing and production. While in the layout view, the user can incorporate a number of useful features such as scale bars and north arrows. These elements are crucial to map-making, and provide clients with appropriate reference information.

PHREEQC-2

PHREEQC version-2 performs a wide variety of low-temperature aqueous geochemical calculations and simulates a variety of reactions and processes in natural waters or laboratory experiments. Moreover, the model provides an information about speciation, saturation and oxidation/reduction of a solution which is the first step in interpreting water chemistry using thermodynamic approach (Hounslow, 1995b). PHREEQC interactive for Windows uses Aquachem samples as input solutions for modeling.

Rockware Aq.QA:

Aq.QA was created with water engineers and aqueous geochemists in mind or for that matter, anyone who keeps water chemistry data in a spreadsheet. AqQA is used to (www.Rockware.com) to   :

- Create Piper diagram, Stiff diagram, Ternary, and 8 other plot types
- Instant unit conversion -- shift effortlessly among units
- Check water analyses for internal consistency
- Manage water data in a spreadsheet

Grapher: Grapher is easy to understand technical graphing software for anyone who needs to create publication-quality graphs quickly and easily. With Grapher software, graphing is accurate and fast. This program creates and displays graphs in 2D, 3D, and any other spatial dimension beyond the third (hyperspace). Quickly create stunning and informative 2D and 3D graphs. Choose from over 80 different graph types and communicate your message to any audience with Grapher's extensive graphing abilities. Click on the below graph groupings to see the different plots Grapher creates.

EasyQuim: This command enables retrieving the information and exporting data into program EasyQuim, which is a free software developed as a plug-in in MS Excel (thus offering a great portability) to draw convectional graphical methods (Piper, salinity, Schoeller-Berkaloff and modified Stff diagrams) as well as tables for CBE, icb index, SAR index and ionic ratios. Finally, the code supplies input data exportable to other GIS platforms to visualise Stiff diagrams.

Aquachem: Aquachem is used as a water quality database with functionality for numerical analysis, graphical presentation and modeling of water quality data. In addition, it has a built-in link to the geochemical modeling program PHREEQC for calculating equilibrium concentration or activities of chemical species and saturation indices of phases in a solution (Schlumberger, 2006). Moreover, it is used to cluster the hydrogeochemical data into distinct groups of water types and source rock deduction by plotting using piper and stiff diagram.

CHAPTER V

HYDROCHEMICAL ASSESSMENT

The quality of groundwater reflects the mineralogical composition of the rocks with which the water has been in contact. As water moves slowly through the subsurface its composition gradually changes, reflecting the increasing saturation of some ions or the end products of various rock-weathering interactions. This chapter examines the general groundwater chemistry of the area, and the processes affecting the groundwater chemistry.

5.1 Data Sets

Water quality sampling and analysis for the following parameters were done during the field work period. 20 pumps samples were analyzed for major ion concentrations: Total Hardness (Calcium Ca^{2+} and Magnesium Mg^{2+}), Alkalinity (Carbonates CO_3^{2-} and Bicarbonates HCO_3^-), Chlorides (Cl^-), Sulphates (SO_4^{2-}), Nitrates (NO_3^-). Physical elements: pH and EC were measured in situ.

5.2 Measurement Scale

Milliequivalent: A milliequivalent (mEq), which is $\frac{1}{10000}$ th of an equivalent, is the unit of measure often used for electrolytes (an electrolyte is a substance that produces an electrically conducting solution when dissolved in a polar solvent, such as water). It indicates the chemical activity, or combining power, of an element relative to activity of 1 mg of hydrogen (as 1 Eq of Hydrogen is equal to 1g of Hydrogen). Concentrations of different dissolved chemical compounds in a water body are usually expressed in milligrams per litre (mg/l). This expression of concentration is very convenient. However, when such dissolved chemical compounds (e.g NaCl, KCl, MgSO4) are electrolytes and dissociate/separate in water to form cations and anions, it is necessary to express their cations and anions in the milliequivalent (mEq or meq). Such expression is used to assert the concentration or the strength of cations and anions separately. This expression is frequently used in different diagrams such as Stiff diagram, Piper diagram, Durov diagram, etc.

(Equivalent concentration) = (mass concentration)* (ionic charge) / (molecular weight)

$$i.e.\ Concentration\ in\ mEq/l\ = \frac{Concentration\ mg/l * valance}{Formula\ weight\ of\ the\ ion}$$

5.3 Reliability Checking for Hydrochemical Data

Only 10 out of 20 water quality data fulfilled the acceptable requirement of < 10%. It is apparent from most samples that mass balance of ionic species was not achieved. While most charge balance error from various locations waters was reasonable, that of pump-1 was way off 42.64%.

Table 5.1: Charge Balance Error of Various Water Samples

ID	∑Cations	∑Anions	CBE (%)	Data Quality
P1	3.8368	1.5428	42.64	Poor
P2	4.3517	2.575	25.65	Poor
P3	2.9417	1.8218	23.51	Poor
P4	4.0202	2.533	22.69	Poor
P5	2.2403	2.1759	1.46	Good
P6	3.3581	3.0938	4.10	Good
P7	3.1585	3.3609	-3.10	Good
P8	3.7967	3.2905	7.14	Good
P9	4.1934	3.4974	9.05	Good
P10	3.6034	2.8435	11.79	Poor
P11	2.6395	2.6099	0.56	Good
P12	3.9453	2.6107	20.36	Poor
P13	3.3587	2.3794	17.07	Poor
P14	3.0233	2.3248	13.06	Poor
P15	2.3251	2.237	1.93	Good
P16	2.1972	2.149	1.11	Good
P17	2.6638	1.597	25.04	Poor
P18	3.6318	2.2634	23.21	Poor
P19	3.3728	3.5694	-2.83	Good
P20	2.8865	2.4228	8.73	Good

This may suggest different minerals buffer could be controlling the water of this location. Therefore, future studies should focus on the ionic contributions of these important species. Despite these obvious descrepancies, the data provided in this study are of high quality. In any case, there is always some error in the measurement of cation and anion concentration. More importantly, this is one of the very first research study to interface computational methods and experimental techniques in water analysis in Sylhet City Corporation (Table 5.1).

Furthermore, results of this analysis indicate samples with a complete set of major ionic data have charge balance errors ranging from -3% to 42 %, with an average value of 12%. The magnitude of the charge balance error was above the acceptable limit in 10 samples/pumps. As shown in Figure 6a-6t, all samples show an overbalance in favour of the cations, which suggests

that not all significant anions are represented in the ion balance calculation. This suggests that either there are significant aions that are not included in the major ion analysis suite, or that there is an inconsistent data quality issue related to sample storage or laboratory analysis.

5.4 Display of Water Quality Data

5.4.1 Stiff Diagram

In this research, the concentrations of the major ions were used to describe the different groundwater associations depicted by the different pumps (Figure 5.1a-5.1t).

Stiff Diagram for Pump-1:

Stiff diagram of pump-1 shows that the Mg cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-1 is the Mg–HCO_3 water type.
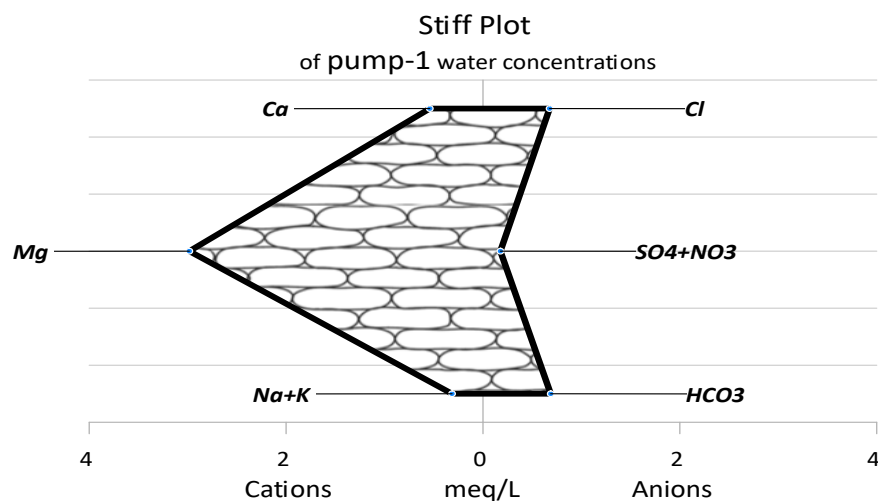

Figure 5.1a: Stiff Diagram for Pump-1

Stiff Diagram for Pump-2:

Stiff diagram of pump-2 shows that the Mg cation is the highest among the cations whilst the Cl^- is the predominant anion. This means that the most predominant water type in pump-2 is the Mg–Cl water type.
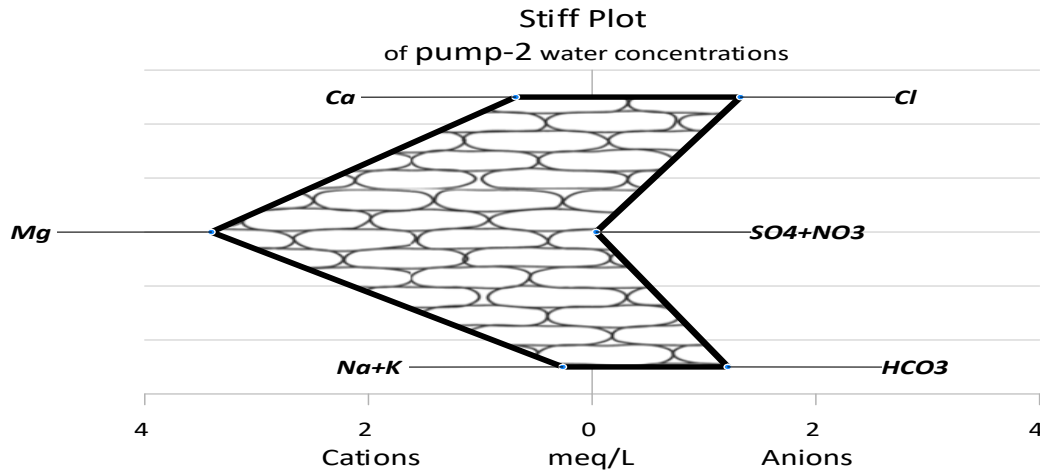
Figure 5.1b: Stiff Diagram for Pump-2

Stiff Diagram for Pump-3:

Stiff diagram of pump-3 shows that the Mg cation is the highest among the cations whilst the Cl⁻ is the predominant anion. This means that the most predominant water type in pump-3 is the Mg–Cl water type.

Figure 5.1c: Stiff Diagram for Pump-3

Stiff Diagram for Pump-4:

Stiff diagram of pump-4 shows that the Mg cation is the highest among the cations whilst the Cl⁻ is the predominant anion. This means that the most predominant water type in pump-4 is the Mg–Cl water type.
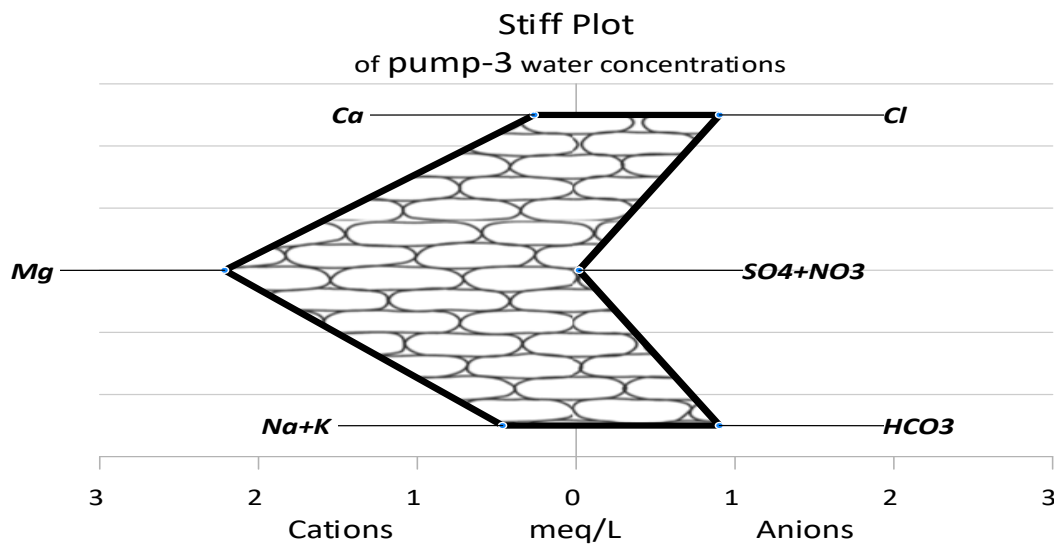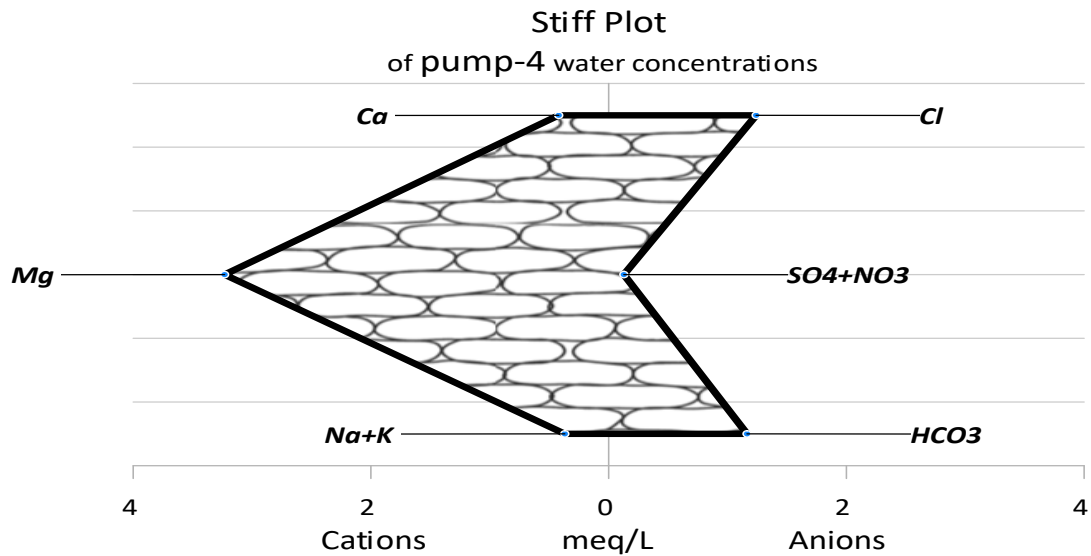
Stiff Plot
of pump-4 water concentrations

Ca ————————— Cl

Mg ————————— SO4+NO3

Na+K ————————— HCO3

4	2	0	2	4
Cations		meq/L		Anions

Figure 5.1d: Stiff Diagram for Pump-4

Stiff Diagram for Pump-5:

Stiff diagram of pump-5 shows that the Mg^{2+} cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-5 is the Mg–HCO3 water type.

Stiff Plot
of pump-5 water concentrations

Ca ————————— Cl

Mg ————————— SO4+NO3

Na+K ————————— HCO3

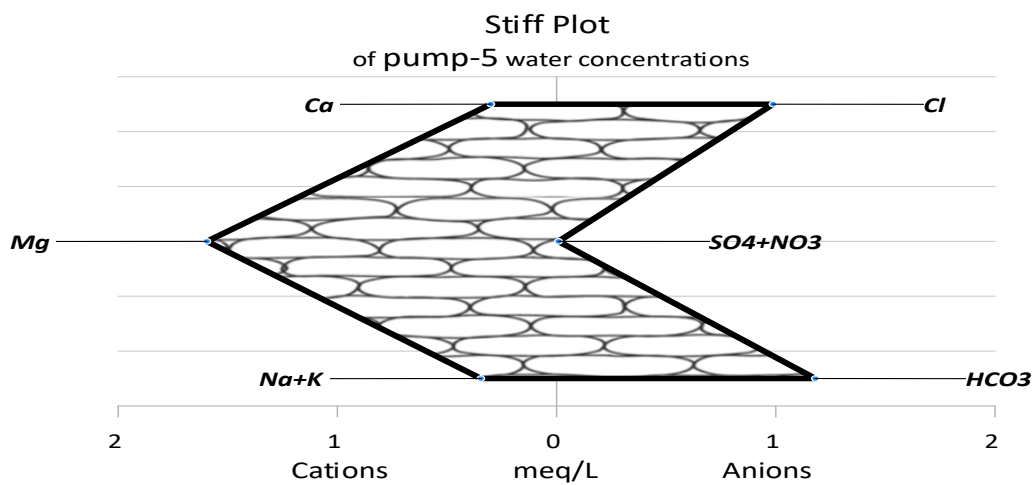| 2	1	0	1	2
Cations		meq/L		Anions

Figure 5.1e: Stiff Diagram for Pump-5

Stiff Diagram for Pump-6:

Stiff diagram of pump-6 shows that the Mg cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-6 is the Mg–HCO3 water type.

Figure 5.1f: Stiff Diagram for Pump-6

Stiff Diagram for Pump-7:

Stiff diagram of pump-7 shows that the Mg^{2+} cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-7 is the Mg–HCO3 water type.
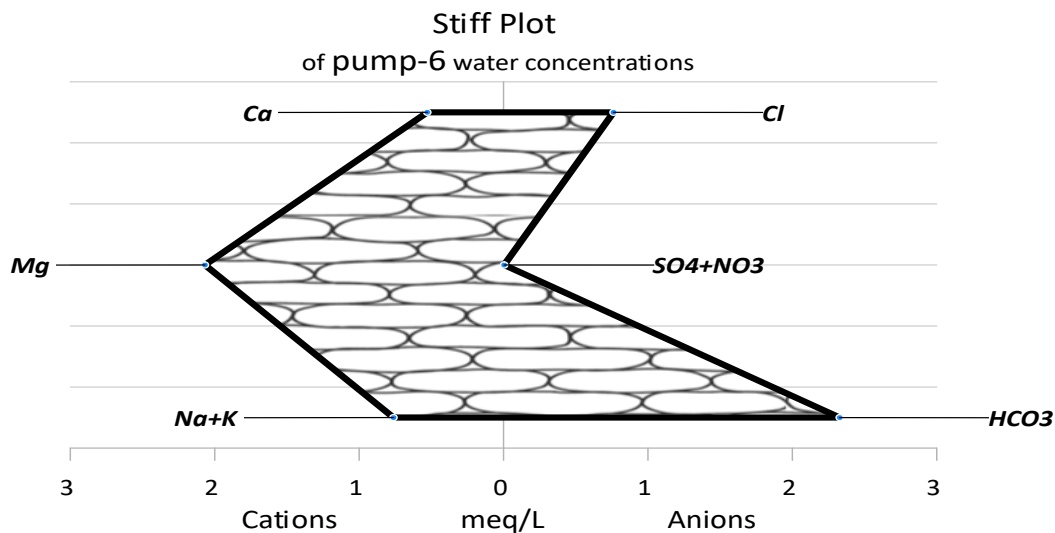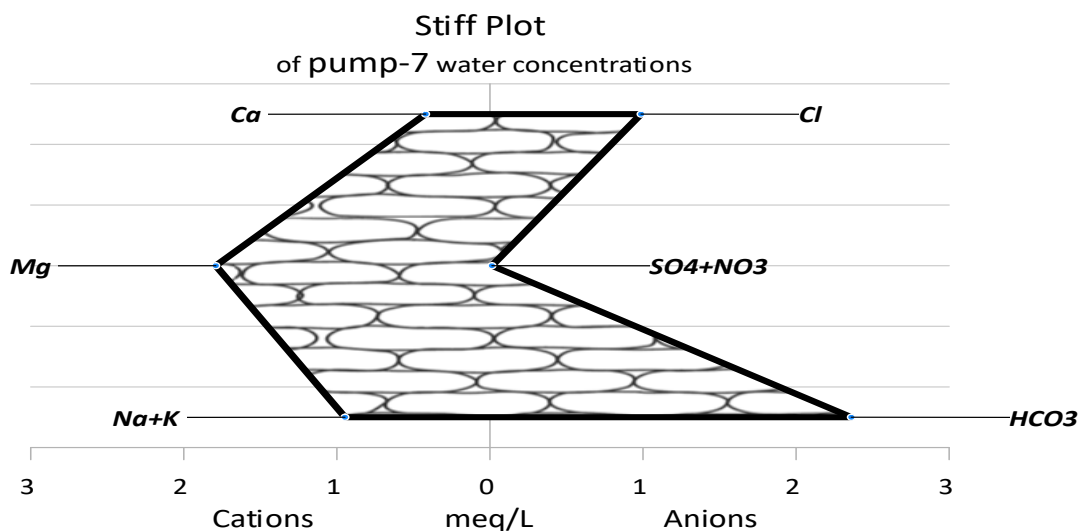

Fig 5.1g: Stiff Diagram for Pump-7

Stiff Diagram for Pump-8:

Stiff diagram of pump-8 shows that the Mg cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-8 is the Mg–HCO_3 water type.

Stiff Plot
of pump-8 water concentrations

Figure 5.1h: Stiff Diagram for Pump-8

Stiff Diagram for Pump-9:

Stiff diagram of pump-9 shows that the Mg^{2+} cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-9 is the $Mg–HCO_3$ water type.

