2013

Geo-chemistry of Ground Water in Rajshahi City and Improving its Quality for Drinking Purpose

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University of Rajshahi

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A Thesis
Submitted to the Institute of Environmental Science at the
University of Rajshahi in Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY
IN
ENVIRONMENTAL SCIENCE

BY

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JUNE 2013

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June 2013

Dedicated To
My Parents Abdus Sattar Sikder
and Fatama Begum
For
Teaching Me Everything

DECLARATION

I declare that the thesis entitled **"Geo-chemistry of Ground Water in Rajshahi City and Improving its Quality for Drinking Purpose"** is the result of my original research work and submitted to the Institute of Environmental Science at the University of Rajshahi, Bangladesh for the degree of Doctor of Philosophy in Environmental Science.

I further declare that this thesis has not been submitted in part or full previously for the award of any other degree or diploma in any institution and to the best of my knowledge and belief, the research contains no material previously published or written by another person, except where due reference has been made in the text of the thesis.

এস,এম, হেলাল উদ্দি
২৫.১১.২০১৬
(S. M. Helal Uddin)
Ph.D. Researcher

Certificate

This is to certify that Mr. S. M. Helal Uddin is the sole author of the desertification entitled **"Geo-chemistry of Ground Water in Rajshahi City and Improving its Quality for Drinking Purpose".** This desertification or part thereof has not been the basis for the award of any degree, diploma or associated with any other similar title.

We are forwarding this desertification to be examined for the degree of Doctor of Philosophy in the Institute of Environmental Science (IES) at the University of Rajshahi, Bangladesh. The data presented in the thesis are genuine and original. Mr. Helal Uddin has fulfilled all the requirements according to the rules of the University for submission of a desertification for the Ph.D. degree and made distinct contribution to the environmental science.

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ACKNOWLEDGEMENTS

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S. M. Helal Uddin

ABSTRACT

The study was aimed at improving the fundamental understanding of the geochemistry of groundwater in Rajshahi City with a focus on constituents that pose a human health risks. The study was attempted to evaluate the major ionic chemistry, weathering and solute acquisition processes controlling water composition, and suitability of water quality for drinking purpose. A total of 240 (180 shallow and 60 deep) tubewells water samples were collected from 40 locations during pre, post-monsoon and monsoon season covering two years. Also a total of 30 aquifer soil samples were collected at depths (10-45 meter) from 30 locations during monsoon season in 2010 to know soil characteristics. A detailed laboratory analysis was carried to determine the characteristics of groundwater and aquifer soil samples of Rajshahi City. Also multivariate statistical analyses were conducted using various softwares (SPSS, AQUACHEM etc.) and the results were plotted to determine hydrochemistry, water quality and water type.

The concentrations of Ca^{2+} and Cd^{2+} were the highest and lowest quantities among cations in the aquifer soil samples, respectively and their mean amounts were 166.08 and 0.133 mg/kg, respectively. Among anions, HCO_3^- and NO_3^- were the maximum and minimum concentrations and their concentrations were 580 and 3.87 mg/kg, respectively. The results of the analyzed aquifer soil samples showed that the mean concentrations of cationic parameters were followed the order: $Ca^{2+}> Mg^{2+}> Na^+> K^+> Fe^{3+}> Mn^{2+}> Zn^{2+}> Cu^{2+}> Pb^{2+}>As(total)> Cd^{2+}$ and that of the anions were: $HCO_3^-> Cl^-> SO_4^{2-}>NO_3^-$.

The analyzed results of the hydro-chemical composition of the shallow and deep tubewells water in the Rajshahi City showed that the groundwater of the study area was slightly acidic to neutral pH, hard to very hard and fresh category. Ca^{2+} was the dominant ionic species among the cations in both the shallow and deep tubewells water and their mean concentrations were 78.354 mg/L for the shallow and 78.541 mg/L for deep tubewells. HCO_3^- was the dominant species with an average of 245.30 mg/L for shallow and 188.362 mg/L for deep tubewells water. The analyzed results show that the mean concentrations of cations and anions in both shallow and deep tubewells water samples were followed the order: $Ca^{2+}> Mg^{2+}> Na^+> K^+> Fe^{3+}> Mn^{2+}> Pb^{2+}> Zn^{2+}> Cu^{2+}> As(total)> Cd^{2+}$ and $HCO_3^-> Cl^-> SO_4^{2-}> NO_3^-$, respectively. Most of the groundwater samples contained concentration of TH, HCO_3^-, Ca^{2+}, Mn^{2+}, Fe^{3+} and Pb^{2+} that exceeded

the permissible limit for World Health Organization (WHO) and Bangladesh Drinking Water Standard (BD-DWS). About 40% groundwater samples exceeded As(total) concentration for the WHO standard limit. The study observes that most of the physico-chemical parameters were found to be higher in the pre and post-monsoon seasons compared to the monsoon season may be the cause of decreasing the volume of water in aquifer.

The analysis results using AQUACHEM software Version 5.1 illustrate that most of the samples fall in the field of Ca^{2+}-HCO_3^- water type in the quadrilateral diagram during the pre, post-monsoon and monsoon. The negative values of Chloro Alkaline Indices suggested the reverse ion exchange process was the major chemical reaction controlling the chemistry of the groundwater. The scatter diagrams of Ca^{2+} versus HCO_3^- and also $m(Ca^{2+} + Mg^{2+})/mHCO_3^-$ versus Cl^- indicate that Ca^{2+} and HCO_3^- were derived from calcite weathering. The average C-ratio and P_{CO_2} were 0.85 and 0.03545 atm in groundwater, respectively which suggests that the carbonic acid was the weathering agent of calcite. Four methods namely the Saturation Indices, Stiff diagram, Gibbs plots and factor analysis were used to understand the geochemistry, which illustrated that the rock water interaction was the major geochemical process controlling the chemistry of groundwater of the study area.

Ca, Mn, Fe, As(total) and Pb ions were found the principal contaminants among the cations in almost all groundwater samples. The consumption of contaminated water poses serious threats to human health. Excessive intake of these contaminants through drinking water may cause illness. The water quality of the area was not suitable for drinking purpose and is suggesting to treat the water before drink. Hence, the experiments were carried out for removing excessive Ca, Mn, Fe, As(total) and Pb ions from the water using batch and column adsorbent experiments with different adsorbents such as sand, sand-stone and various amounts of magnetite (Fe_3O_4) enriched sand. 2g magnetite enriched sand adsorbent showed the best removal efficiencies among the adsorbents and the removal percentage were about 97 and 83% for As(total) and Pb ions from the initial concentration containing 0.50 mg/L As(total) and 3 mg/L Pb ions spiked groundwater, respectively. But in case of Mn ion, the sand adsorbent showed better removal efficiency over magnetite enriched sand adsorbent and the removal percentage was 92% from the initial concentration containing 3.0 mg/L Mn ion spiked groundwater. In column

adsorption experiments, 2g magnetite enriched sand-stone adsorbent also showed the better removal efficiencies over on sand-stone adsorbent and the removal percentage were about 77 and 70% for Ca and Fe ions from the initial concentration containing 100 mg/L Ca and 3 mg/L Fe ions spiked water, respectively. The overall adsorption study results show that the treated water contained Ca, Mn, Fe, As(total) and Pb ions were well below the permissible limit of WHO and BD-DWS.

Thus the study suggests that the sand-stone enriched with magnetic adsorbent could be used for removal contaminants from water and thus the water quality would be enhanced and ensured safe water in the area. A detailed study on kinetics and mechanism of sand-stone enriched magnetite adsorbent would have to be considered for further development of the adsorbent process. Finally, the sand-stone enriched with magnetic adsorbent could be considered as economically suitable indigenous materials for removing contaminants from water in the area.