Stiff Plot
of pump-9 water concentrations

Figure 5.1i: Stiff Diagram for Pump-9

Stiff Diagram for Pump-10:

Stiff diagram of pump-10 shows that the Mg^{2+} cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-10 is the Mg–HCO3 water type.
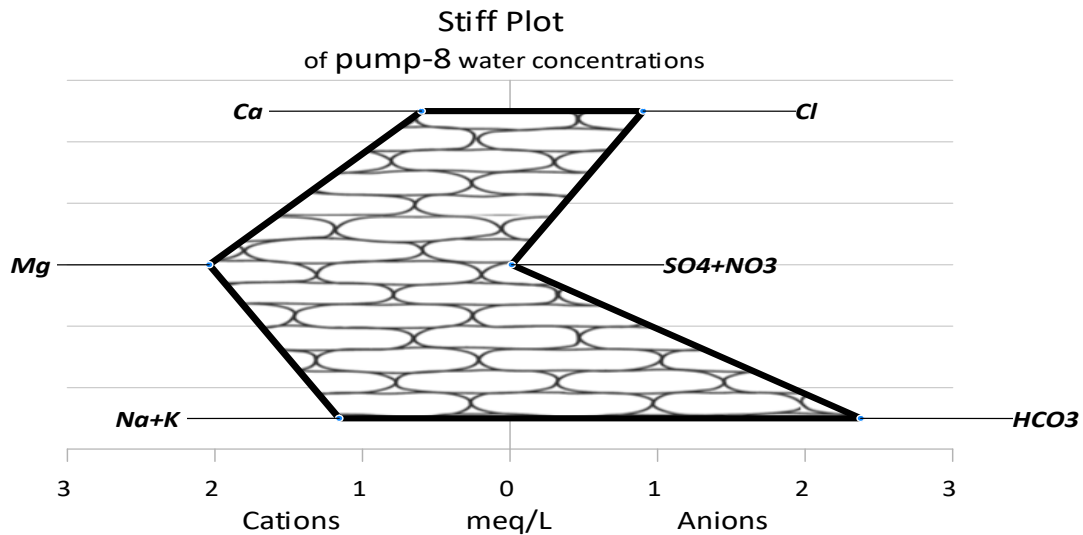
Figure 5.1j: Stiff Diagram for Pump -10

Stiff Diagram for Pump-11:

Stiff diagram of pump-11 shows that the Mg^{2+} cation is the highest among the cations whilst the Cl^- is the predominant anion. This means that the most predominant water type in pump-11 is the Mg–Cl water type.
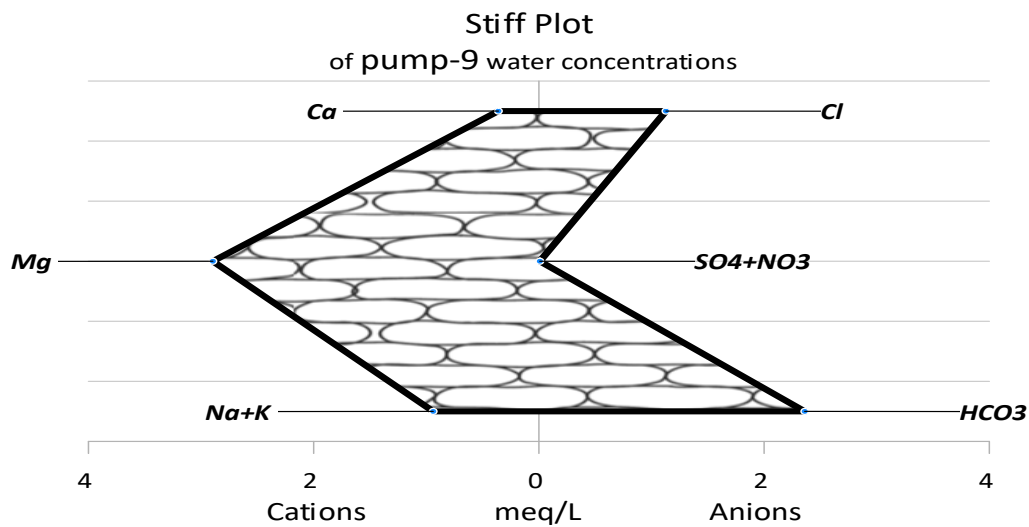

Figure 5.1k: Stiff Diagram for Pump -11

Stiff Diagram for Pump-12:

Stiff diagram of pump-12 shows that the Mg^{2+} cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-12 is the Mg–HCO3 water type.

Figure 5.1l: Stiff Diagram for Pump -12

Stiff Diagram for Pump-13:

Stiff diagram of pump-13 shows that the Mg^{2+} cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-13 is the Mg–HCO3 water type.
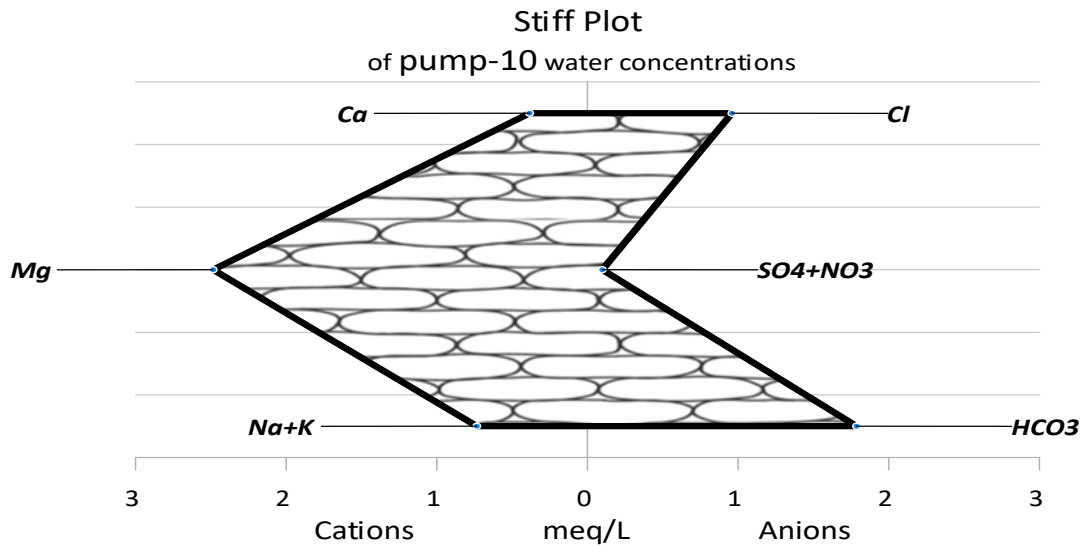

Figure 5.1m: Stiff Diagram for Pump -13

Stiff Diagram for Pump-14:

Stiff diagram of pump-14 shows that the Mg^{2+} cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-14 is the Mg–HCO3 water type.
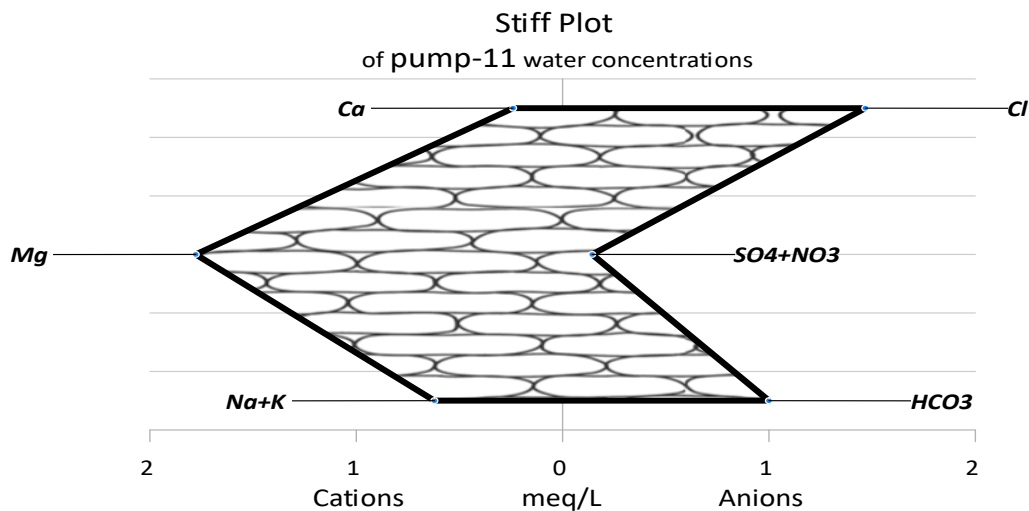
Figure 5.1n: Stiff Diagram for Pump -14

Stiff Diagram for Pump-15:

Stiff diagram of pump-15 shows that the Mg^{2+} cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-15 is the Mg–HCO3 water type.

Figure 5.1o: Stiff Diagram for Pump -15

Stiff Diagram for Pump-16:

Stiff diagram of pump-16 shows that the Mg^{2+} cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-16 is the Mg–HCO3 water type.
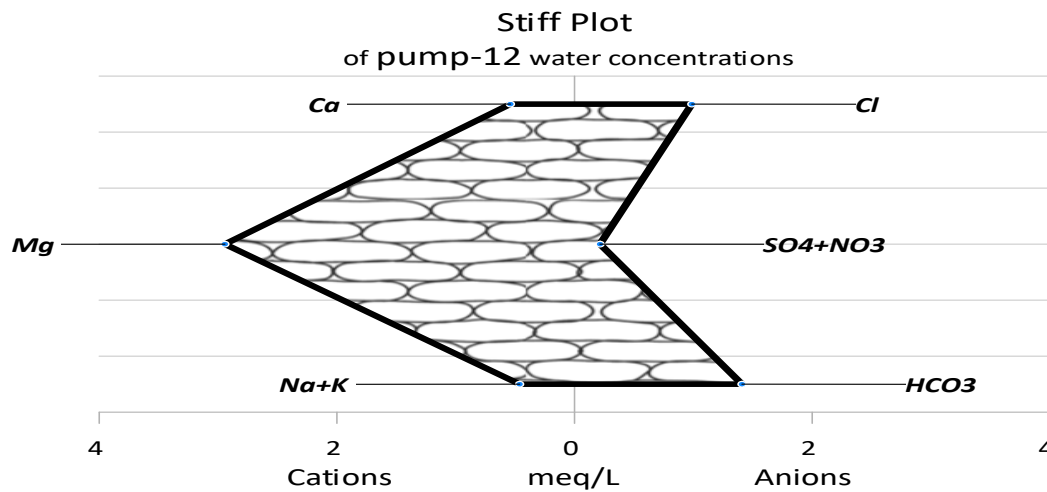
Figure 5.1p: Stiff Diagram for Pump -16

Stiff Diagram for Pump-17:

Stiff diagram of pump-17 shows that the Mg^{2+} cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-17 is the Mg–HCO3 water type.
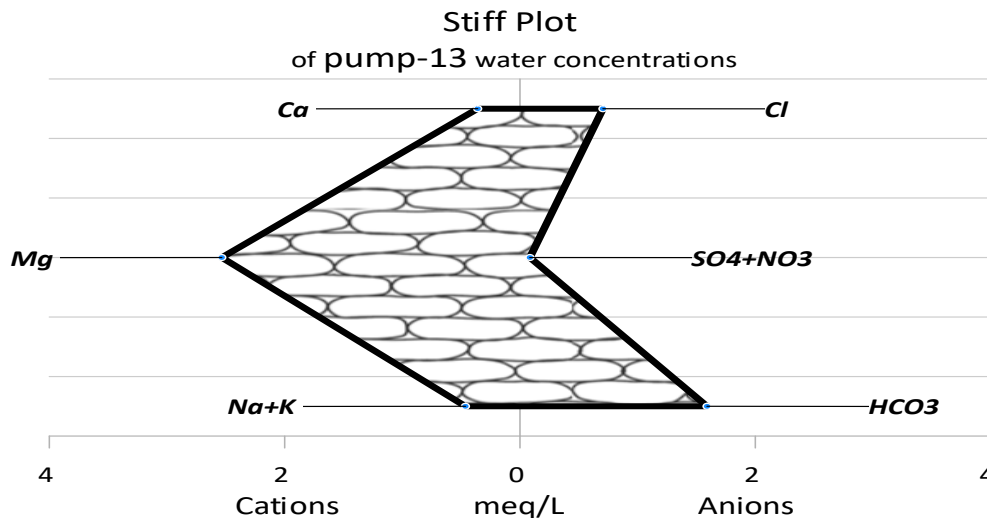

Figure 5.1q: Stiff Diagram for Pump -17

Stiff Diagram for Pump-18:

Stiff diagram of pump-18 shows that the Mg^{2+} cation is the highest among the cations whilst the HCO_3^- is the predominant anion. This means that the most predominant water type in pump-18 is the Mg–HCO3 water type.

Figure 5.1r: Stiff Diagram for Pump -18

Stiff Diagram for Pump-19:

Stiff diagram of pump-19 shows that the Mg^{2+} cation is the highest among the cations whilst the Cl^- is the predominant anion. This means that the most predominant water type in pump-19 is the Mg–Cl water type.
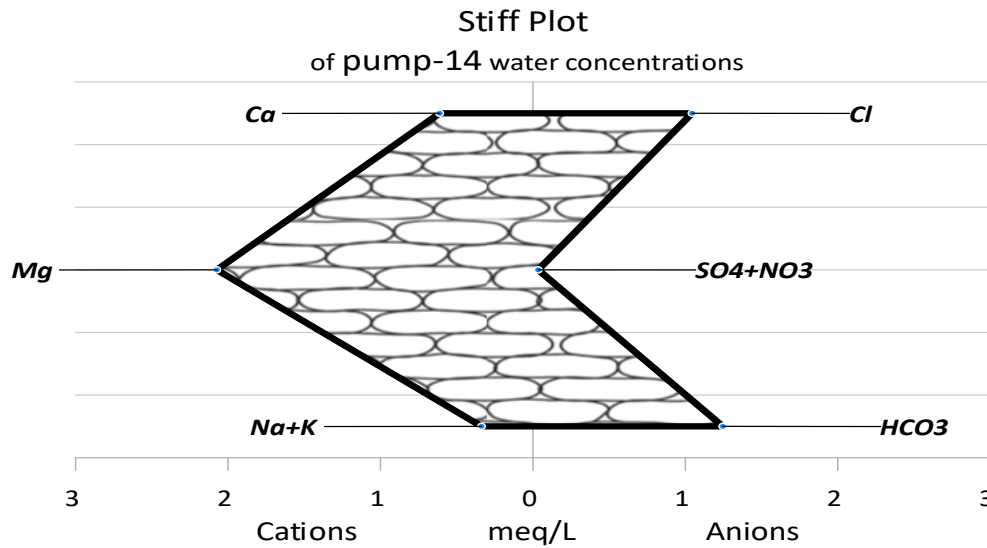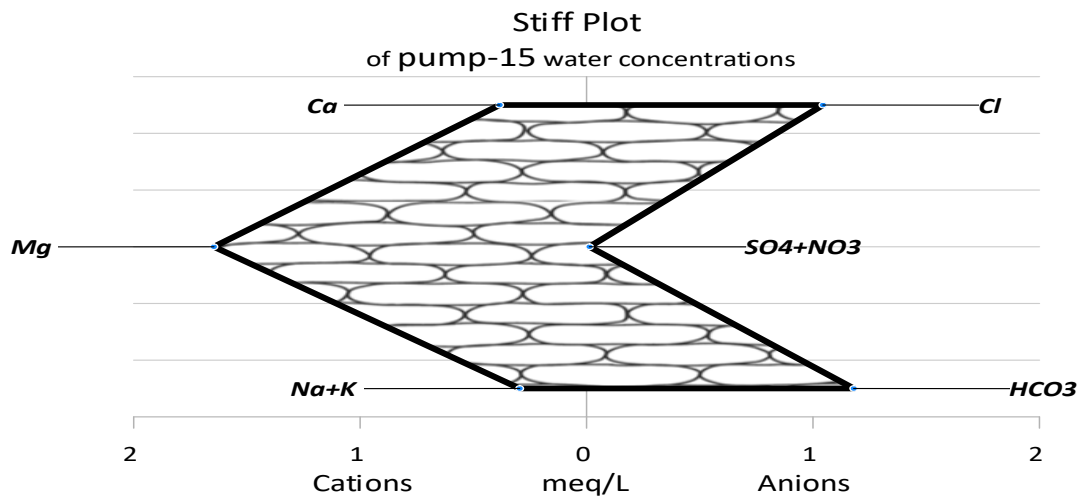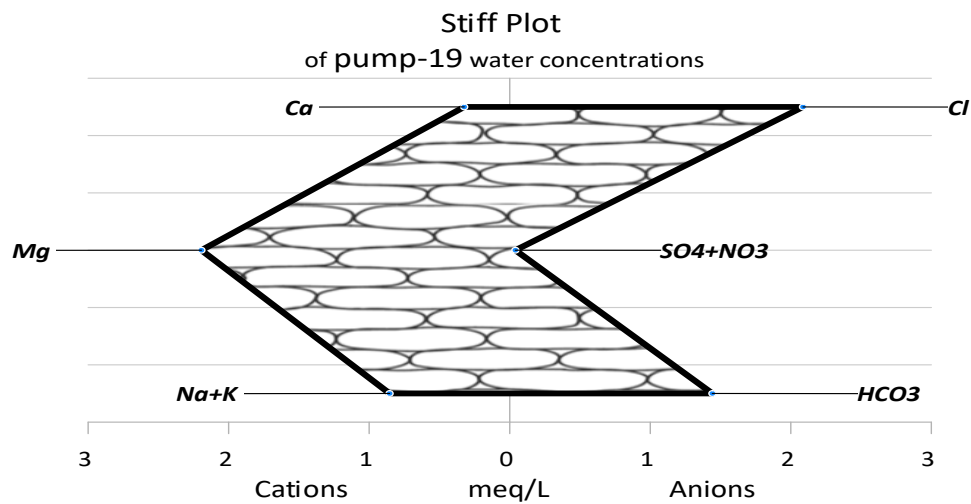

Figure 5.1s: Stiff Diagram for Pump -19

Stiff Diagram for Pump-20:

Stiff diagram of pump-20 shows that the Mg^{2+} cation is the highest among the cations whilst the Cl^- is the predominant anion. This means that the most predominant water type in pump-20 is the Mg–Cl water type.
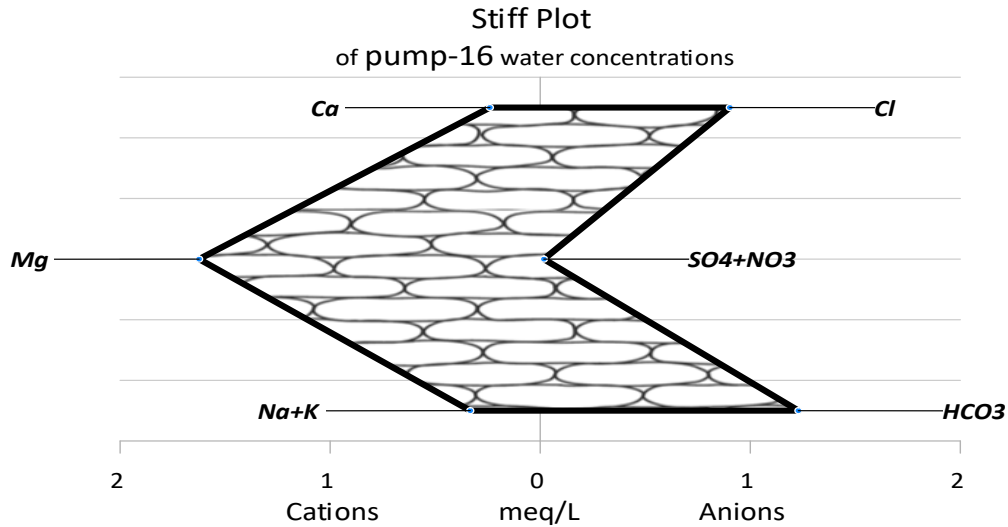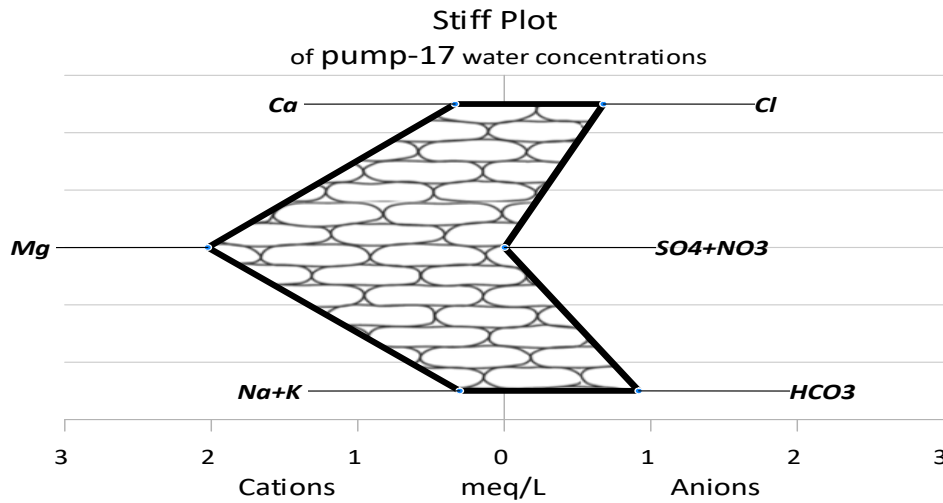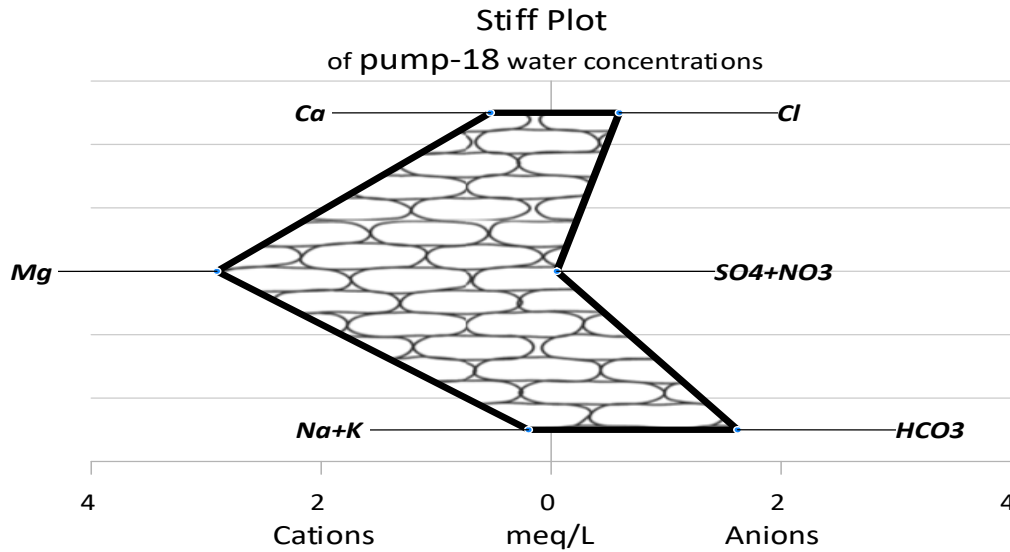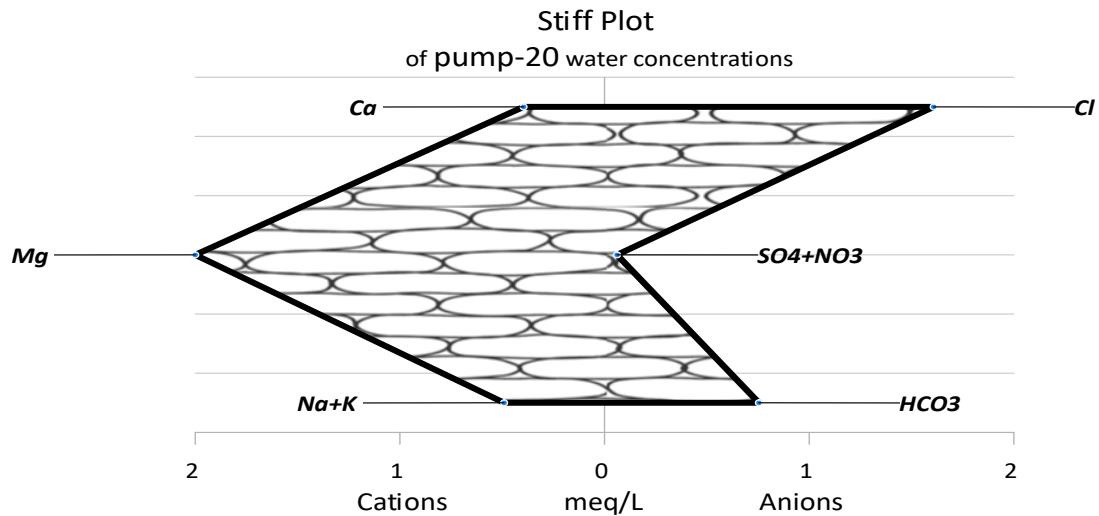
Figure 5.1t: Stiff Diagram for Pump -20

Figures 5.1 a-t, show the typical water type using stiff diagrams for different directions around the pumps. Stiff plots indicate magnesium bicarbonate and magnesium cloride types water. The shape of these plots are generally and they are suggesting same that there is no change in the ionic composition of groundwater around pumps of SCC. The dominant MgCl and $MgHCO_3$ type water indicates that ion exchange and rock dissolution processes influence the groundwater chemistry of the area. In the study area, the cation abundance relates and agrees well with the Collin's bar diagram (of the following) by that the dominant cation is magnisium while the dominant anion is bicarbonate. This water has the same source and is from the same aquifer system.

5.4.2 Collin's Bar Diagram

Collins diagrams (Collins, 1923) present the relative major ions composition in percent milliequivalent per liter. In it major cations are plotted on the left and major anions are plotted on the right. Both the cations and anions have a total of 100%. The cations are plotted on the left and the anions are plotted on the right. In Collin's bar diagram, the cations and anions concentration in epm or meq/l are represented by height of bars and the concentration of ions are marked by horizontal breaks (Figure 5.2 a-t).

The heights of the bar are proportional to total cations and anions meq/l values. As the sum of cations and anions should be equal to the height of the bar. Any height difference occurs between cations and anions bar may be due to error in analysis or some ions occuring in significant quantity

is not being represented. The cations are represented as Ca^{2+}, Mg^{2+}, Na^+, K^+, and the anions as Cl^-, SO_4^{2-} and HCO_3^-.

Collin's Bar Diagram of Pump-1

Figure 5.2a: Collin's Bar Diagram of Pump-1

Collin's Bar Diagram of Pump-2

Figure 5.2b: Collin's Bar Diagram of Pump-2

Collin's Bar Diagram of Pump-3

Figure 5.2c: Collin's Bar Diagram of Pump-3

Collin's Bar Diagram of Pump-4

Figure 5.2d: Collin's Bar Diagram of Pump-4

Collin's Bar Diagram of Pump-5
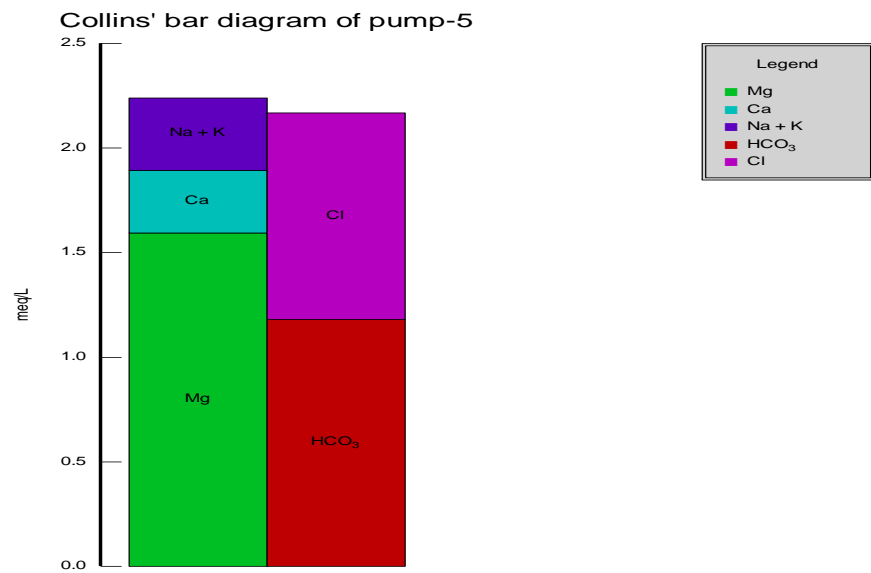
Figure 5.2e: Collin's Bar Diagram of Pump-5

Collin's Bar Diagram of Pump-6
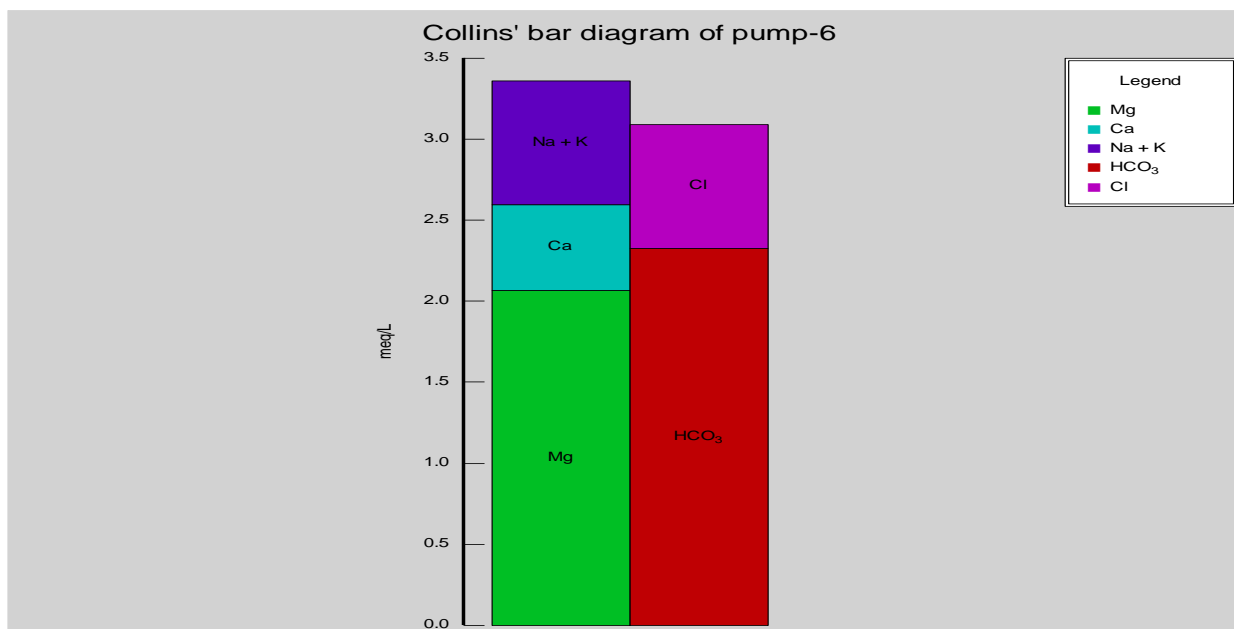
Figure 5.2f: Collin's Bar Diagram of Pump-6

Collin's Bar Diagram of Pump-7
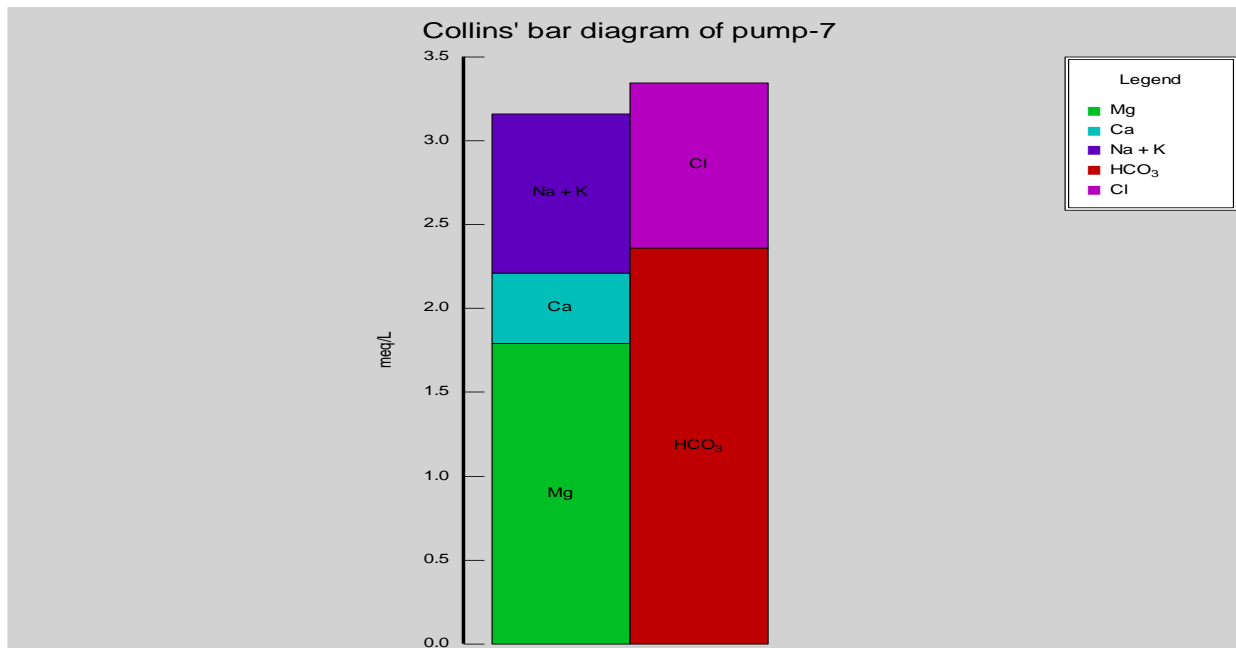
Figure 5.2g: Collin's Bar Diagram of Pump-7

Collin's Bar Diagram of Pump-8
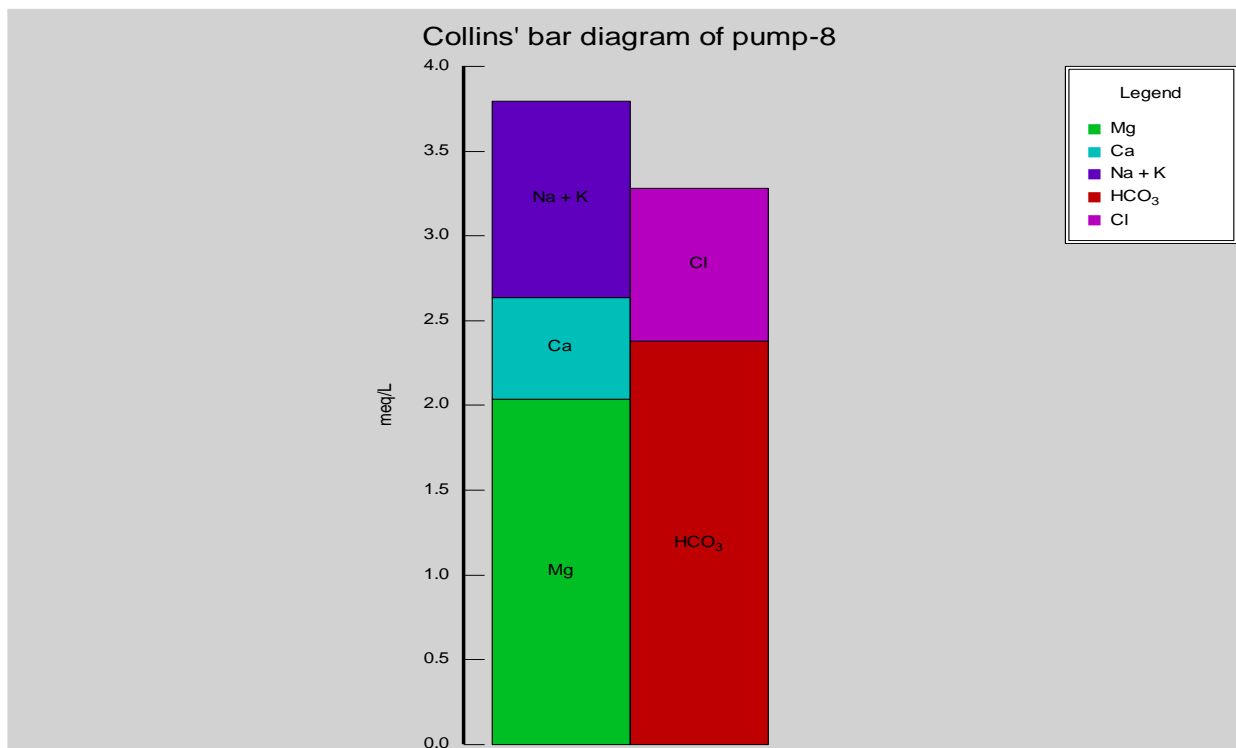
Figure 5.2h: Collin's Bar Diagram of Pump-8

Collin's Bar Diagram of Pump-9
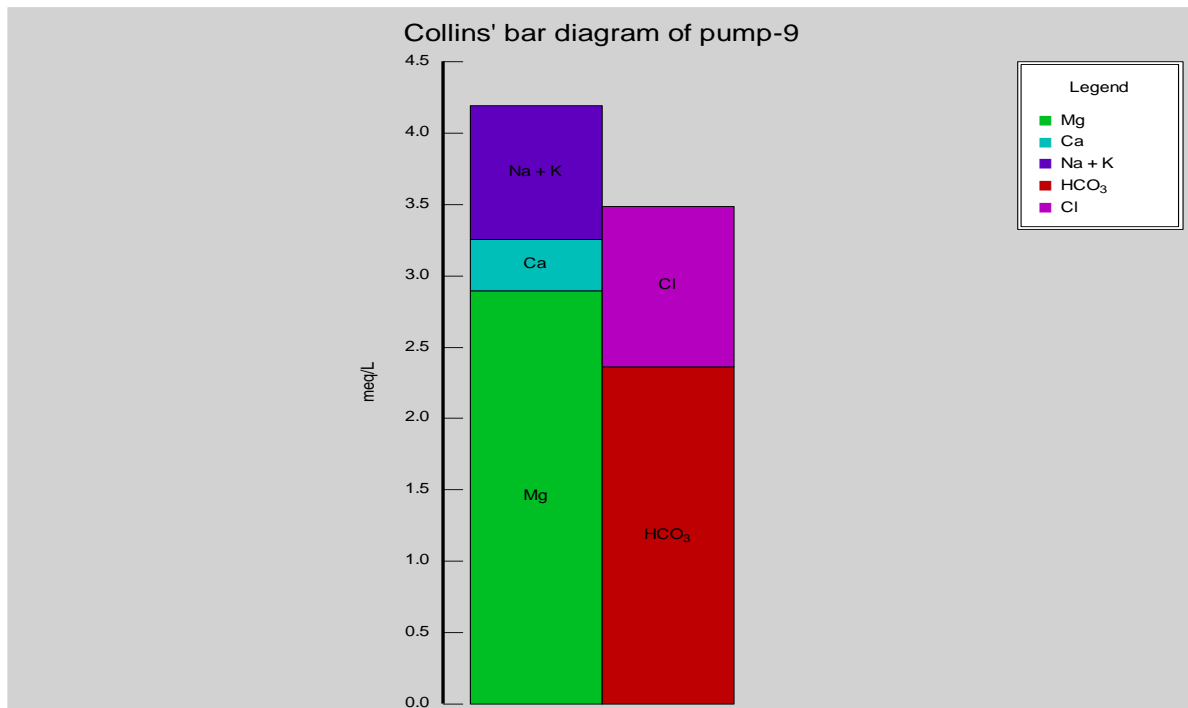
Figure 5.2i: Collin's Bar Diagram of Pump-9

Collin's Bar Diagram of Pump-10
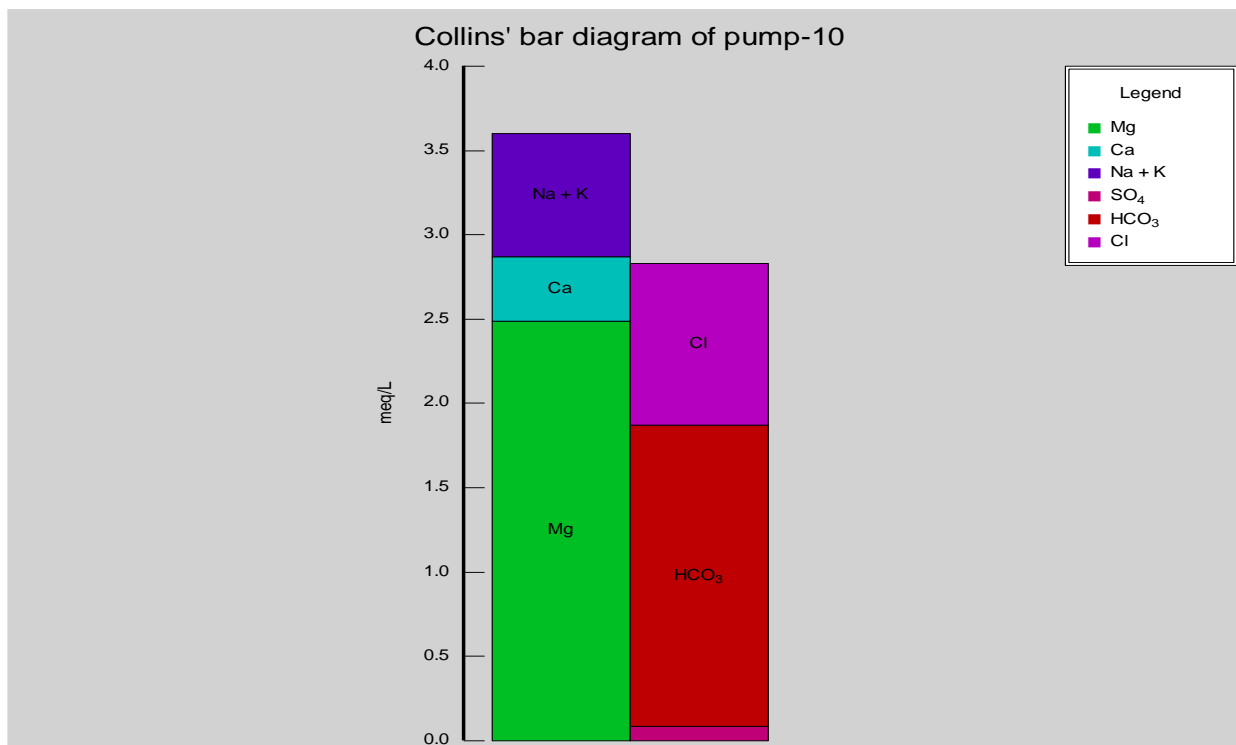
Figure 5.2j: Collin's Bar Diagram of Pump-10

Collin's Bar Diagram of Pump-11
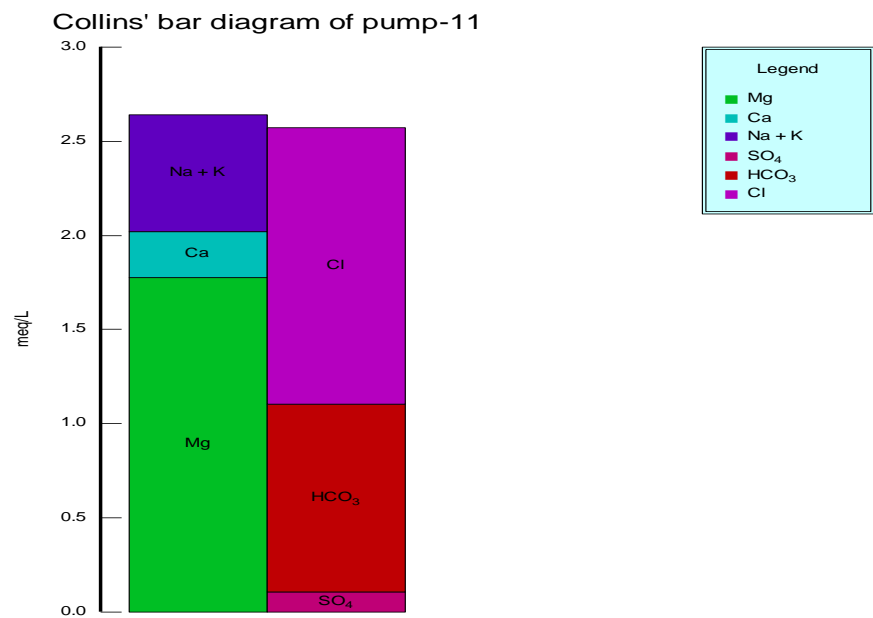
Figure 5.2k: Collin's Bar Diagram of Pump-11

Collin's Bar Diagram of Pump-12
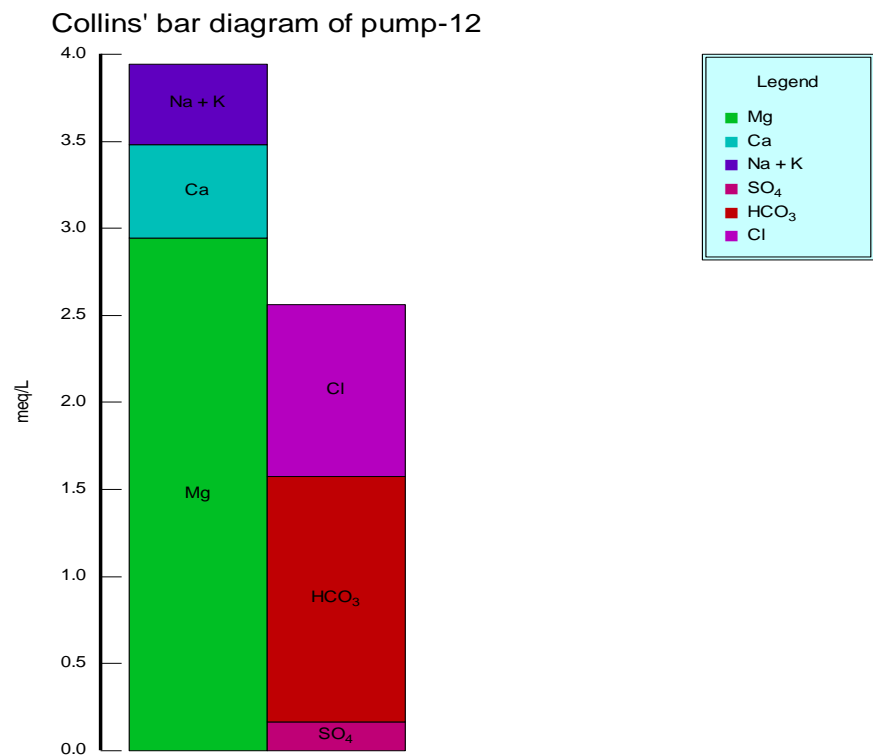
Figure 5.2l: Collin's Bar Diagram of Pump-12