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ABBREVIATIONS

AAS-Atomic Absorption Spectrophotometer

ASS-Aquifer Soil Sample

MSL- Mean Sea Level

BD-DWS- Bangladesh Drinking Water Standard

CAI- Chloro Alkaline Indices

CFU- Coliform Forming Unit

DTW-Deep Tubewells Water

EC- Electrical Conductivity

FC-Faecal Coliform

MEUF-Micellar Enhanced Ultra-Filtration

PEUF- Polymer Enhanced Ultra-Filtration

RWASA-Rajshahi Water Supply and Sewarge Authority

RSD-Relative Standard Deviation

SI- Saturation Indices

STW-Shallow Tubewells Water

TDS- Total Dissolved Solid

TC- Total Coliform

TSS-Total Suspended Solid

TH-Total Hardness

TS-Total Solids

UV Spectrophotometer-Ultra Violet Spectrophotometer

UF- Ultra Filter

WHO-World Health Organization

Chapter One

Introduction

INTRODUCTION

1.1 Introduction

Water is very important for human health, agriculture, industry, ensuring integrity and sustainability of the Earth's ecosystem, which is an undisputed fact. Groundwater is an important natural resource for domestic, industrial, commercial and irrigation purposes. Safe drinking water is absolutely essential for healthy living. It is the single largest source of drinking water in most of the developing countries and estimated that approximately one third of the world's population is depending on groundwater where the general assumption of groundwater is being safe to drink (Nickson *et al.*, 2005). About 96% of the total population in Bangladesh has access to drinking water from tubewells (WHO Regional Office for South-East Asia, 2002).

Groundwater refers to water that occurs in the zone of saturation below the water-table, the water-table being the surface that divides rocks in which the pores are completely filled with water from those that are partially filled with air (Drever, 1997). It is perceived to be a safer source of drinking water with adequate protection and excellent microbial and chemical quality that requires minimum treatment. Groundwater resources in arid and semi-arid regions play a vital role on the socioeconomic development.

Geochemistry is the science that uses the tools and principles of chemistry to explain the mechanisms behind major geological systems such as the Earth's crust and its oceans (Albarede, 2003). More specifically, it is the study of the absolute and relative abundances of chemical elements in the rocks, minerals, ores, soils, water and atmosphere of the earth and the distribution and movement of these elements from one place to another as a result of their chemical and physical changes (Konard, 1967). Of them changes, chemical studies provide insights into the mechanisms of ancient sedimentary rocks and the fluids contained in them. Today, important work in geochemistry involves the study of geochemical cycles in the atmosphere, marine and estuarine waters, and the earth's crust. There are many studies in relation to the effects of massive amounts of pollutants on the environment. Geochemistry of groundwater is an important factor for determining its use for various purposes such as domestic, irrigation and industrial uses. It depends on a number of factors, such as general geology, degree of

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chemical weathering of the various rock types, quality of recharge water and inputs from sources of other water-rock interaction (Domenico, 1972; Hem, 1989; Schuh *et al.,* 1997; Toth, 1984). This process that is responsible for altering the chemical composition of groundwater varies with respect with space and time. This process also helps to obtain an insight into the contributions of rock/soil-water interaction and anthropogenic influences on groundwater. So, interaction of groundwater with aquifer minerals through which it flows greatly controls the groundwater chemistry (Hussein, 2004).

Almost 71% of the earth's surface area is covered by water. Total water resources of the world are estimated at 1.36×10^8 million ha-m (Shiklomanov and Rodda, 2003). Of these global water resources about 97.20% is saline water, mainly in oceans and only 2.80 % is available as fresh water. Out of 2.80% fresh water, about 2.20% and 0.60% water are available as surface water and groundwater, respectively. Even out of the 2.20% of surface, about 2.15% is confined in glaciers icecaps and only 0.01% (1.36×10^4 million ha-m) is available in lakes and streams, the remaining 0.04% is being in other forms. Out of the 0.60% of stored groundwater, only about 0.25% (34×10^4 million ha-m) can be economically extracted with the present drilling technology (Deshpande, 1963).

Most of the developing countries, population depend on groundwater for drinking, irrigation and domestic water uses, but yet the groundwater quality and its management have not received much attention. Millennium Development Goals (MDG) are an ambitious agenda for reducing poverty and improving lives that world leaders agreed on at the Millennium Summit in September, 2000. Of the eight goals, ensure environmental sustainability is the most important goal. The MDG have attempted to address the current unacceptable levels of lack of access to safe drinking water by aiming to halve the proportion of people without sustainable access to safe drinking water by 2015.