Collin's Bar Diagram of Pump-13
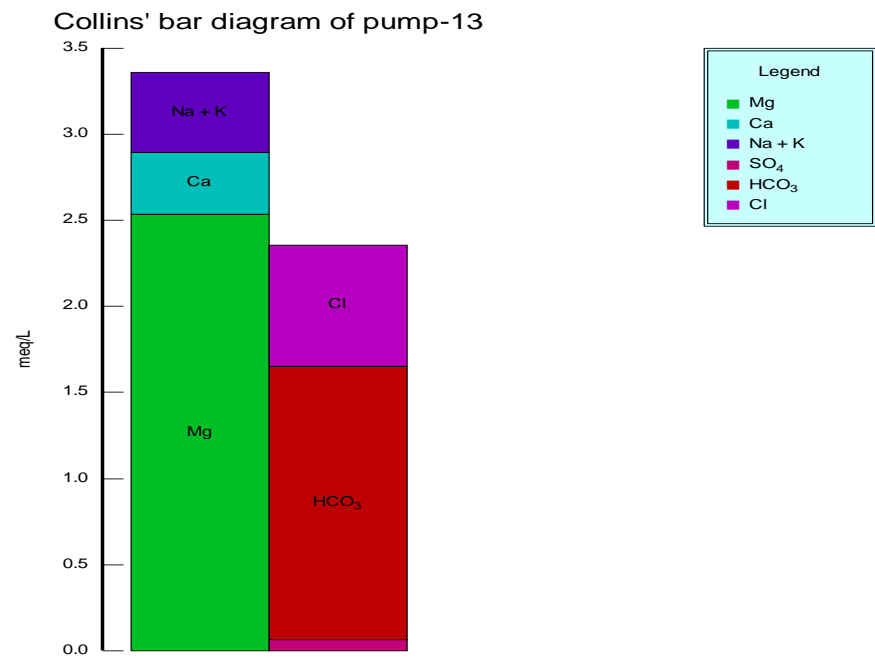
Figure 5.2m: Collin's Bar Diagram of Pump-13

Collin's Bar Diagram of Pump-14
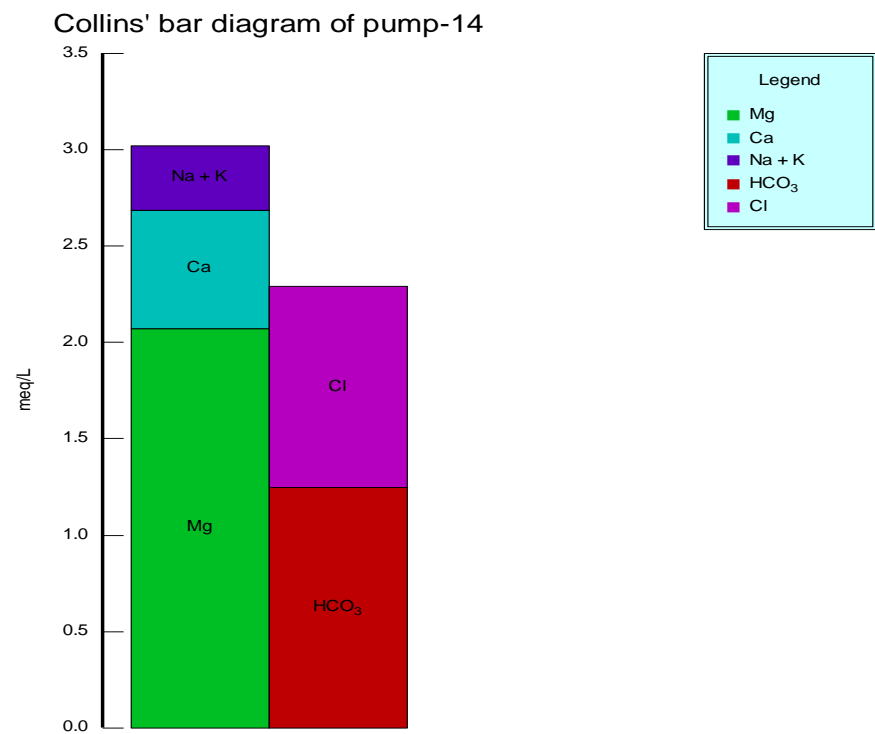
Figure 5.2n: Collin's Bar Diagram of Pump-14

Collin's Bar Diagram of Pump-15
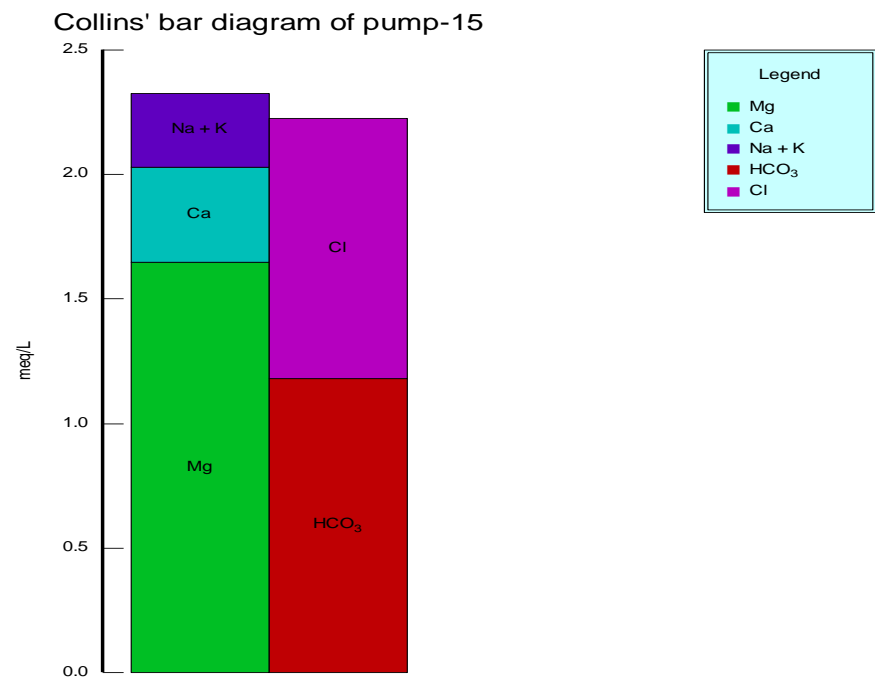
Figure 5.2o: Collin's Bar Diagram of Pump-15

Collin's Bar Diagram of Pump-16
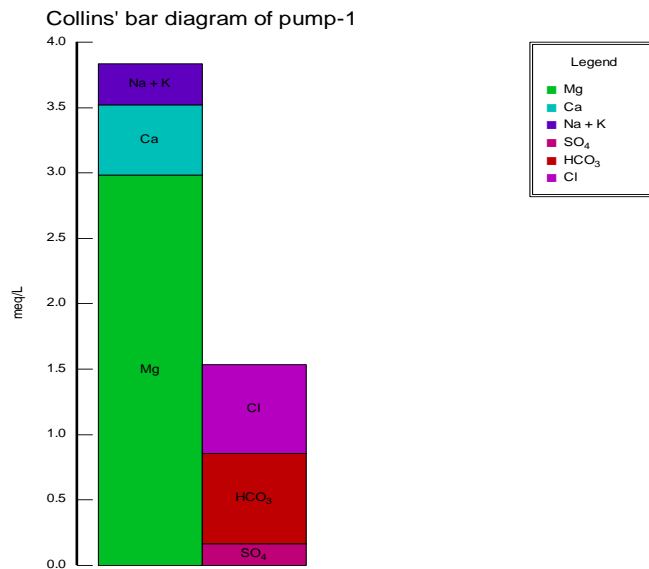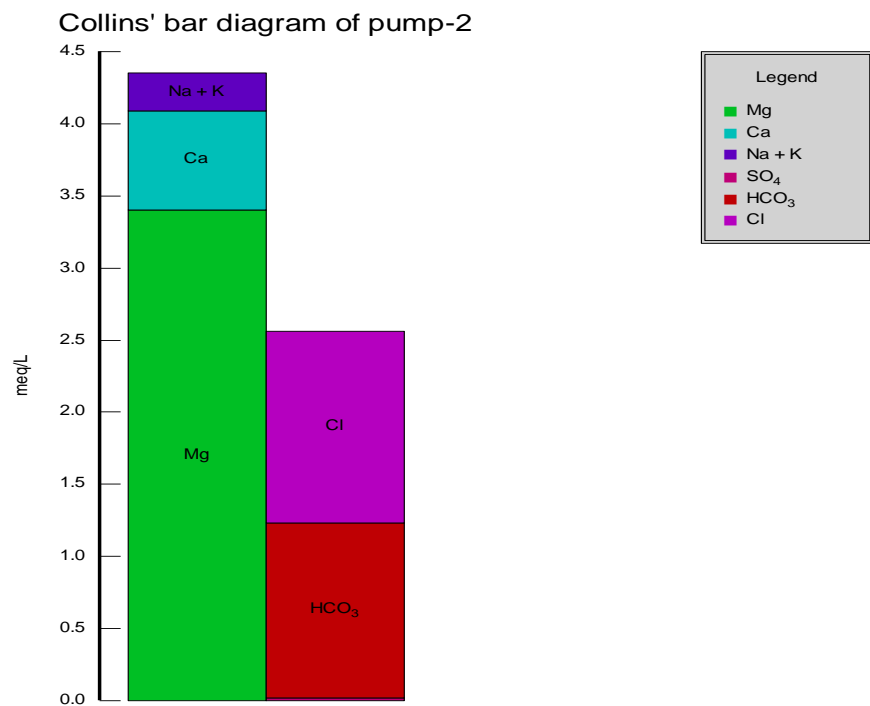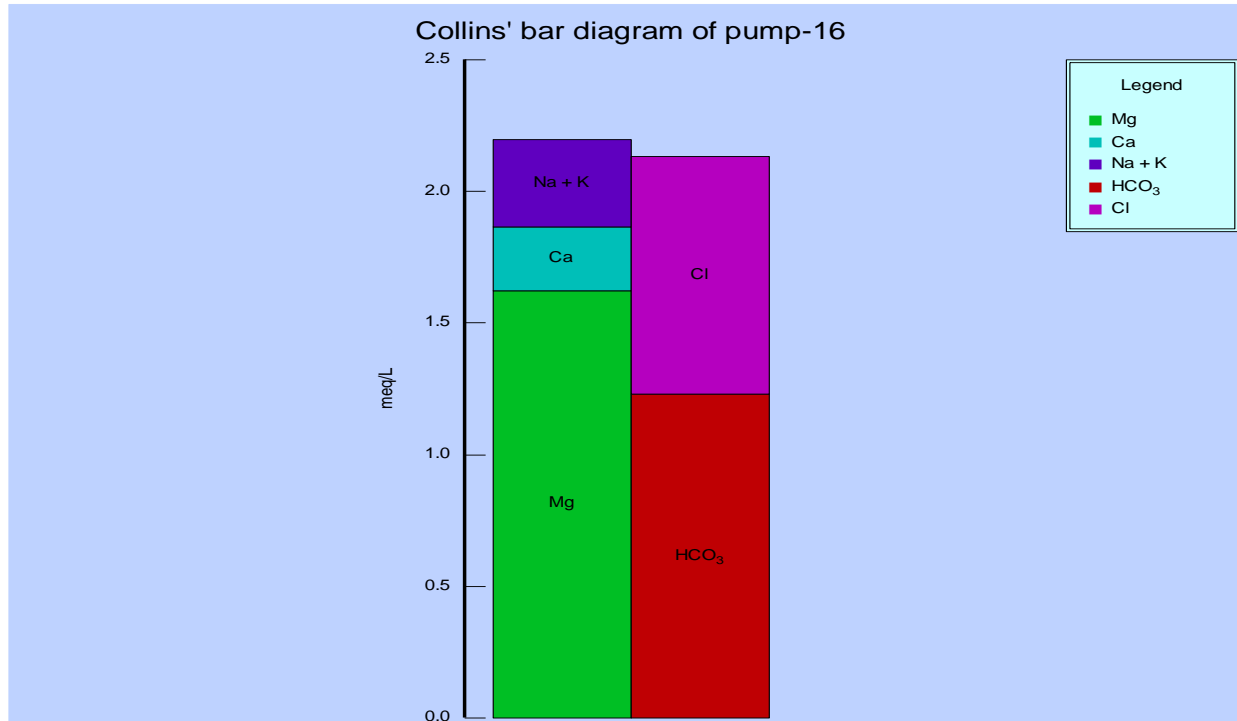

Figure 5.2p: Collin's Bar Diagram of Pump-16

Collin's Bar Diagram of Pump-17
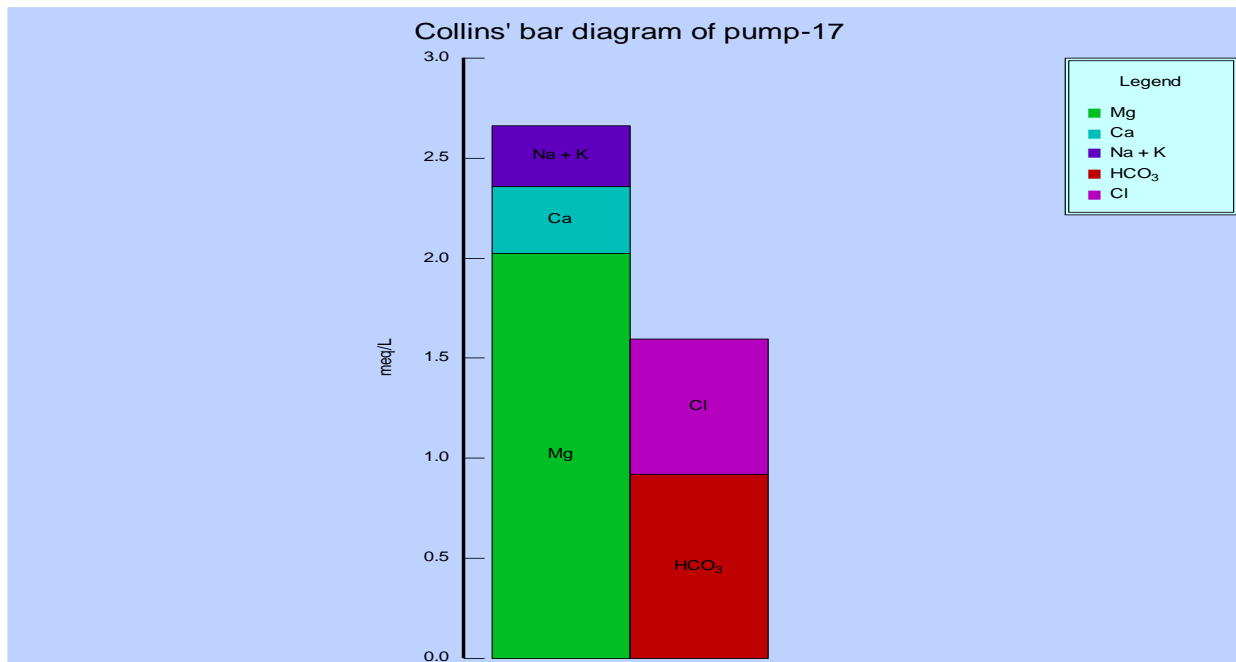
Figure 5.2q: Collin's Bar Diagram of Pump-17

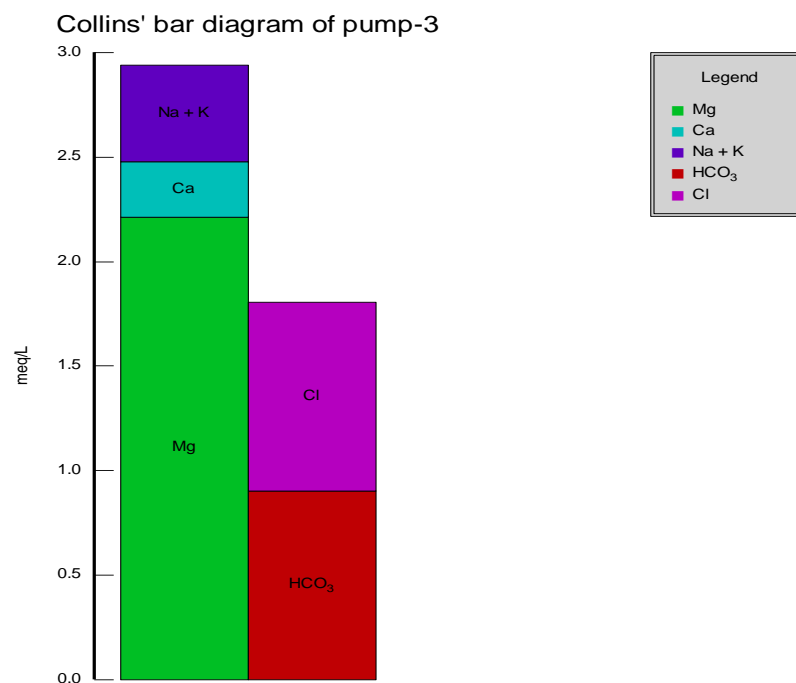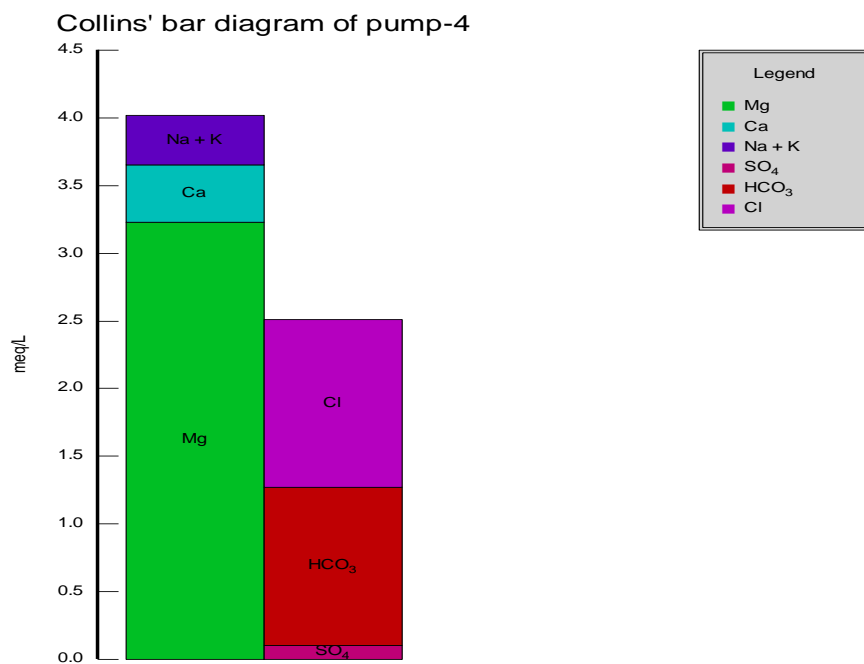**Collin's Bar Diagram of Pump-18**
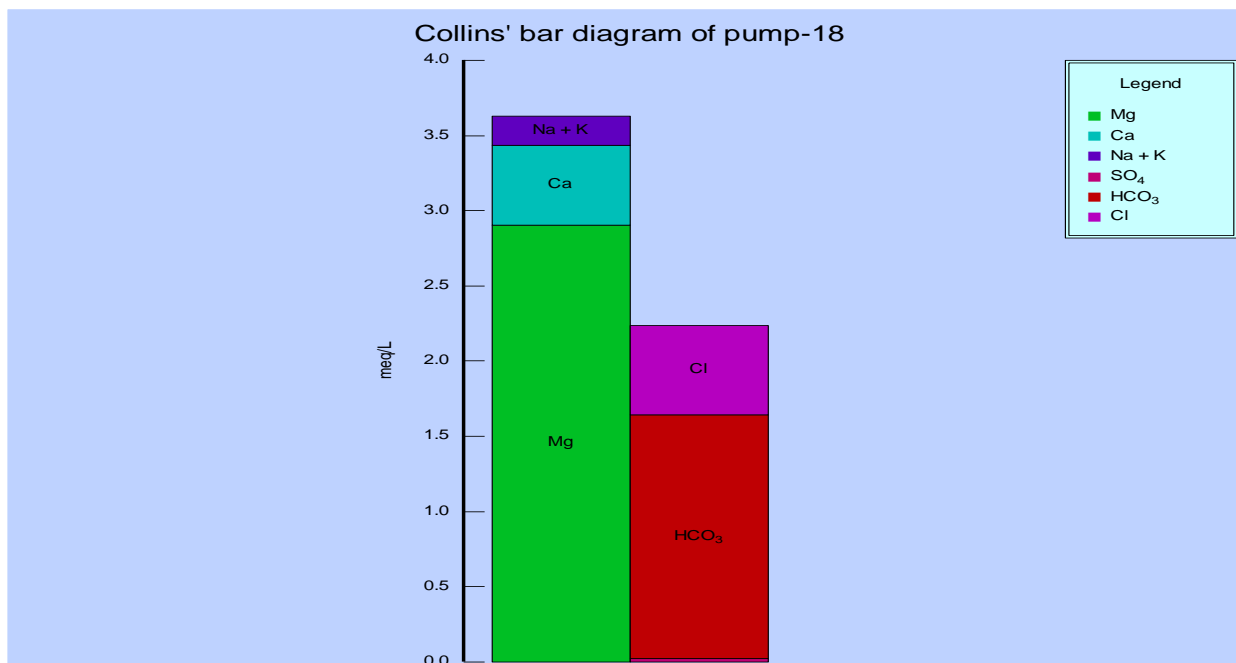
Figure 5.2r: Collin's Bar Diagram of Pump-18

Collin's Bar Diagram of Pump-19
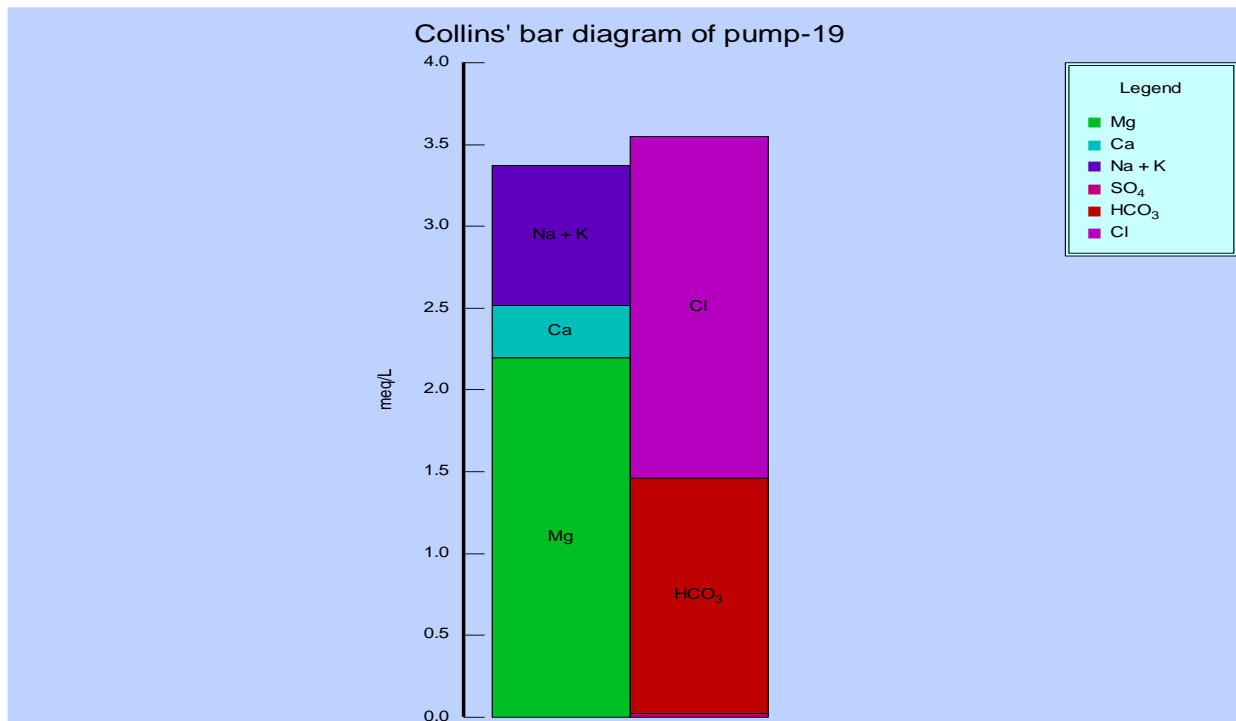
Figure 5.2s: Collin's Bar Diagram of Pump-19

Collin's Bar Diagram of Pump-20
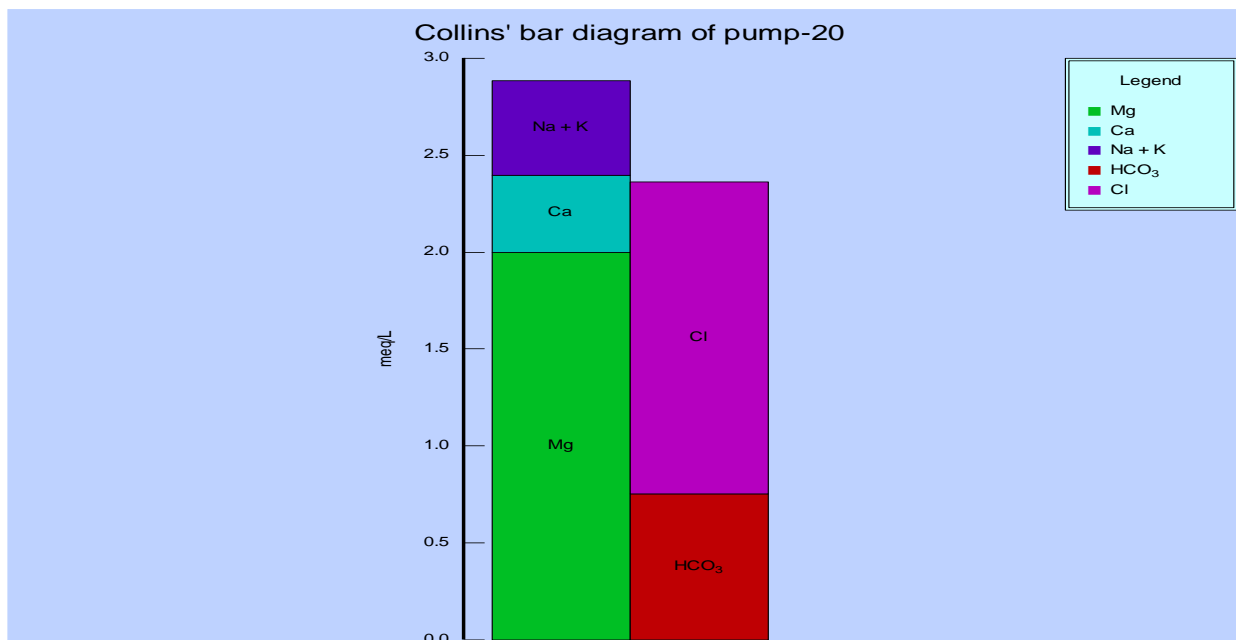
Figure 5.2t: Collin's Bar Diagram of Pump-20

5.4.3 Gibbs Diagram

Several factors control groundwater chemistry, which can be related to the physical situation of the aquifer, bedrock mineralogy and weather condition. The TDS vs. $Na^+/(Na^+ + Ca^{2+})$ and TDS vs. $Cl^-/(Cl^- + HCO_3^-)$ scatter plot can be used to identify the occurrence of rock-water interaction processes (Gibbs, 1970). The diagram is divided into three fields, the rock-water interaction, precipitation and evaporation. In these diagrams the samples falling in the centre of the curve indicate an origin from rock-water interaction. Figure 5.3a and 5.3b represent Gibbs TDS vs. $Na^+/$ $(Na^+ + Ca^{2+})$ and TDS vs. $Cl^-/(Cl^- + HCO_3^-)$ scatter plots plotted using groundwater samples from the study area .

Figure 5.3a and 5.3b shows that almost all the samples falls in the rock area. The Gibbs's diagrams suggest that chemical weathering of the rock forming minerals are the main processes which contribute the ions to the water. It is interesting to note that during post-monsoon, precipitation has no dominating effect and no points falls on the precipitation dominating area. Anthropogenic activities may also increase the TDS value (Hem, 1985) and the samples tend to fall on evaporation dominance area.
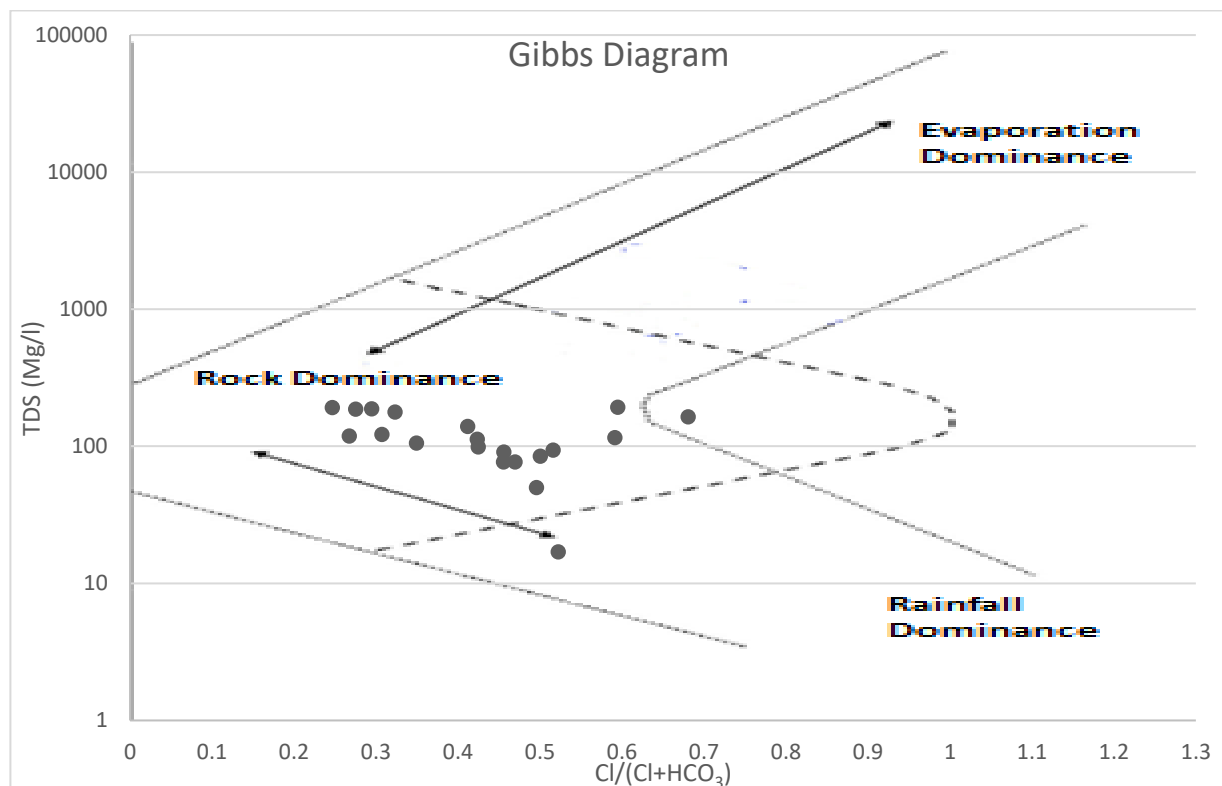
Figure 5.3a: Gibbs Plotfor Anions in the Study Area
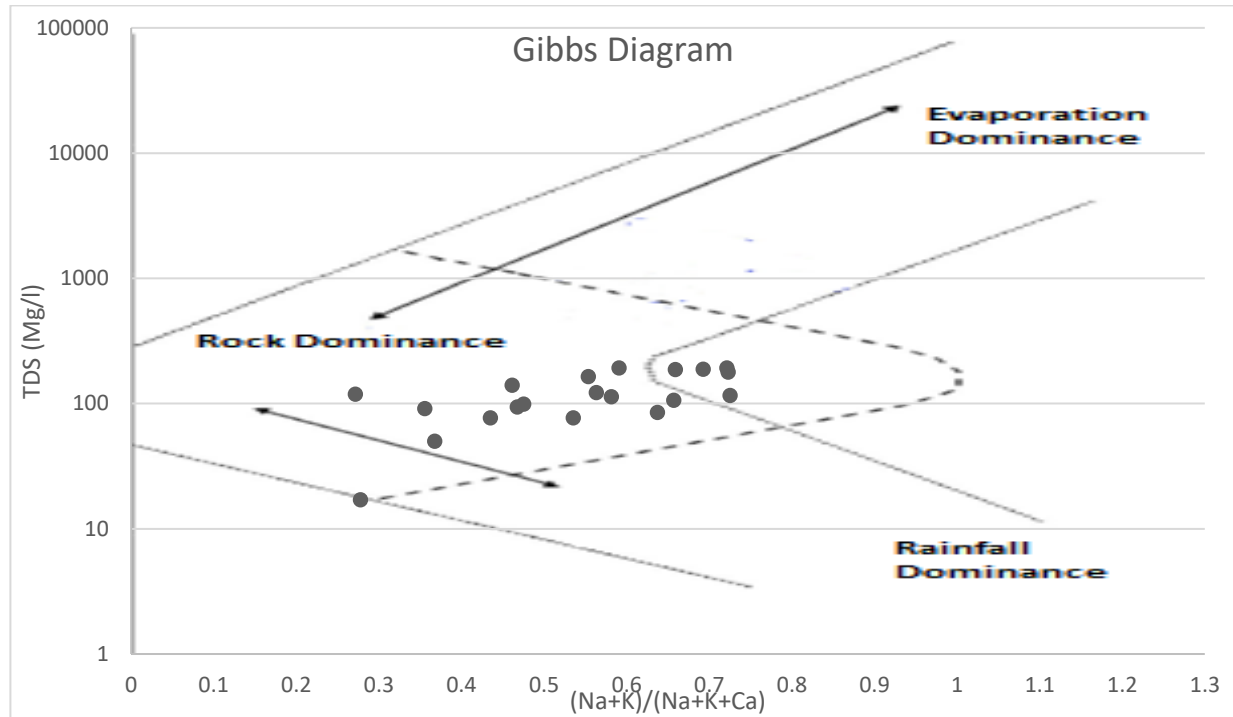
Figure 5.3b: Gibbs plot for Cations in the study area

The Gibbs plots also show that most of the groundwater samples fall in the centre of the curve. For the study area indicates that the ions composition is controlled by rock dominance origin and it close to the boundaries and by rock weathering in the center of the plain, which is indicative of the dominance rock-water interaction as the main process in the study area. During the process of rock-water interaction a variety of chemical processes occur such as weathering and dissolution, ion exchange processes, oxidation and reduction. This confirms that water–rock interaction is the mechanism that is responsible for the chemical composition of the groundwater. The Na^+ and Cl^- are the dominant ions in the center of the plain while Ca^{2+} and HCO_3^- are the dominant ions in the boundaries. Hwang et al., (2017) shows that most of the cations and anions groundwater have a rock-dominance origin. This characteristic indicates the dissolution of ions in groundwater through the interaction between groundwater ansd rock or soil is more dominant than precipitation or any other sources.

5.4.4 Schoeller Diagram

The Schoeller-Berkaloff plots of Figure 5.4 corroborate that the waters are generally high in Ca^{2+}, HCO_3^-, Na^+ and Mg^{2+} and low in K^+ and SO_4^{2-} concentrations, reflecting the possible mixing of the deep aquifers with the pump waters.

In Figure 5.4, all the samples are plotted on Schoeller semi-logarithmic diagrams for each pump. This plot illustrates the difficulty in using purely graphical means to water samples. The chemical characteristics of water compositions on the basis of major ion concentrations were evaluated on a Schoeller diagram. Accordingly, the dominant type of water in the region is considered to be Ca-HCO_3 (calcium-bicarbonate type). However, this type of water is also rich in Na, Ca and especially Mg. Regarding Schoeller diagram, the current status of local underground water is good for drinking purposes. By commencing mining excavation with designed capacity in near future, the minerals will come into contact with air and water resulting in dissolution, especially in ponds, which, in turn, will increase the concentration of toxic metals in groundwater. Considering future uses of this water including for drinking, irrigation, industrial purposes, etc., precautions must be taken in to consideration.
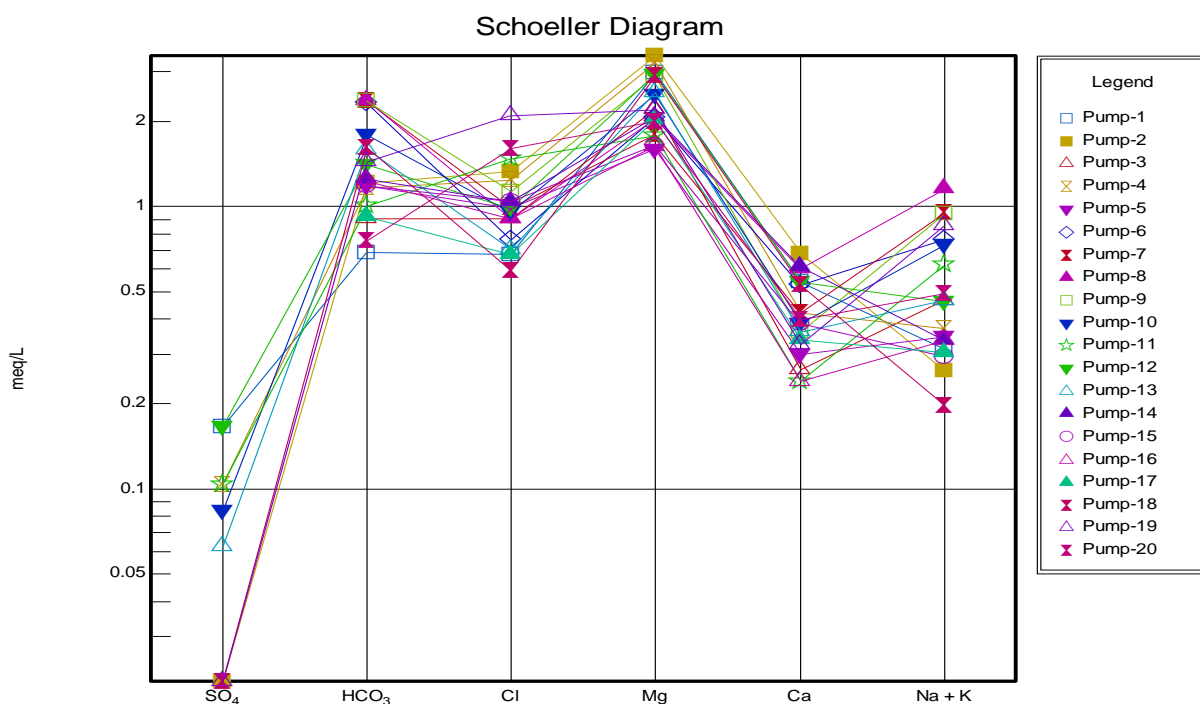
Figure 5.4: Chemical Analysis of Underground Water of the Study Area Plotted on the Schoeller Diagram

5.4.5.1 Sodium Percentage (Na⁺ %)

The Na^+ in irrigation water is usually denoted as Na^+ % and can be determined using the formula Wilcox, (1955) given below, where the concentrations are expressed in meq/l.

$$\text{Sodium percentage } (\%Na+) = \frac{Na^+ + K^+}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} * 100$$

The classification of groundwater samples with respect to the Na^+ % is shown in Table 5.2 . The Na^+% in the study area ranged between 7% and 71%, with an average of 38% in the groundwater. It is observed that the most of groundwater samples fall within the category of good (30%) to permissible (42%) and a few samples fall under excellent (13%) and doubtful (15%) category. As per the Indian standards (BIS 2003), a maximum Na content of 60% is recommended for irrigation water.

Table 5.2: Classification of SCC Groundwater Based on Na^+ %

Range	Categories	Representing pumps
<20	Excellent	1,2,3,4,5,12,13,14,15,16,17,18,20
20–40	Good	6,7,8,9,10,11,19
40–60	Permissible	Nil
60–80	Doubtful	Nil
>80	Unsuitable	Nil

5.4.5.2 Wilcox's Diagram

Following Wilcox, (1955) (Figure 5.5), classifying groundwater based on $\%Na^+$ and EC shows that all of the groundwater samples fall in the fields of very good to good. The agricultural yields are observed in fields. In study area water belonging to doubtful to unsuitable and doubtful. This is probably due to the presence of Na salts, which cause osmotic effects in soil plant system. Hence, air and water circulation is restricted during wet conditions and such soils are usually hard when dry (Saleh, Al-Ruwaih, & Shehata, 1999). The results (Table 5.2) also show that the groundwater is good for. This may be due to the increased anthropogenic activities, various industrial activities under the study area. For the study area, the chemical data of groundwater samples are plotted in the Wilcox's diagram (Figure 5.5) and it is observed that about all of the samples are "very good to good" category of the study area.
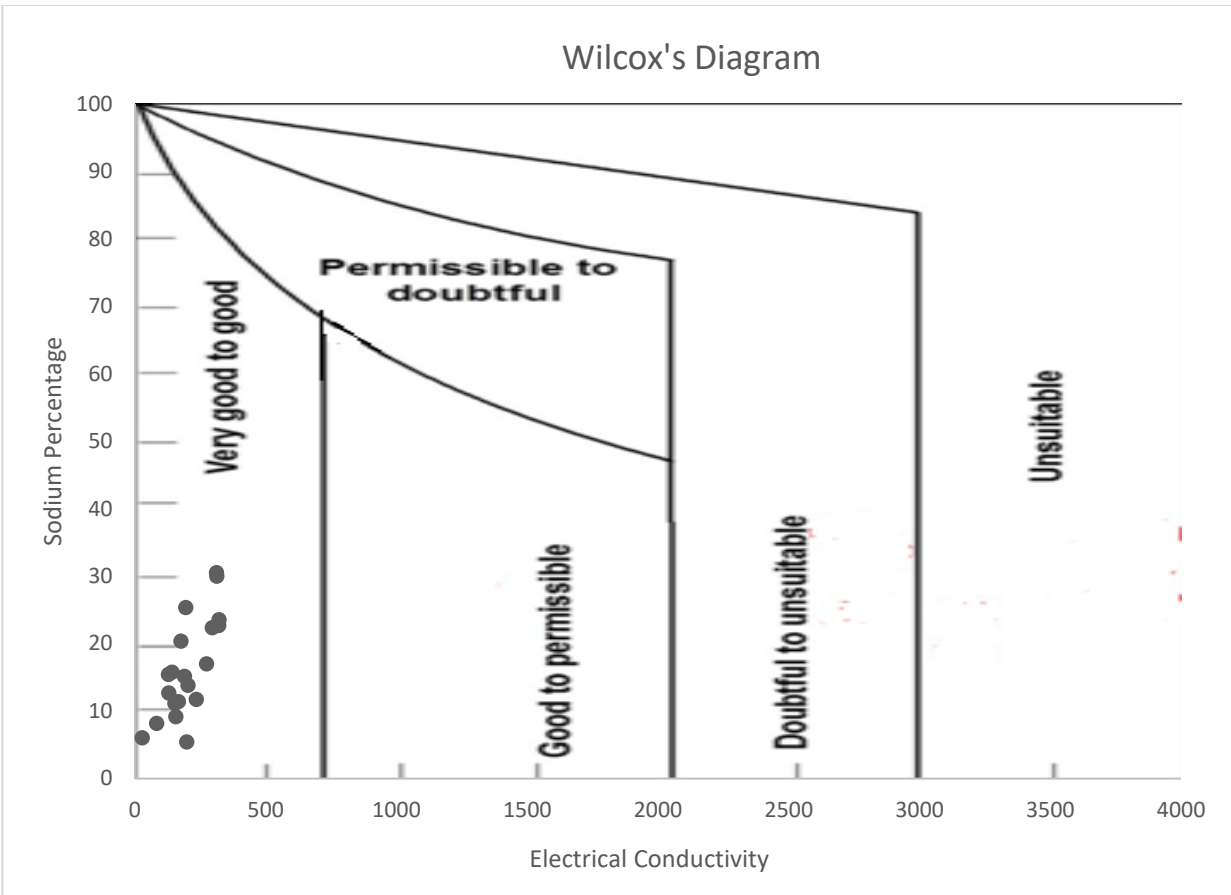
Figure 5.5: Wilcox's Classification of Groundwater Quality for Irrigation

5.4.6.1 Alkali and Salinity Hazard (SAR)

Sodium Absorption Ratio (SAR) is an important parameter for determining the suitability of groundwater for irrigation because it is a measure of alkali/sodium hazard to crops. SAR is calculated by the following formula (where the concentration of all ions are in meq/l),

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

The calculated value of SAR in this area ranges from 0.73 to 8.95 and has been classified as moderately suitable for irrigation. When SAR values are greater than 9, irrigation water will cause permeability problems on shrinking and swelling in clayey soils (Saleh et al., 1999). The higher the SAR values in the water, the greater the risk of Na^+ which leads to the development of an

alkaline soil (Todd, 1980), while a high salt concentration in water leads to formation of saline soil.

The plot of data on the US salinity diagram (Richards et al., 1954), in which the EC is taken as salinity hazard and SAR as alkalinity hazard, shows that all of the groundwater samples fall in the field of excellent water quality (Table 5.3). This is due to enrichment of EC and Na^+ concentrations (Figure 5.6). The elevated EC and Na^+ concentrations could be attributed to bedrock formation, saline soil, agricultural activities, storage of animal waste and local contamination of domestic sewage. The moderate waters can be used to irrigate salt-tolerant and semitolerant crops under favorable drainage conditions. The bad waters are generally undesirable for irrigation and should not be used on clay soils of low permeability. Bad waters, however, can be used to irrigate plants of high salt tolerance as there is a decline of fertile lands.

The SAR concentration ranges from 0.13277 to 0.984633 with a mean of 0.43535. Table 5.3 shows that all 20 samples have SAR ratio less than 10. The rating of water samples in relation to salinity and sodium hazard reflects that the high sodium ion concentration in the water at some of the stations/pumps may produce harmful levels of exchangeable sodium in the soil.