Due to the ever-increasing demand for drinking and irrigation water and inadequate of surface water, the importance of groundwater is increasing exponentially everyday. At the same time intense urbanization has placed a high demand on groundwater resources in arid and semi arid regions as a result groundwater quality has been deteriorated (Jalali, 2005). Groundwater quality comprises of the physical, chemical and biological qualities. A detailed geochemical study of groundwater is used to understand the role of various elements in watersheds, including all the major ions such as Na, Mg, Al, Fe, Mn, S, K,

Ca, Cr, Ni, Cu, Zn, Pb, Hg and how the elemental fluxes are exchanged through atmospheric terrestrial aquatic interactions. Hydro-geochemical composition of groundwater can also be indicative of its origin and history of the passage through underground materials with which water has been in contact. Groundwater contains dissolved minerals from the soil layers during recirculation through which it passes. It may also contain some harmful contaminants through the process of seepage from the surface water and biological activities. The water bodies are continuously subjected to a dynamic state of change with respect to lithological characteristics and geo-climatic conditions. This dynamic balance in the aquatic system is upset by human activities, resulting in contamination or pollution which is unsustainable development.

The quality of groundwater is equally important to its quantity owing to suitability and intended use of water for various purposes. The variation of groundwater quality in an area is a function of physical, chemical and biological parameters that are greatly influenced by geological formations and anthropogenic activities (Jiang and Yan, 2010; Nisi *et al.*, 2008; Perumal and Thamarai, 2008; Singh and Chandel, 2006; Subramani *et al.*, 2005a; Tatawat and Chandel, 2008). Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium. Prolonged exposure to heavy metals such as Ni, Cu, Zn and Cd can cause deleterious health effects in humans (Reilly, 1991). Heavy metals are the elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Srivastava and Majumder, 2008). There are several impacts on potential human health due to intake poor quality of water. Therefore, water quality issues and its management options need to be given greater attention in developing countries. The management of groundwater quality is essential for sustainable water uses for various purposes. Because purified water is fit for a specific purpose such as drinking water, industrial processes, medical and many other purposes. Water treatment technique may reduce the concentration of particulate matter including suspended particles, bacteria, viruses and a range of dissolved elements. In general, the methods used include physical process such as filtration and sedimentation, biological processes such as slow sand filters or activated sludge, chemical process such as flocculation and chlorination and the use of electromagnetic radiation such as ultraviolet light.

1.2 Scope of the research

Consumption of water per capita is one of the major indicators of life-standard in modern and civilized society. For this reason, the assessment of water quality and the study for the improvement of the water supply system is essential. Rajshahi Water Supply and Sewerage Authority (RWASA) supplies water through pipe network but people do not rely on the quality of this water. Most of the people prefer tubewells water for drinking purpose. The geochemistry of groundwater in Rajshahi City has been assessed principally by the consideration of the abundance and ratios of chemical parameters within shallow and deep tubewells water and how these related to hydro-geochemical process and to mineral suite within the aquifer material. The hydro-geochemical analysis employed in this study encompasses the suite of physico-chemical, major ion, minor ion, water type etc. Arsenic has been identified as a tremendous menace for the public health of the country. So, a detailed study is to be needed regarding water quality situation in the City area and to earn adequate knowledge about heavy metals in groundwater for getting rid of the problem by adequate treatment process.

1.3 Aim and objectives of the research

The aim of this study was to understand the geochemistry of groundwater of Rajshahi City and improve the water quality for drinking purpose for the City dwellers. In the present study, a detailed investigation was carried out with the objectives to define hydro-geochemical processes controlling groundwater quality based on major ion chemistry, conventional graphical plots, multivariate statistical analysis and the seasonal variations of groundwater quality in the study area.

To achieve the main objective of the present research, the other objectives are as follows:

1. To understand the chemistry of groundwater of Rajshahi City.
2. To identify the source of ionic species in groundwater.
3. To determine the water type of groundwater.
4. To assess the seasonal variations of groundwater.
5. To evaluate groundwater quality in study area.
6. To evaluate the water treatment efficiencies of indigenous materials.

Chapter Two

Literature Review

LITERATURE REVIEW

The literature reports are vast as regards the most important and brilliant development of the extensive studies of the geochemistry. A substantial amount of investigations are related to evaluate hydro-geochemical processes controlling groundwater quality based on ion chemistry. The following summarizes only the recent reports on the soil chemistry groundwater composition, water type, dissolution of minerals etc so far published. An attempts is also made to record the dissolution process of minerals from the various sources. This section is also reported different treatment processes for removal of arsenic, iron, manganese, lead etc from the groundwater.