Table 5.3: Sodium Hazard Classes Based on SAR

Range	Categories	Representing pumps
<10	Excellent	1-20
20–18	Good	Nil
18-26	Doubtful	Nil
>26	Unsuitable	Nil

For the purpose of analysis and classification, the total concentration of soluble salts (salinity hazard) in irrigation water can be expressed in terms of specific conductance. Classification of groundwater based on salinity hazard is shown in Table 5.3. It is found from EC that all of the samples are permissible for irrigation purpose. Excessive solutes in irrigation water are a common problem in semi arid areas where water loss through evaporation is maximal. Salinity problems encountered in irrigated agriculture are most likely to arise where drainage is poor, which allows the water table to rise close to the root zone of plants, causing accumulation of Na^+ salts in the soil solution through capillary rise following surface evaporation.

5.4.6.2 US Salinity Laboratory (USSL) diagram

This diagram is used in interpreting the analysis of irrigation water. Water can be grouped into 16 classes. It uses Sodium Absorption Ratio (SAR) in vertical axis and conductance in horizontal axis as shown in Figure 5.6. All concentration values are expressed in equivalents per million. Salinity, sodicity and toxicity generally need to be considered for evaluation of the suitability of groundwater for irrigation. Sodium absorption ratio is also used to determine the suitability of groundwater for irrigation as it gives a measure of alkali/sodium hazard to crops.
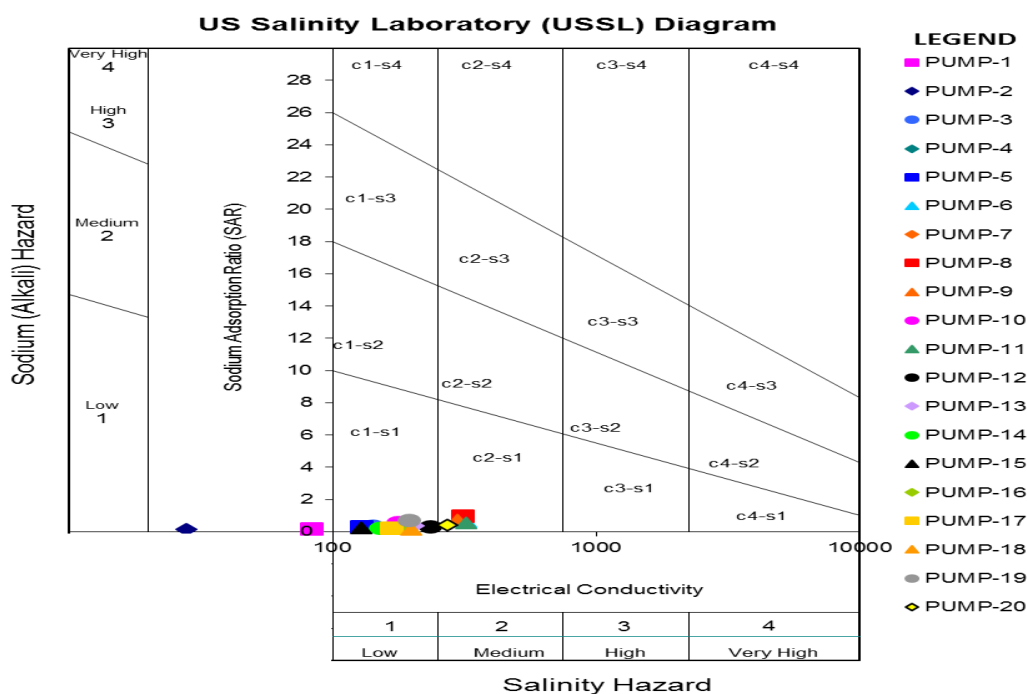
Figure 5.6: USSL Diagram for Classification of Groundwater Quality for Irrigation

5.5 Mineral saturation index

To further examine the state of the minerals present within the samples of our chosen study area, we employed PHREEQC hydrochemical simulation software to calculate the (Saturation Index) SI values of the main minerals at high TDS values during brine extraction (Table 5.4). As indicated in the table, the SI values for the main minerals under these conditions were < 0, indicating that these minerals were in unsaturated states. Furthermore, upon the continuous exploitation of underground water in the study area, the SI values of anhydrite, gypsum, and halite in the water samples were gradually reduced.

Table 5.4: Thermodynamic Speciation (Saturation Indices of Some Minerals and the Tartial Pressure of CO_2)

No. of pumps	Anhdrite	Aragonite	Calcite	Dolomite	Gypsum	Halite	Log(P_{CO2})
P1	-3.71	-1.81	-1.66	-2.29	-2.45	-3.41	-2.29
P2	-3.72	-1.57	-1.42	-1.97	-3.42	-8.47	-2.05
P3	-3.98	-1.99	-1.84	-2.63	-3.68	-8.03	-2.17
P4	-3.84	-1.70	-1.56	-2.09	-3.54	-8.00	-2.07
P5	-3.92	-1.81	-1.67	-2.40	-3.62	-8.15	-2.06
P6	-3.71	-1.30	-1.15	-1.58	-3.41	-7.88	-1.76
P7	-3.80	-1.39	-1.24	-1.73	-3.50	-7.68	-1.76
P8	-3.67	-1.24	-1.09	-1.52	-3.36	-7.63	-1.76
P9	-3.91	-1.47	-1.33	-1.62	-3.61	-7.63	-1.76
P10	-3.86	-1.55	-1.41	-1.87	-3.55	-7.81	-1.88
P11	-4.01	-1.98	-1.84	-2.68	-3.71	-7.71	-2.13
P12	-3.73	-1.51	-1.36	-1.86	-3.42	-8.00	-1.98
P13	-3.88	-1.62	-1.48	-1.98	-3.57	-8.15	-1.93
P14	-3.63	-1.49	-1.35	-2.03	-3.33	-8.13	-2.03
P15	-3.80	-1.70	-1.56	-2.36	-3.50	-8.19	-2.05
P16	-4.00	-1.89	-1.74	-2.52	-3.70	-8.19	-2.04
P17	-3.87	-1.87	-1.73	-2.54	-3.57	-8.38	-2.16
P18	-3.73	-1.45	-1.31	-1.74	-3.43	-8.62	-1.92
P19	-3.92	-1.71	-1.57	-2.18	-3.62	-7.40	-1.97
P20	-3.81	-1.89	-1.75	-2.66	-3.51	-7.78	-2.25
Min	-4.01	-1.99	-1.84	-2.68	-3.71	-8.62	-2.29
Mean	-3.825	-1.647	-1.503	-2.1125	-3.475	-7.762	-2.001
Max	-3.63	-1.24	-1.09	-1.52	-2.45	-3.41	-1.76

CHAPTER VI

RESULTS AND DISCUSSIONS

This chapter presents the results and discussion based on the groundwater chemistry and the methods that were used to further classify and characterize hydro-chemical processes responsible for the quality of the water.

6.1 Descriptive Statistics

The level of understanding of underground water and its quantity is very important because it is the main reason for determining the suitability for domestic, drinking, agricultural and industrial purposes. Hydro-geochemistry is influenced by the rock-water interaction along with other chemical processes occurring in the region. The analyzed water quality parameters with their basic statistics are summarized in Table 6.1 while Table 6.2 shows the prescribed limits of WHO (World Health Organization, 2009) and Bangladesh Standard Value (BDS-1240,2001 BSTI). Examination of the statistical characteristics of the chemical analyses shows that the pH values of groundwater ranged from 5.70 mg/l to 7.40 mg/l with an average value of 7.11 mg/l. This exposes that the groundwater is slightly acidic to alkaline in nature. The process of buffering Calcite and Dolomite are dominant 6.5 to 7.5 for the pH (Blowes et al., 1994; International Association of Theoretical and Applied Limnology., 1923; Jurjovec, Ptacek, & Blowes, 2002). The pH data appears to be largely homogeneous, displaying little variability (SD = 0.43) over the pumps of the study area. This variability may be responsible for the ion exchange process performed in soil and rock matrices. Adomako et al., (2011) suggests that slightly acidic waters could be due to excessive use of ammonium and fertilizer from agricultural activities in the experimental areas. TDS value ranged from 17.00 mg/l to 193.00 mg/l with a mean of 120.40 mg/l. These observed TDS values may arise from a combination of factors including mineral weathering and anthropogenic activities (Sandow Mark Yidana, Bawoyobie, Sakyi, & Fynn, 2018). The value of EC varied from 28 mmohs/cm to 321 mmohs/cm with an average value of 200.65 mmohs/cm, which is directly related to the ionic concentrations present in the groundwater. This information does not support higher salinity and total dissolved concentration (Selvakumar, Chandrasekar, & Kumar, 2017). The variability of EC (SD = 50.25) were high over the study area.

Table 6.1: Degree of Dispersion and Standard Specifications of Ionic Concentrations for Groundwater Samples in the Study Area*

Parameters	Mean	SD	Min	Max	CV (%)
EC	200.65	83.66	28.00	321.00	41.69
TDS	120.40	50.25	17.00	193.00	41.74
pH	7.11	0.43	5.70	7.40	6.03
K^+	1.36	0.53	0.82	2.19	31.55
Na^+	11.45	6.37	4.00	26.00	55.63
Mg^{2+}	28.43	6.62	19.73	41.38	23.28
Ca^{2+}	8.47	2.60	4.81	13.70	30.73
Cl^-	37.20	12.74	21.00	74.00	34.25
SO_4^{2-}	1.80	2.73	0.00	8.00	151.45
CO_3^{2-}	0.00	0.00	0.00	0.00	0.00
HCO_3^-	87.70	33.34	42.00	145.00	38.01
NO_3^-	0.95	0.69	0.10	2.80	72.41

* All values are in mg/l, except pH, SD = Standard Deviation, CV = Coefficient of variation

The concentration of bicarbonate (HCO_3^-) is observed from 42 to 145 mg/L with the mean value of 87.70 mg/l. High HCO_3^- concentration indicates the presence of carbonate containing minerals. Presence of HCO_3^- is one of the main cause of alkalinity in water (Rajput & Goyal, 2017). Weathering of silicate and carbonate minerals along with degradation of organic matter might contribute a high concentration of HCO_3^- ions in groundwater (Rina, Datta, Singh, & Mukherjee, 2012). Na^+ varied from a low of 4.00 mg/l to a high of 26.00 mg/l with the mean value of 11.45 mg/l. Na^+ is conservative in nature and it is bound with clay minerals due to the exchange of ions (Saxena, 1983). K^+ ranged from 0.82 to 2.19 mg/l with the mean value of 1.36 mg/l. Ca^{2+} value varied from 4.81 to 13.70 mg/l with the mean value of 8.47 mg/l. Mg^{2+} varied from 19.73 mg/l to 41.38 mg/l with the mean value of 28.43 mg/l. Ca^{2+} and Mg^{2+} along with HCO_3^- determine the hardness of the groundwater. At soil zone of Ca^{2+} and Mg^{2+} precipitation occurs due to temporary hardness and these precipitated salts might get leached from the soil zone with rainwater or these ions contribute to the high concentration of irrigation water and underground water (C. K. Singh et al., 2017).

The Chloride (Cl^-) ion concentration varied between 21 mg/l to 74 mg/l. $SO4^{2+}$ ranged from 0.00 to 8.00 mg/l with the mean value of 1.80 mg/l, which is very important in many irrigated agricultural areas and has extensive environmental problems. These unusual concentrations may indicate pollution by organic waste (Rajput & Goyal, 2017). High Cl^- concentration might be due

to the high evaporation rate in the region. Higher concentrations of Na^+, Cl^-, and SO_4^{2+} in the area of SCC indicate dissolution of evaporite minerals. The high concentration of nitrate is probably due to wastewater leakage from industrial activities, urbanization, and agricultural practices.

Ranges of nitrate concentration in groundwater from 0.10 mg/l to 2.80 mg/l with an average value of 0.95 mg/l. The average concentrations of major ions in groundwater are in the following order: anions: - Bicarbonate (87.70) > Chloride (37.20) > Sulphate (1.80) > Nitrate (0.95) while cations: - Magnesium (28.43) > Sodium (11.45) > Calcium (8.47) > Potassium (1.36). The standard deviations of major ions in groundwater are in the following order: anions: - Bicarbonate (33.34) > Chloride (12.74) > Sulphate (2.73) > Nitrate (0.69) while Cations: - Magnesium (6.62) > Sodium (6.37) > Calcium (2.60) > Potassium (0.53). Na+ and HCO3-, among the major ions, show the highest variability for cation and anion, respectively (Table 6.1).
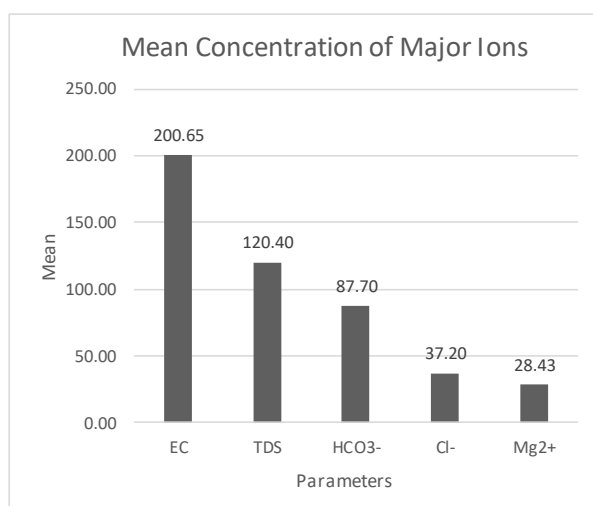
Figure 6.1a: Mean Concentrations of Major Parameters
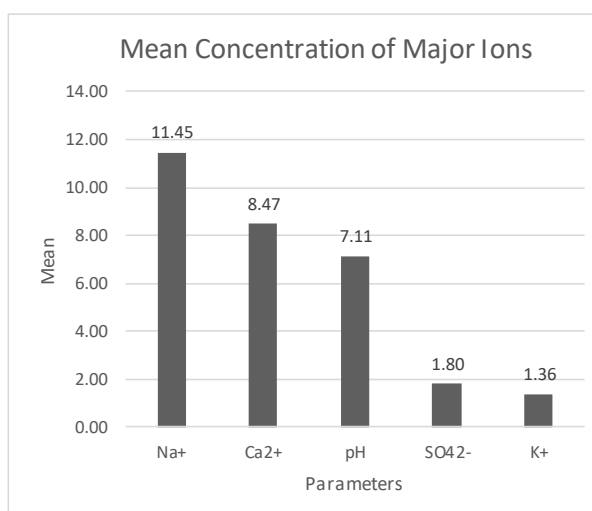
Figure 6.1b: Mean Concentrations of Major Parameters

The apparently high degree of dispersion in the Na^+ concentration may suggest a variety of geogenic and anthropogenic sources, which may vary in the space of the area. The Mg^{2+} displays a similar trend of variability, which is quite higher than that observed for the alkaline earth elements analyzed in this study. This may suggest that the possible sources of variation in the concentrations of the alkali elements (Na^+, Mg^{2+}) are quite variable compared to Ca^{2+} and Mg^{2+} in the study area. The dominance of Na+ over Ca^{2+} and Mg^{2+} may also be related to ion exchange processes between saturated and unsaturated zones (Fetter, 2005). Extensive diversity of

groundwater parameters indicates that groundwater features are influenced by the anthropogenic activities along with climatic factors and geogenic factors such as rock-water interaction (C. K. Singh et al., 2017).

Table 6.1 also depicts that the standard deviation of some of the parameters are higher than the average value (in terms of CV), and it indicates that the geochemistry of the study area is not homogenous. The diversity of water quality data indicates that SO_4^{2-} content were highly varied (CV>100%), then Na^+ and NO_3^- (50% < CV < 100%) and the rest are in decrement order (CV<50%). Central value of each parameter alone with scatterness are presented in the Figure 6.2a- Figure 6.2e for the comprehension at a glance.
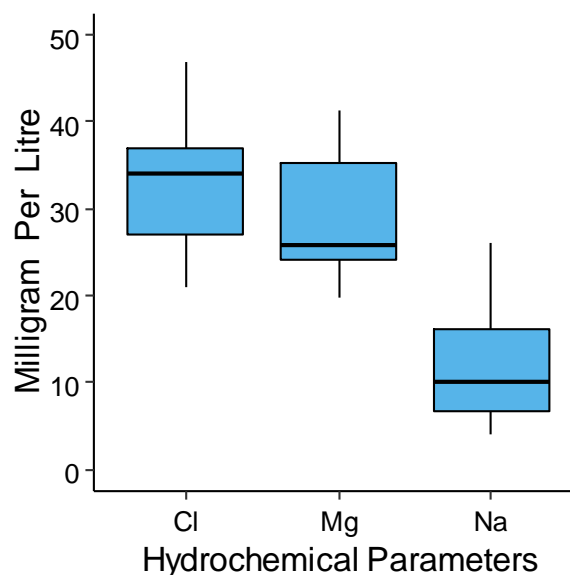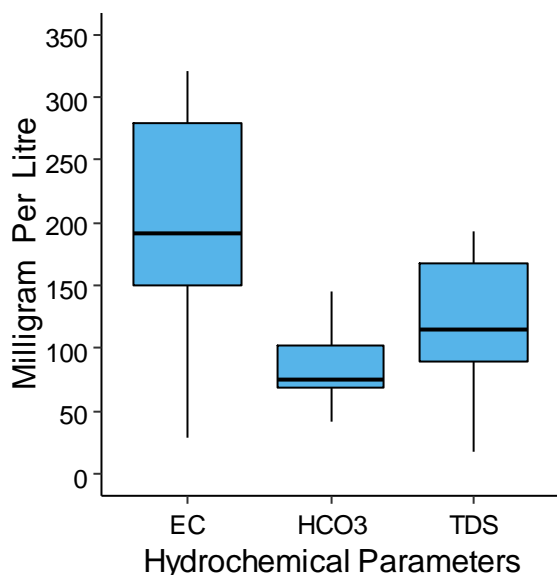
Figure 6.2a: Boxplots of EC, HCO3 and TDS   Figure 6.2b: Boxplots of Cl, Mg and Na
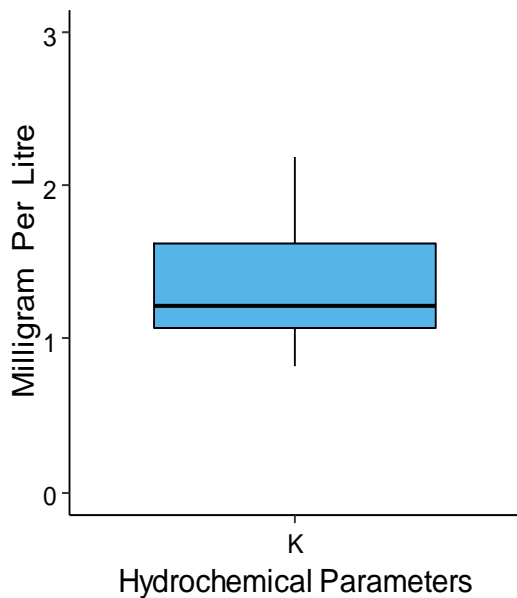
Figure 6.2c: Boxplots of K   Figure 6.2d: Boxplots of pH
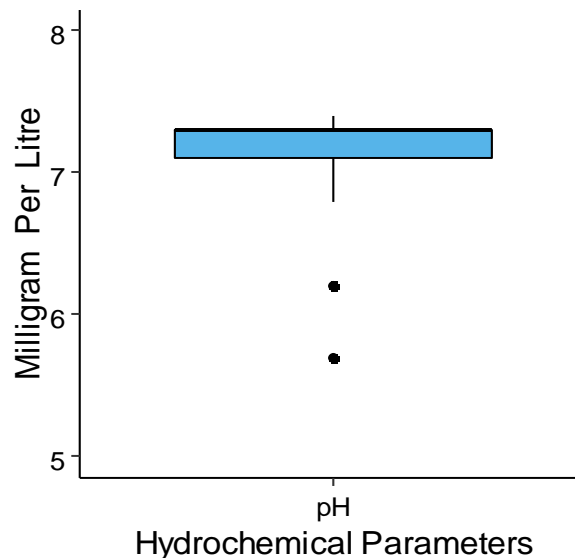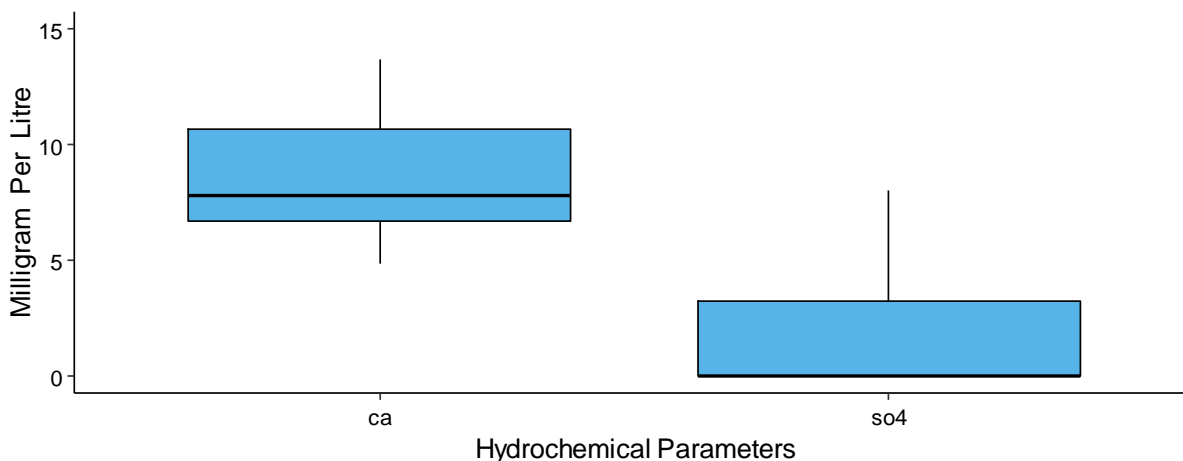
Figure 6.2e: Boxplots of Ca and SO4

6.2 Quality of Ground Water

As given in Table 6.2 pH, electrical conductivity (EC), and TDS were statistically analyzed and the result are compared to drinking water suitability standards. It results suggest that all sample have EC under 500 µS/cm (fresh water). According to WHO the desirable value of EC is 1500 µS/cm. The pH is a numeric scale from 0-14 to determine the acidity and basicity of the water solution. The pH of pure water is neutral when the value of pH is equal to 7. Solutions with a pH more than 7 are basic and solutions with pH less than 7 are acidic. According to WHO the desirable

value of pH is between 6.5-8.5. In this sudy, two samples were lower than this limit. One is moderately acidic (pH = 5.7) and another is slightly acidic (pH = 6.2) (Lambers, Piessens, Bloem, Pronk, & Finkel, 2006). According to WHO, all of other 18 samples were in an acceptable range of pH for useable water (6.5 – 8.5). High pH value suggests an interaction between soil and rainwater, thus imparting alkaline characteristics to the groundwater (Saxena, 1983). In the study area, this is rare to be observed.