Geochemical studies of groundwater provide a better understanding of possible changes in quality as development progress (Bhardwaj *et al.*, 2010; Gupta *et al.*, 2008; Gupta *et al.*, 2009; Jalali, 2006; Nagaraju *et al.*, 2006; Sreedevi, 2004; Subba Rao, 2006). Geochemical process, occurring within the groundwater and their reactions with the aquifer materials, are responsible for changes in groundwater chemistry and quality (Drever, 1988; Hem, 1991; Subba Rao and Surya Rao, 2009; Wen *et al.*, 2008). So, it is impossible to control the dissolution of undesirable constituents in the waters once they enter into the ground (Johnson, 1979; Sastri, 1994).

Many naturally occurring major and trace elements in drinking water can have a significant effect on human health either through deficiency or excessive intake (Frengstad *et al.*, 2001). Thus, it is necessary to understand the hydrochemical parameters of groundwater and hydro-geochemical properties of the aquifer to utilize and protect valuable water sources effectively and predict the change in groundwater environments. The study of quantity of water alone is not sufficient to solve the water management issues because of its uses for various purposes depend on its quality. Hence, the hydro-geochemical characters of groundwater in different aquifers over space and time have proven to be important in solving the problems (Atwia *et al.*, 1997; Ballukraya and Ravi, 1999; Panigrahy *et al.*, 1996; Ramappa and Suresh, 2000). Therefore, the fundamental knowledge of the controlling process in groundwater chemistry is a pre-requisite condition for rational management of water resources.

Over the last few decades, competition for economic development, associated with rapid

growth in population, urbanization, and intensive agricultural activities have caused a high demand on groundwater resources in arid and semi-arid regions in the world, whillist in Bangladesh, groundwater resource is at greater risk of contamination (Giridharan *et al.*, 2008; Jalali, 2007a; Moghaddam and Najib, 2006; Tayfur *et al.*, 2008).

Groundwater supplied from 75 deep tubewells through pipe networks of 512 km reticulated over an area of 93.34 square kilometers and also withdrawn from 3811 shallow tubewells in Rajshahi City (R WASA, 2013). Groundwater water demand is increasing day by day in the City and the current water demand is likely to reach around 118,077 m^3/day, where supply water is about 55,440 m^3/day (R WASA) which would be 2,40,000 m^3/day by 2020 (DDC, 2002). About 70% of the population has access to pipe water (supply water) and the rest (30%) of demand is mitigated through shallow tube wells in the City area (R WASA, 2013). But the most unfortunate thing is that the tap water is being supplied without any treatment. Recently a surface water treatment plant has been established at Shampur in the City which cover about 10% of the total supply water.

A number of research works were carried out on geochemistry of groundwater (Balasubramanian and Sastri, 1994), groundwater level fluctuation and quality monitoring, and its suitability for drinking and agriculture purposes (Subramani *et al.*, 2005a) and the occurrence of various rock types and their mineral composition (Subramani *et al.*, 2005b). A number of studies on groundwater quality with respect to drinking and irrigation purposes have been carried out in the different parts of the world including Bangladesh (Lakshmanan *et al.*, 2003; Mondal and Singh, 2004; Rabemanana *et al.*, 2005; Das and Kaur, 2007; Singh *et al.*, 2007 and Sadashivaiah *et al.*, 2008). The reports showed the analysis of major cations such as Na, Mg, K, Ca and anions including HCO_3^-, Cl^-, SO_4^{-2}, NO_3^-, and physical parameters i.e. pH, EC, TDS and TH are important for drinking purpose. Chemical and microbial parameters are mainly responsible for maintaining the water quality, because some elements such as Mn, As, Cd, Pb etc., have potentially harmful for human health even presence in low concentration. Faced with more and more stringent regulations, nowadays heavy metals are the environmental priority pollutants and are becoming one of the most serious environmental problems. Water may also be contaminated by bacteria, algea and or even

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or pollutants, such as pesticides and herbicides and it can create disease easily.

Poor quality of water consumption is detrimental to human health (Edmunds and Smeldey, 1996; Frengstad *et al.*, 2000; Reimann and DeCaritat, 1998). Groundwater quality determination can be evaluated by various softwares (AQUACHEM, PHREEQC etc.) and diagrams such as Chanda, Dourov, Piper, Stiff (Chadha, 1999; Durov, 1948; Piper, 1944; Stiff, 1951) etc. So, the toxic heavy metals and other impurities should be removed from the water to protect the people and the environment. With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides etc., wastewaters contained with heavy metals are directly or indirectly discharged into the environment increasingly in the developing countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. Simple procedures such as boiling or the use of a household activated carbon filter are not sufficient for treating all the possible contaminants that may be present in water from an unknown source. In this section all the important parameters and heavy metals are discussed about their toxic effect and treatment processes.

Zinc (Zn) is a trace element that is essential for human health. It is important for the physiological functions of living tissue and regulates many biochemical processes. However, too much Zn can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia (Oyaro *et al.*, 2007). Copper (Cu) does essential work in animal metabolism. But the excessive ingestion of Cu brings about serious toxicological concerns such as vomiting, cramps, convulsions, or even death (Paulino *et al.*, 2006). Cadmium (Cd) has been classified by U.S. Environmental Protection Agency as a probable human carcinogen. Cd exposes human health to severe risks. Chronic exposure of Cd results in kidney dysfunction and high levels of exposure will result in death.

Lead (Pb) has been serious polluters of water since Roman times and perhaps earlier. It has been major water pollutants during the 20th century and continues to create serious problems in the 21st century. It can cause central nervous system damage. It can also damage the kidney, liver and reproductive system, basic cellular processes and brain

functions. The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages (Naseem and Tahir, 2001). Also, studies have linked Pb exposures even at low levels with an increase in blood pressure (Zietz *et al.*, 2007) as well as with a reduced intelligence quotient in children (Needleman and Gatsonis, 1990) and with attention disorders (Yule and Rutter, 1985). The possible long-term effects of chronic exposure to Pb present in drinking water are the subject of considerable public concern (Zietz *et al.*, 2007). It is a neurotoxin and responsible for the most common type of human metal toxicosis (Berman, 1980).

Manganese (Mn) is best characterized as a neurotoxin; occupational exposures are associated with a characteristic syndrome called manganism, which involves both psychiatric symptoms and parkinsonian features (Calne *et al.*, 1994; Dobson *et al.*, 2004; Yamada *et al.*, 1986). For high intake Mn having adverse neurotoxic health effect, WHO recommends guideline value of 0.40 mg/L (WHO, 2008) to protect against neurological damage, drinking water standard from aesthetic considerations is even more stringent, 0.10 mg/L. Mn issue however has attracted relatively less attention in Bangladesh.

Arsenic is viewed as being synonymous with toxicity. Arsenic contamination in groundwater is one of the biggest natural calamities, which has become threat to human health throughout the world. High arsenic concentrations have been reported recently in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India. Among 21 countries in different parts of the world affected by groundwater arsenic contamination, the largest population at risk is in Bangladesh followed by West Bengal in India. Arsenic is considered a highly toxic element and abundant in our environment with both natural and anthropogenic sources (Smedley and Kinniburgh, 2002). Nickson *et al.*, (1998) reported that as many as million water wells drilled into Ganges alluvial deposits in Bangladesh and India (West Bengal) may be contaminated with arsenic. Arsenic contamination level in groundwater in many parts of the world has aroused attention due to it much higher concentrations than that of the World Health Organization's (WHO) drinking water standard. This situation has become more serious in Bangladesh, India (West Bengal), and Nepal in the Indo-region as a result of resource pressures from growing populations as well as surface water contamination (Kanel *et al.*, 2005; Smedley and Kinniburgh, 2002). Many studies have

revealed that arsenic in groundwater, even at trace levels has proven to be harmful to human health and the environment.

Hardness is very important property of water from its domestic application point of view. It is mainly an aesthetic concern because of the unpleasant taste. It also reduces the efficiency of soap and causes scale formation in pipes. Long-term consumption of very high hard water might lead to an increased incidence of urolithiasis, anencephaly, parental mortality, some types of cancer, and cardiovascular disorders (Agrawal and Jagetia, 1997). Hard water also causes problem in boilers in industries however, it can be easily remove by the addition of slake lime [$Ca(OH)_2$]. The World Health Organization did not have any recommendations for levels of Ca and hardness in drinking water (WHO, 2008). However, researchers have suggested that a minimum of 20 mg/L (Novikov *et al.*, 1983) and an optimum of about 50 (40-80 mg/L) mg/L (Kozisek, 1992; Rachmanin *et al.*, 1990) calcium present in drinking water may be the most suitable for human consumption. Kozisek (2006) showed that there is a higher risk of gall stones, kidney stones, urinary stones, arthrosis and arthropathies in populations supplied with water of hardness higher than 300 mg/L (Kozisek, 2006).