According to WHO, the optimum value of TDS is 1000 mg/l and none of the samples exceed this ideal permissible limit. However, the high level of TDS presence in the water can be objectionable to the consumers and can result in taste and excessive scaling of water pipes, heaters, boilers, and household appliances. TDS can be unacceptable to consumers due to its flat, insipid taste; it is often the ecorrosive to the water supply system (WHO, 1996).

Table 6.2: Standard Specifications of Ionic Concentrations for Groundwater Samples in the Study Area*

Parameters	Mean	WHO	BS
EC	200.65	1500	-
TDS	120.40	1000	1000
pH	7.11	6.5-8.5	6.5-8.5
K^+	1.40	12	12
Na^+	15.45	200	200
Mg^{2+}	28.43	30	30-35
Ca^{2+}	8.47	100	75
Cl^-	37.20	250	150-600
SO_4^{2-}	1.85	250	400
CO_3^{2-}	0.00	-	-
HCO_3^-	89.70	500	240
NO_3^-	0.95	10	10

* All values are in mg/l, except pH and WHO = World Health Organization (WHO, 2018), BS = Bangladesh Standard (Kormoker, Proshad, & Mahmud Khan, 2017; Monir, Khan, Quamruzzaman, Kabir, & Hossain, 2012; Roy et al., 2018; Zaman, Akter, & Muhit, 2015).

The desirable limit of K^+ for drinking water is specified by WHO as 12 mg/l. It is observed that none of our samples is exceed this limit. According to WHO the desirable value of Mg^{2+} are 30 mg/l and 100mg/l, respectively. In this study, eight samples are exceeding the limit for magnasium. Surplus of calcium and magnesium shows the water hardness and it is not good for portable.

According to WHO, the desirable limit of Cl⁻ is 250 mg/l, and no samples/pumps exceeded the maximum acceptable concentration of Cl⁻ for drinking water and no samples/pumps exceeded the maximum acceptable concentration of SO_4^{2+} for drinking water (250 mg/l). Sulfate values vary from 0 mg/l to 8 mg/l and all samples are in limit according to the WHO standard. It indicates that the effects of the s accumulation soluble salts in the soil, anthropological activities and extreme sulfate fertilizer. The chemical analysis showed that none of the water samples have values higher than 10 mg/l, therefore higher than the desirable limit of NO_3^- for drinking water (10 mg/l). The high concentration of nitrate in water is poisonous and causes methemoglobinemia (blue baby disease) in children and gastric carcinomas (Fewtrell, 2004). NO_3^- in groundwater is mostly associated with anthropogenic activities along with some natural processes (Dentener et al., 2006). This are not concern for the study area. Dissolution of gypsum and anhydrite might contribute SO_4^{2-} in groundwater while fertilizers and leaching of municipal waste or agricultural runoff might contribute a high concentration of NO_3^- in groundwater.

6.3 Correlation Analysis

As given in the Table 6.3, out of 66 pairs of water quality attributes, 11 pairs were found significantly correlated ($p<0.05$) and the frequency of correlation indicated that the water characteristics could be grouped into factors based on their correlation patterns. Correlation gives an idea of rapid water monitoring methods (Kumar & Singh Chandel, 2010). There is very strong positive significant ($p <0.05$) correlation at between EC and TDS (r = 0.99), sodium (r = 0.74) and moderate positive correlation between EC and , bi-carbonate (r = 0.53). The origin belongs to dissolved salts from the aquifer matrix is due to a long residence time of groundwater, evaporite depositions in sedimentary sequence, etc. Waterlogging of fields cause higher salination of groundwater in arid or semi-arid areas where the rate of evaporation is quite high (S. Shrestha & Kazama, 2007).

Table 6.3: Correlation Coefficient among Hydrochemical Parameters

	EC	TDS	pH	K⁺	Na⁺	Mg²⁺	Ca²⁺	Cl⁻	SO₄²⁻	HCO₃	NO₃⁻
EC	1.00										
TDS	**0.99***	1.00									
pH	0.31	0.31	1.00								
K⁺	-0.27	-0.26	**-0.48***	1.00							
Na⁺	**0.74***	**0.74***	0.40	-0.28	1.00						

Mg²⁺	-0.28	-0.28	-0.13	-0.30	-0.16	1.00					
Ca²⁺	-0.09	-0.09	0.11	-0.14	-0.15	**0.51***	1.00				
Cl⁻	0.06	0.06	-0.20	0.20	0.24	-0.09	-0.08	1.00			
SO₄²⁻	-0.06	-0.06	-0.44	0.02	-0.13	**0.60***	0.17	0.04	1.00		
HCO₃⁻	**0.53***	**0.53***	**0.70**	**-0.55**	**0.56**	0.02	0.25	-0.12	-0.15	1.00	
NO₃⁻	0.14	0.14	-0.29	0.01	-0.11	0.13	0.05	0.39	0.43	-0.20	1.00

*Correlation is significant at the 0.05 level (two-tailed)

There is very strong positive correlation between TDS and sodium (r = 0.74), sodium (r = 0.74) and moderate positive correlation between TDS and bi-carbonate (r = 0.53). TDS in the water is originated from natural sources, sewage, urban run-off, and industrial waste water (Louloudakis, Vernardou, Papadimitropoulos, Davazoglou, & Koudoumas, 2018). The concentration of TDS in water varies considerably in different geological regions owing to differences in the solubility of minerals. pH has positive correlation at $p < 0.05$ with K^+ (0.48),and HCO_3^- (0.70). HCO_3^- has a positive correlation with Na^+ (0.56) and negative correlation with K^+ (-0.55). It may be due to the presence of high amounts of calcium salts in groundwater. Mg^{2+} has a positive correlation with Ca^{2+} (0.51) and SO_4^{2-} (0.60). The findings from the correlation analysis are depicted in Figure 6.3.
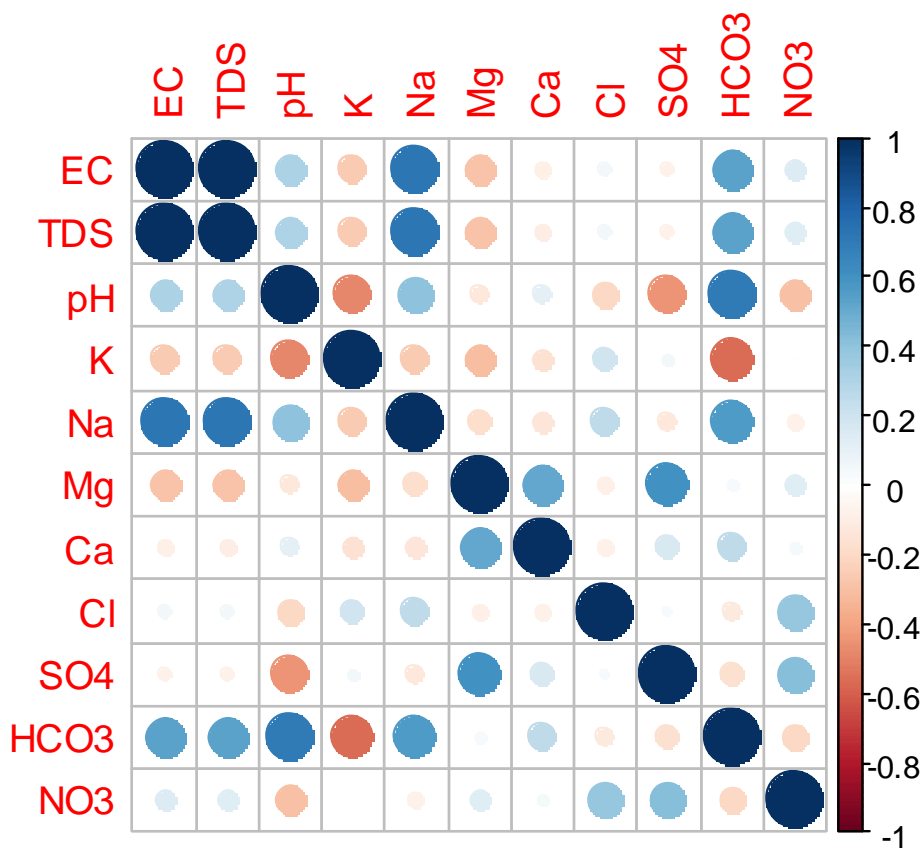
Figure 6.3: Correlation Coefficient Plot

6.4 Partial Correlation Analysis

A partial correlation coefficient enumerates the correlation between two or more variables when removing the effects of one or several other variables (de la Fuente, Bing, Hoeschele, & Mendes, 2004). The partial correlation coefficient matrix for the pumps of SCC area is given in Table 5.4. The partial correlation coefficients among eleven water quality parameters namely pH, EC, TDS, Ca^{2+}, Mg^{2+}, Na^+, K^+, CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-} and NO_3^- were calculated for correlation analysis. When removing the effects of all other parameters, pH shows negative partial correlation with the carbonates elements K^+, Ca^{2+}, Cl^-, and SO_4^{2-}.

Table 6.4: Spearman Partial Correlation Coefficient among Hydrochemical Parameters

	EC	TDS	pH	K^+	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-
EC	1.00										
TDS	**0.99***	1.00									
pH	0.28	-0.29	1.00								
K^+	-0.18	0.18	-0.10	1.00							
Na^+	-0.09	0.12	0.18	0.01	1.00						
Mg^{2+}	-0.27	0.25	0.04	-0.50	0.24	1.00					
Ca^{2+}	0.26	-0.26	-0.04	0.32	-0.29	0.59	1.00				
Cl^-	0.15	-0.17	-0.24	0.18	0.55	-0.04	0.05	1.00			
SO_4^{2-}	0.24	-0.23	-0.39	0.29	0.01	**0.64***	-0.29	-0.19	1.00		
HCO_3^-	-0.21	0.22	0.52	**-**0.34	0.12	-0.16	0.38	0.09	0.25	1.00	
NO_3^-	-0.03	0.05	0.11	-0.21	-0.42	-0.04	0.05	0.55	0.36	-0.23	1.00

*Correlation is significant at the 0.05 level (two-tailed)

A strong positive partial correlation between $Mg2+$ and SO_4^{2-} shows that most ions are involved in various physiochemical reactions, such as oxidation-reduction and ion exchange in the groundwater aquifer system (Udayalaxmi, Himabindu, & Ramadass, 2010). This analysis also shows a moderate positive correlation of EC with pH, SO_4^{2-}, Ca^{2+}. EC has also a moderate partial negative correlation with Mg and HCO3. It has a strong positive correlation with TDS (r=0.99). The NO3− shows a moderate correlation with SO_4^{2-} (0.36), Cl^- (0.55), K^+ (-0.21), and Na (-0.42) indicating that agricultural practices are significant in the study area. As the partial correlation is calculated by removing the effects of other ingradiants, we need to interpret them properly. The findings from the partial correlation analysis are depicted in Figure 6.4.
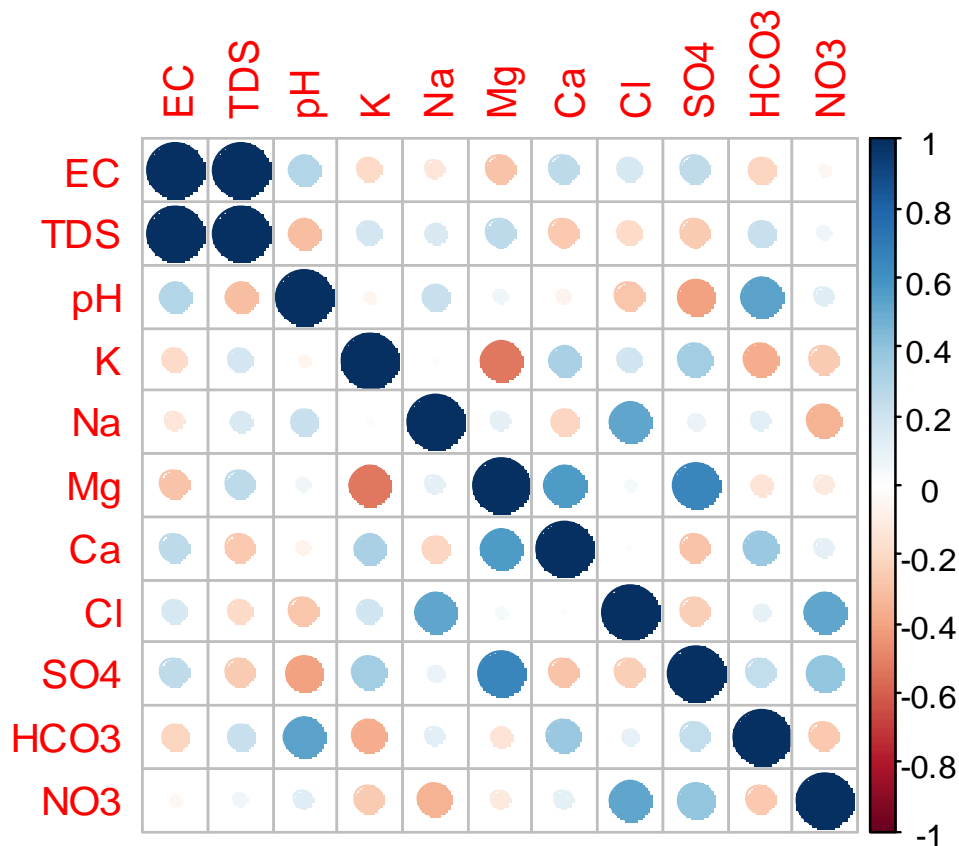
Figure 6.4: Partial Correlation Coefficient

6.5 Component Matrix with Total Variance Explained

Principal component analysis (PCA) was performed on standardized data sets (12 parameters $\times$ 20 monitoring sites) to reduce the dimensions of the original data sets and to identify latent factors affecting water quality. The number of significant principal components (PCs) is determined based on both scree plots and eigenvalue. Eigenvalue that indicates that PCs with eigenvalues are considered important when the correlation matrix is used in the analysis (Cattell, 1966). Factor scores represent the cumulate contribution of all parameters loaded on a particular factor/principal component. Positive and negative scores in the PCA indicate that most of the water samples are mainly affected or unaffected by the presence of extracted loadings (Bhuiyan et al., 2011). In this study, as presented in Table 6.5, PCA extracted three significant PCs with eigenvalues > 1, explaining about 71% of the total variance in corresponding water quality data sets of the study area. The examination of the Scree plot as shown in Figure 6.5 provides a visualization of the

variance associated with each factor, the steep slope shows the biggest factors. It is clear from the figure that there are three dominant factors of the total variance of the hydrochemistry of water.

Table 6.5: Rotated factor loadings for groundwater samples in the study area (Extraction method**)

Parameters	PC1	PC2	PC3
EC	0.434	0.175	0.239
TDS	0.434	0.173	0.241
pH	0.373	-0.005	-0.232
K	-0.229	0.427	0.059
Na	0.405	-0.029	0.225
Mg	-0.238	-0.353	0.433
Ca	-0.105	-0.387	0.402
Cl	0.009	0.421	0.203
SO4	-0.204	0.020	0.460
HCO3	0.392	-0.349	0.158
NO3	-0.063	0.427	0.388
Eigenvalue	4.05	2.07	1.70
Variance Explained (%)	36.81	18.78	15.45
Cummulative Variance (%)	36.81	55.59	71.04

** Three components extracted from matrix; Extraction method = Principal component analysis; Loadings greater than 0.3 are in bold.

The rules of classifying the factor loadings as "strong," "medium," and "weak," corresponding to absolute loading values of >0.75, 0.75– 0.50, and 0.50–0.30, respectively (Liu, Lin, & Kuo, 2003). It clearly shows that first few factors explain a relatively larger amount of variance. Whereas, the subsequent factors explain the small amount of variance. Those factors variance exceeded 70% and they are sufficient to explain the mechanisms that controlling groundwater chemistry (Nagaraju, Sunil Kumar, Thejaswi, & Sharifi, 2014).
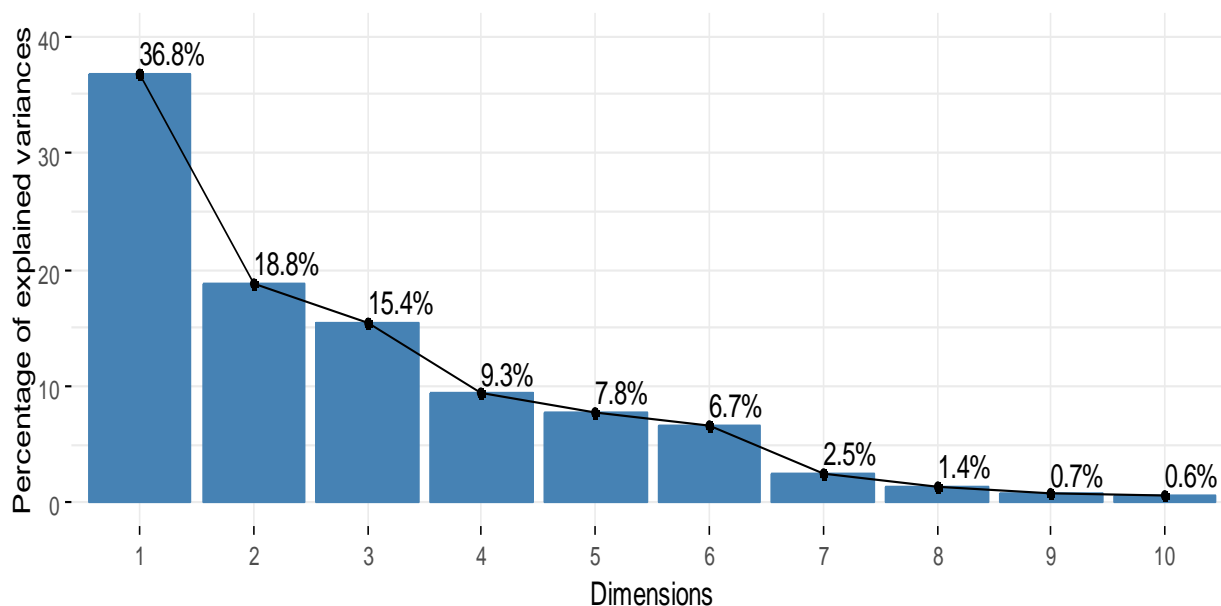
Figure 6.5: Scree plot with % of explained variance

PC1, accounting for 36.8% of the total variance, had moderate positive loadings on EC, TDS, pH and HCO3, and significant loading for other parameters. The source of these elements is natural mineralization process originated from the dissolution of minerals. PC2, accounting for 18.72% of the total variance, has moderate positive loadings on K, Cl, and NO3 and moderate negative loadings on Mg, Ca and HCO3. This factor could be related to the alkalinity of groundwater due to bicarbonate ions. In addition, PC3 accounts for about 15.4% and it is positively and moderately loaded with Mg (0.433), Ca (0.402), SO4 (0.460) and NO3 (0.388), this could be related from domestic waste and agricultural activities. (Table 6.5).

Many methods have been developed to provide multivariate data insights using interactive visualization, scatterplot, Parallel Coordination Plot (PCP) and Radar Chart as important representatives. On the radar chart (many other names, such as the Spider Chart, Star Chart, and Kiviat diagram) is a data visualization system that describes the multi-dimensional data on the two-dimensional plane (Claessen & van Wijk, 2011). It depicts and allows the comparison of several variables over time (Stafoggia et al., 2011). Rotated PCA was considered because of the logical grouping of variables under different factors and their high frequency of correlation with individual characteristics. Radar charts highlight those parameters that are undergoing the most or the least effect on the contribute to PCs. With the use of overlying data, changes in any parameters are visually depicted (Figure 6.6). Radar (spider) chart illustrates the loadings of PCA of water

quality parameters of three dominant PCA. Data for the current PC3 (red) are overlaid on data from the two previous factors (orange = PC3, green = PC2). Data represent (anti-clockwise from right) the loadings of the parameter.
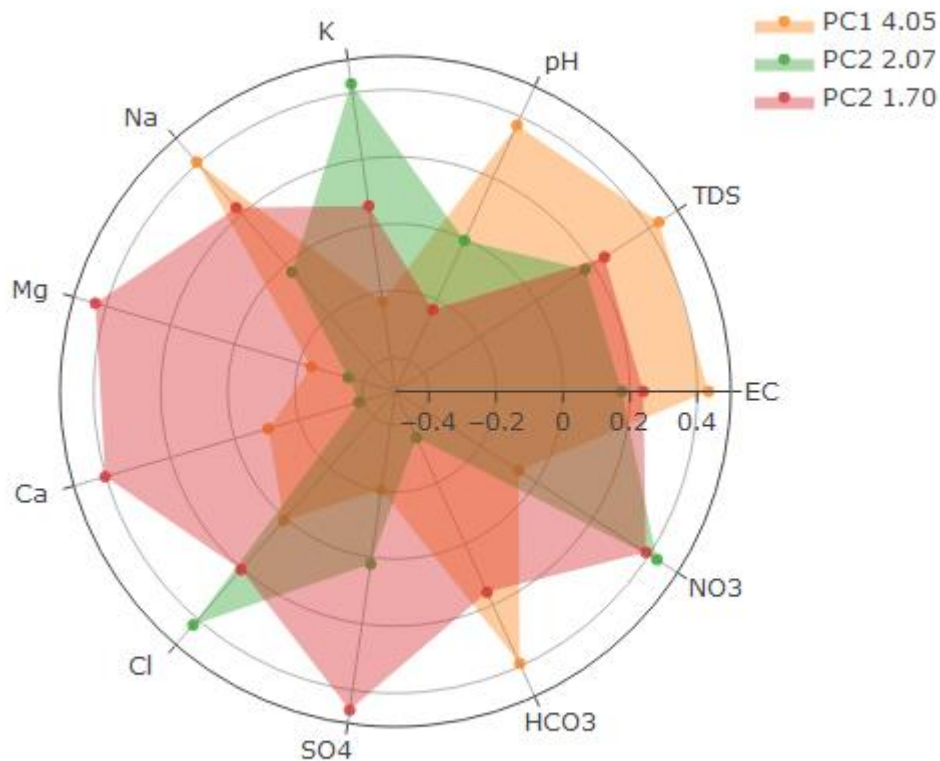
Figure 6.6: Rotated Factor Loadings of Three Water Quality Factors Extracted by PCA

6.6 Cluster Analysis

The affiliation among the pumps was obtained through cluster analysis. Cluster analysis (CA) was employed to identify groups of similar monitoring sites and explore spatial heterogeneity of water quality. As the distance between the pair of pumps increases, it indicates less similarity between the pumps with respect to water quality parameters. The physicochemical parameters were used as variables to show the heterogeneity among the pumps as a result of consequence in their relationship and the degree of contamination. The Euclidian distance between the pair of pump location. It is one of the methods to measure the similarity between the pumps location. By looking

into the squared Euclidian distance table, it was observed great variability between the pumps (Appendix 6.2).

Essentially, data points with the smallest distances between them are grouped together. Then the data with the next smallest distances are added to each group, etc. until all observations end up together in one large group. The cluster is interpreted by observing the pattern produced. These may have some practical meaning in terms of the research problem. For this reason, hierarchical cluster analysis was used to detect the similarity groups between the sampling sites. Since hierarchical agglomerative cluster analysis was used, the number of clusters was also decided by the practicality of the results as there was information available on the study sites. It generated a dendrogram, grouping the 20 sites into five distinct clusters (Figure 6.6).

The distance ranged from 1.14 to 8.08. The smallest distance observed was 0.642 between P5 and P15 followed by 1.33 between P5 and P17. The highest distance observed was 8.08 between P8 and P2 followed by 7.79 between P2 and P6 (Appendix 6.2).
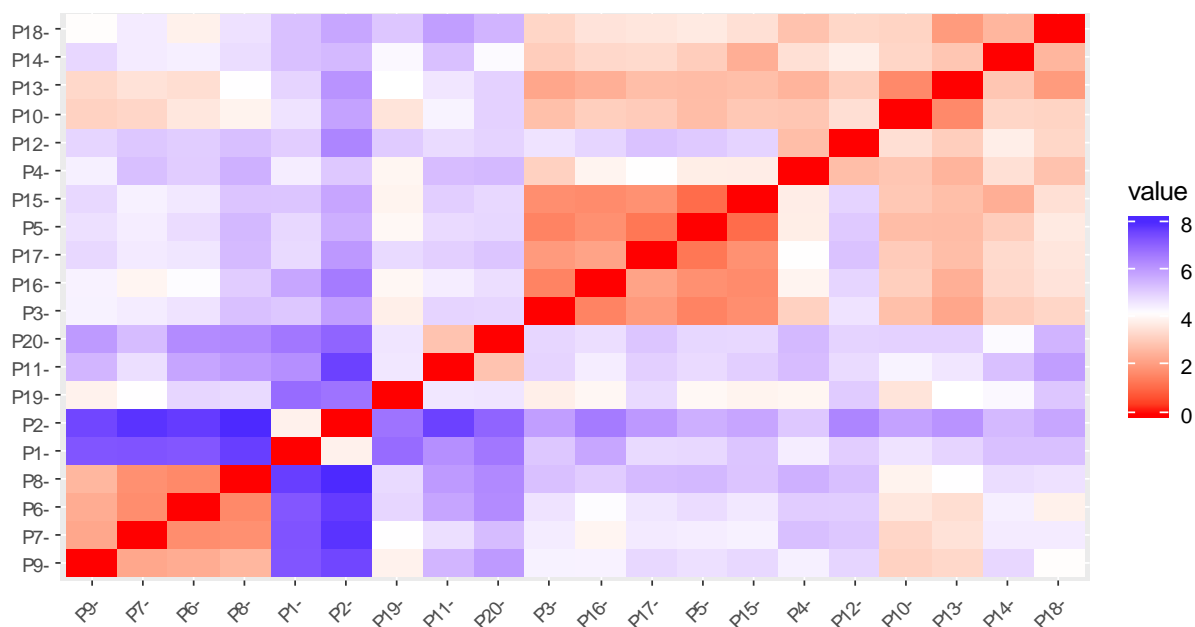
Figure 6.9: Dissimilatiy Matrix Based on Euclidean Distance

Results in Table 6.6 shows the history of the clustering process. In our case, CA has indicated five clusters or groups (Cluster 5/Group E the major cluster and Cluster 1/Group A the minor clusters). Even though Group E is uniform, there was some variability seen in the dendrogram. Group A

included two lower-most sites P1 (Raaj Para Pump House) and P2 (M. C. College Pump House), exhibiting similar variation located in Ward-20 and north-eastern part of Sylhet City Corporation. It consists of 10% of the total sample points. The presence of minor clusters could have been a result of the mixing of water types. Group B included sites P6-P9, located on Ward-9 which is situated in eastern part of Sylhet City Corporation and it consists of 20% of the total sample points.

Table 6.6: Cluster Groups and their members

Group	Members (Location/Sample No.)	N (%)
A	P1, P2	2 (10)
B	P6, P7, P8, P9	4 (20)
C	P11, P19, P20	3 (15)
D	P3, P5, P15, P16, P17	5 (25)
E	P4, P10, P12, P13, P14, P18	6 (30)

Within Group C, the three sites below reservoirs (Pumps P11, P19, and P20) were clustered which is located on Ward-6, Ward-14, and Ward-18 and it consists of 15% of the total sample points. Group D included the (P3 and P5) which is located on Ward-5 and Ward-8 and also P15, P16, and P17 which is located on Ward-9 were just below the Ward-8, western part of Sylhet City Corporation. It consists of 25% of the total sample points. Group E included the six higher-most sites (P4, P10, P12, P13, P14, and P18) located on Ward-1, Ward-5, Ward-6, and Ward-19. Figure 13 shows the dendrogram of clustered lakes. It consists of 30% of the total sample points hence there is one dominant cluster. From the distribution of the points however, Group C, Group D, and Group E are located in areas where the hydrogeology is complex or influenced by other processes. As a result, there was high variation in water parameter. It is yields a dendrogram (Figure 6.10) and grouping all 20 sampling sites of the study area into five statistically significant clusters.

6.7 Dendrogram HCA
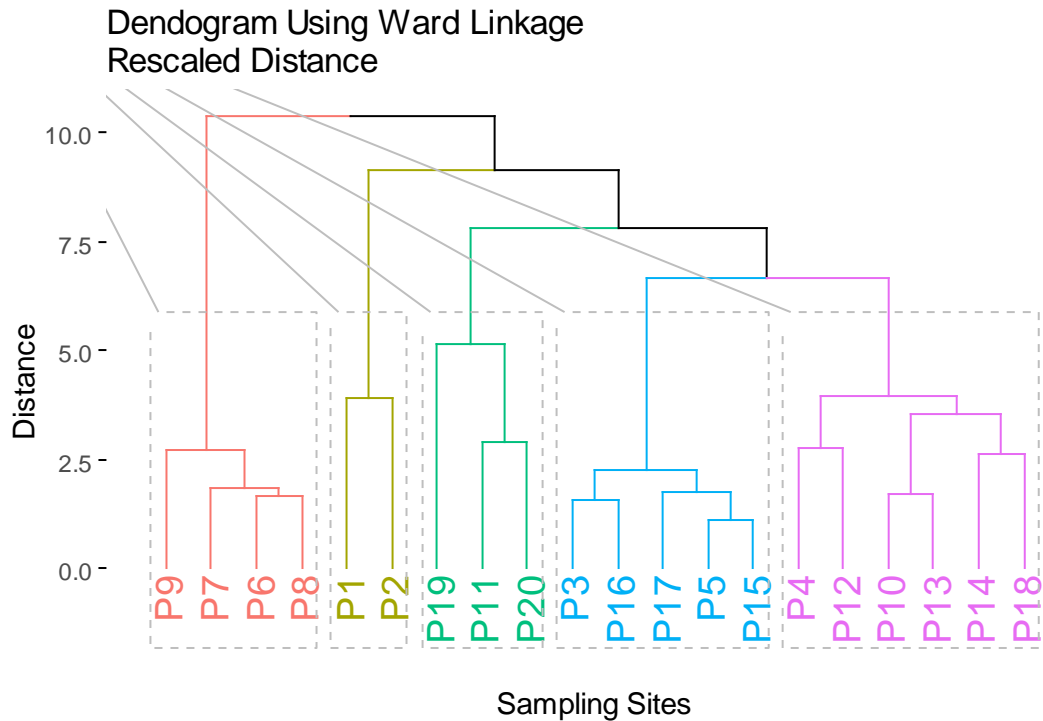
Figure 6.10: Dendogram of Cluster Analysis on Water Quality Parameters

The mean value of EC was highest in Group B. This may be because of the rock composition that determines the chemistry of the watershed soil and ultimate the water quality of the pump. For example, limestone leads to higher EC because of the dissolution of carbonate minerals in the study area. The mean value of EC was lowest in Group A. As water quality/purity depends on EC (purer the water the lower the conductivity). The water of Group A was purer than other groups (Almahrooqi, 2012).

The chemistry of this area may have varied enough. In Group B TDS was high and it was lower among in Groups. Higher TDS in the water not only changes the taste of the water but also increases the risk of health problem. Low TDS level in water does not have any side effects. Low level of TDS represents a better quality of water. But if the TDS level in water is less than 10, some of the essential minerals from the water which are necessary get removed (Kozisek, 2005). pH is also similar to TDS and EC for Group A and Group B. Sodium and potassium are highest on Group A and Group B. In addition, chloride was highest in Group A and lowest in Group D.

Magnesium is highest in Group A and lowest in Group D, calcium is also same for these two groups. It explains that it dissolved from most soils and rocks, especially limestone, dolomite, and gypsum. Usually, they have no effect on the suitability of water for irrigation or stock water. Sulfate is only detected in three groups A, C, and E.

Table 6.7: Mean Value of Ionic Concentrations for Groundwater Samples in the Study Area*

Parameters	Group A	Group B	Group C	Group D	Group E
EC	55.50	310.00	263.00	150.80	186.50
TDS	33.50	186.25	157.67	90.20	112.00
pH	5.95	7.35	7.03	7.22	7.27
K^+	1.93	1.07	1.83	1.37	1.12
Na^+	5.50	21.25	14.00	7.20	9.17
Mg^{2+}	38.82	26.71	24.19	23.01	32.76
Ca^{2+}	12.26	9.56	6.41	6.11	9.50
Cl^-	35.50	33.50	61.00	32.00	32.67
SO_4^{2-}	4.50	0	2.00	0	3.50
CO_3^{2-}	ND	ND	ND	ND	ND
HCO_3^-	58.00	143.75	65.00	66.00	89.67
NO_3^-	0.60	0.43	1.83	0.54	1.32

* All values are in mg/l, except pH

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

This chapter includes several section. In the first section the main inputs and results of the holistic assessment conducted in this study of water quality are presented. The second section summarizes a viable recommendation about water quality status.

7.1 Conclusions

Water demand for domestic and other purposes is increasing rapidly and causing over-pumping of the water resources in the study area. As a result, water quality issues like groundwater contamination is a major concern for water resources development projects as well as for people's health by drinking water. Due to the rapid increase in urbanization and industrialization, the water bodies are getting polluted fast and scarcity of drinking water are the major problems. Improper maintenance of city sewage lines and industrial effluents are considered to be one of the major reasons for the pollution of water.

Hydrochemical assessment and multivariate statistical methods were successfully applied in this study to evaluate the variation in water quality and to identify possible anthropogenic sources of water quality patterns at selected sites. The results are useful for Sylhet water quality management. HCA has divided the 20 selected sites into five groups, on the basis of equality of water quality characteristics. For example, the number of monitoring sites could be reduced by selecting only one site from each of the five groups.

Findings of the Research

The main findings of the research can be summarized as follows:

7.1.1 Hydrochemical Characteristics

- About 50% of the samples data passed the quality control tests that are were permitted for further analysis using classical hydrochemical plotting and multivariate analysis techniques.

- The predominant water type in the study area is the Mg–HCO$_3$ water, while some locations have Mg-Cl water type.

- The study not only verified the observed water quality for all intended uses, but went further to examine the developed of cause-effect relationships between groundwater quality and environmental data (geology, hydrogeology, land use, pollutant sources). Low mineralization indicated the situation of short stay of underground water in shallow aquifer.

- A critical analysis for the chemical elements speciation and concentration in the ground water as well as the mineral saturation indices indicate that because of continuous exploitation, the halite minerals continue to dissolve, thereby resulting in a continuous increase in the TDS content of the study area.

- The water in the study are have been found good for irrigation.

- Anhydrite, halite, and gypsum are found to be the main source-rocks to explain the ion composition in the water levels. It is mainly due to carbonate weathering and dissolution of evaporite Gypsum. Anthropogenic processes also play a major role in the quality of water.

- Urbanization and agricultural activities are not responsible for water quality. This is because nitrate and sodium absorption ratios present in the study area is not high. The impact of groundwater flow could not be fully assessed because of inadequate data.

- EC (salinity hazard), Sodium percent (Na%), Sodium adsorption ratio (SAR), were used to assess the water quality for irrigation purposes. The hydrochemical data was further analyzed using multivariate statistical methods.

- The map of these results was presented using ArcGIS. The results revealed that most of the samples are within the permissible range for WHO (2011) guidelines for water quality.

7.1.2 Statistical Analysis

1. Univariate and bivariate statistics identified that behavior of the major chemical parameters in groundwater of the SCC area support the findings of the hydrochemical assessments.

2. The multivariate statistical techniques such as cluster analysis and factor analysis have been applied in this study for drawing meaningful information.

3. Three factors were extracted that have effects on the hydrochemistry of groundwater of SCC area. The most important factor with 36% variation could be due to the source of those elements in natural mineralization process originated from dissolution of minerals. The second factor with 18% could be due to alkalinity of groundwater and bicarbonate ions in the water. The third factor with 15% variation could be due to domestic waste and agricultural activities.

4. Factor analysis identified some important factors responsible for the quality of water. The increased level of EC, TDS, pH, Na, HCO3 and Mg were the main contributors to the quality in the study area.

5. Both the hydrochemical and statistical classification techniques indicated the presence of a dominant type of water.

6. Cluster analysis indicated one major cluster (or groundwater type) and two smaller clusters (or groundwater types). Cluster analysis focused on the areas with contrasting hydrogeology from the main area by a measure of parameter similarity.

7.2 Limitations and Recommendations for Future Works

This study may be considered a preliminary assessment of water quality, and therefore serve as a guideline to established framework for trend monitoring and vulnerability studies.

7.2.1 Limitations of the Study

1. As this study aimed at to gain some knowledge about the underlying hydrochemical interactions it did not yet investigate other approaches e.g. supervised classification techniques or other multivariate state-of-the-art chemometrics techniques or pattern recognition processes including multiple linear regression (MLR), canonical corresponding analysis, discriminant analysis, etc.

2. To ensure utmost reliability and validity in conducting a laboratory-based study on hydrochemical properties of water, a large sample size is required, which is absent in here.

3. Frequent monitoring of the pumps is required for proper evoluation. This is not possible in this study.

4. The classification may be questioned as some of the data points were not electroneutrality balanced.

5. There is no opportunity to compare the present study with others as such studies are not available for the targeted area.

6. No comparison was made between the groundwater and surface water which is necessary for proper evaluation.

7.2.2 Recommendations

1. The overall quality of groundwater is not harmful but continious evaluation is necessary for proper maintainance.

2. It is recommended to delineate a good field area and it should be included in the master plan of the towns and land-use management plan of sorrounding area. This will helps to avoid anthropogenic effects.

3. It is obvious that domestic uses and drinking water supply using groundwater mainly causes over-pumping, evaporation and anthropogenic pollution of shallow groundwater. Hence, it is suggested to surface water with proper treatment.

4. The study area is covered by different geological formations. Therefore, detailed study of mineral and chemical composition of the rocks is recommended.

5. Series of study shoi and compared to the update data to examine the effects of the update data.

6. Incorporate hydrological parameters into the chemical assessment e.g. water levels, thermal profiles, depth profiles (this was attempted in the field but not successful).

7. To verify the output of the geostatistical assessments and to identify spatial correlations on a small scale.

8. A detailed study needs based on all pumps under SCC.

9. Some of the pumps are maintained by government who have a limited budget. So, one option may be handover the pumps to private institutions, NGO's for batter maintenance.

Appendix

Appendix Table 5.1: Ions in milliequivalents Per Litre (mEq/L)

ID	Cations (mEq/L)				Anions (mEq/L)					$\sum$Cations	$\sum$Anions
	K^+	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	NO_3^-		
P1	0.0529	0.2610	2.9830	0.5399	0.6770	0.1666	ND	0.6883	0.0109	3.8368	1.5428
P2	0.0455	0.2175	3.4050	0.6837	1.3260	0.0208	ND	1.2130	0.0152	4.3517	2.575
P3	0.0287	0.4350	2.2140	0.2640	0.9026	0.0000	ND	0.9018	0.0174	2.9417	1.8218
P4	0.0210	0.3480	3.2310	0.4202	1.2410	0.1041	ND	1.1640	0.0239	4.0202	2.533
P5	0.0409	0.3045	1.5950	0.2999	0.9872	0.0000	ND	1.1800	0.0087	2.2403	2.1759
P6	0.0230	0.7391	2.068	0.528	0.7616	0.0000	ND	2.3279	0.0043	3.3581	3.0938
P7	0.0343	0.9130	1.7910	0.4202	0.9872	0.0000	ND	2.3607	0.0130	3.1585	3.3609
P8	0.0269	1.1310	2.0390	0.5998	0.9026	0.0000	ND	2.3770	0.0109	3.7967	3.2905
P9	0.0256	0.9130	2.8950	0.3598	1.1280	0.0000	ND	2.3607	0.0087	4.1934	3.4974
P10	0.0386	0.6960	2.4850	0.3838	0.9590	0.0833	ND	1.7860	0.0152	3.6034	2.8435
P11	0.0560	0.5655	1.7780	0.2400	1.4670	0.1041	ND	0.9997	0.0391	2.6395	2.6099
P12	0.0274	0.4350	2.9430	0.5399	0.9872	0.1667	ND	1.4090	0.0478	3.9453	2.6107
P13	0.0289	0.4350	2.5350	0.3598	0.7052	0.0625	ND	1.5900	0.0217	3.3587	2.3794
P14	0.0330	0.3045	2.0740	0.6118	1.0440	0.0000	ND	1.2460	0.0348	3.0233	2.3248
P15	0.0343	0.2610	1.6460	0.3838	1.0440	0.0000	ND	1.1800	0.0130	2.3251	2.237
P16	0.0287	0.3045	1.6240	0.2400	0.9026	0.0000	ND	1.2290	0.0174	2.1972	2.149
P17	0.0430	0.2610	2.0240	0.3358	0.6770	0.0000	ND	0.9178	0.0022	2.6638	1.597
P18	0.0228	0.1740	2.9070	0.5280	0.5923	0.0208	ND	1.6220	0.0283	3.6318	2.2634
P19	0.0284	0.8265	2.1940	0.3239	2.0870	0.0208	ND	1.4420	0.0196	3.3728	3.5694
P20	0.0558	0.4350	2.0000	0.3957	1.6080	0.0000	ND	0.7539	0.0609	2.8865	2.4228

Appendix Table 6.1: Ionic Variation of hydrochemical parameters of groundwater samples in the study area*.

ID	EC at 25ºC (mmohs/cm)	TDS	pH	K^+	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	NO_3^-
P1	83	50	6.2	2.07	6	36.25	10.82	24	8	ND	42	0.5
P2	28	17	5.7	1.78	5	41.38	13.7	47	1.0	ND	74	0.7
P3	142	85	7.2	1.12	10	26.90	5.29	32	0.0	ND	55	0.8
P4	156	94	7.1	0.82	8	39.26	8.42	44	5	ND	71	1.1
P5	128	77	7.2	1.60	7	23.81	6.01	35	0.0	ND	72	0.4
P6	320	192	7.3	0.90	17	25.13	10.58	27	0	ND	142	0.2
P7	313	188	7.3	1.34	21	21.76	8.42	35	0	ND	144	0.6
P8	311	187	7.4	1.05	26	24.78	12.02	32	0	ND	145	0.5
P9	296	178	7.4	1.00	21	35.18	7.21	40	0	ND	144	0.4
P10	176	106	7.3	1.51	16	30.20	7.69	34	4	ND	109	0.7
P11	321	193	6.8	2.19	13	21.61	4.81	52	5.0	ND	61	1.8
P12	234	140	7.2	1.07	10	35.76	10.82	35	8.0	ND	86	2.2
P13	203	122	7.3	1.13	10	30.81	7.21	25	3.0	ND	97	1.0
P14	152	91	7.4	1.29	7	25.20	12.26	37	0.0	ND	76	1.6
P15	129	77	7.3	1.34	6	20	7.69	37	0.0	ND	72	0.6
P16	189	113	7.1	1.12	7	19.73	4.81	32	0	ND	75	0.8
P17	166	99	7.3	1.68	6	24.6	6.73	24	0	ND	56	0.1
P18	198	119	7.3	0.89	4	35.33	10.58	21	1	ND	99	1.3
P19	194	116	7.3	1.11	19	26.66	6.49	74	1	ND	88	0.9
P20	274	164	7.0	2.18	10	24.31	7.93	57	0	ND	46	2.8

*All values are in mg/l, except pH, ND = not detected

Appendix Table 6.2: Squared Euclidian distance between the lakes

Case	Squared Euclidean Distance																			
	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17	P18	P19	P20
P1	0.00																			
P2	3.92	0.00																		
P3	5.25	6.00	0.00																	
P4	4.56	5.23	3.21	0.00																
P5	4.94	5.69	1.57	3.85	0.00															
P6	7.33	7.79	4.74	5.15	4.87	0.00														
P7	7.38	7.93	4.58	5.39	4.55	1.77	0.00													
P8	7.74	8.08	5.39	5.68	5.53	1.69	1.82	0.00												
P9	7.36	7.62	4.48	4.51	4.80	2.40	2.31	2.64	0.00											
P10	4.73	5.93	2.83	2.97	2.77	3.70	3.33	3.97	3.23	0.00										
P11	6.29	7.69	5.02	5.44	4.90	5.88	4.82	6.07	5.57	4.45	0.00									
P12	5.13	6.48	4.73	2.79	5.22	5.14	5.25	5.40	4.99	3.53	4.89	0.00								
P13	5.01	6.21	2.28	2.58	2.75	3.49	3.59	4.25	3.37	1.70	4.69	3.15	0.00							
P14	5.37	5.50	3.12	3.55	3.13	4.53	4.59	4.85	4.95	3.32	5.38	3.87	2.98	0.00						
P15	5.29	5.87	1.79	3.84	1.14	4.66	4.48	5.31	4.93	3.02	5.13	5.03	2.81	2.46	0.00					
P16	5.85	6.66	1.57	3.99	1.83	4.29	4.02	5.15	4.47	3.17	4.56	5.00	2.49	3.38	1.73	0.00				
P17	4.90	6.12	2.04	4.22	1.33	4.69	4.61	5.49	4.93	3.09	5.10	5.35	2.79	3.41	1.85	2.22	0.00			
P18	5.38	5.85	3.32	2.89	3.77	3.91	4.59	4.77	4.19	3.27	6.00	3.34	2.04	2.63	3.55	3.63	3.68	0.00		
P19	6.95	6.81	3.87	4.03	4.08	4.98	4.25	4.91	3.95	3.64	4.66	5.17	4.23	4.36	3.98	4.06	4.91	5.27	0.00	
P20	6.73	7.09	4.98	5.51	4.96	6.36	5.46	6.39	6.08	5.06	2.92	5.04	5.06	4.33	4.95	4.84	5.29	5.59	4.70	0.00

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