According to WHO report (2007), 1.1 billion people lack access to an improved drinking water supply and 88% of the 4 billion annual cases of diarrheal disease are attributed to unsafe water and inadequate sanitation and hygiene, and 1.8 million people die from diarrheal diseases each year. The report also illustrate that the estimated that 94% of these diarrheal cases are preventable through modifications to the environment, including access to safe water. It is true that water borne infections are responsible for more than 80% of the diseases in all over the world. Whenever there is contamination of drinking water sources and water logging after rain there is in an outbreak of infection. Hazardous heavy metal contamination of groundwater is one of the most important environmental problems throughout the world.

A number of reports were found available on the internet, journals and books about arsenic contamination of groundwater in Bangladesh, related health hazards and mitigation measures (Chakravarty *et al.*, 2002; Chakraborti *et al.*, 2010; Van Halem *et al.*, 2010; Kongkea *et al.*, 2010; Karim, 2000; Meng *et al.*, 2001; Mostafa *et al.*, 2010; Mostafa *et al.*, 2011; Needleman and Gatsonis, 1990; Nickson *et al.*, 1998;, Selim *et al.*,

2010). Hence, heavy metals in groundwater are injurious to human so, the remediation of hardness, arsenic and other heavy metals from drinking water is imperative to save people from its harmful effects. Because treatment of water can avoid much possible water borne diseases like cholera, typhoid, jaundice and so on.

A number of reports have found on arsenic analysis and related contamination of groundwater in Rajshahi City area (Ahmed *et al.*, 1999; Ahmed *et al.*, 2002; BAMSAW, 2003; Chowdhury, 2004; Hossain, 1997; Mondal, 1998; Sarkar and Heijnen, 2000; Uddin, 1999). Reports of arsenic in groundwater analyses revealed that about 27% samples of shallow tubewells contained arsenic (As) above Bangladesh standard for drinking water (0.05 mg/L) and about 46% samples were above the WHO guideline (0.01 mg/L) (BGS/MML, 1998; BGS/DPHE, 2001). A survey conducted by BAMWSP (2003) reported that 4 out of 25 pumps were found contaminated with arsenic above 0.05 mg/L in Rajshahi City. Thus, the presence of heavy metals, toxic chemicals, bacteria in drinking water need to be treated to save human life.

Water treatment is the process of removing undesirable chemicals, biological contaminants, suspended solids and gases from contaminated water. Simple techniques for treating water at home, such as chlorination, filtration, and solar disinfection, and storing it in safe containers could save a huge number of lives each year (WHO and UNICEF, 2005). Simple procedures such as boiling or the use of a household activated carbon filter are not sufficient for treating all the possible contaminants that may be present in water from an unknown source. But, it is difficult to standardize the solution in the form of processes for water from different sources. There is no unique solution (selection of processes) for any type of water.

The present research deals with the current techniques for the removal of heavy metal ions from contaminated water. A number of technologies have been developed for the removal of arsenic and other heavy metals from drinking water based on various methods namely oxidation, coagulation, precipitation, ion exchange, adsorption, reverse osmosis and membrane techniques (Cheng *et al.*, 1994; Hering *et al.*, 1996, Joshi and Chaudhury, 1996). Chemical precipitation is effective and by far the most widely used process in industry (Ku and Jung, 2001) because it is relatively simple and inexpensive to operate. In precipitation processes, chemicals react with heavy metal ions to form

insoluble precipitates. The forming precipitates can be separated from the water by sedimentation or filtration. And the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes includes hydroxide precipitation and sulfide precipitation.

Ion-exchange processes have been widely used to remove heavy metals from contaminated water due to their many advantages such as high treatment capacity, high removal efficiency and fast kinetics (Kang *et al.*, 2004). Ion-exchange resin, either synthetic or natural solid resin has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution (Alyuz and Veli, 2009). Many researchers have demonstrated that zeolites exhibit good cation-exchange capacities for heavy metal ions under different experimental conditions (Motsi *et al.*, 2009; Ostroski *et al.*, 2009; Taffarel and Rubio, 2009). There are several modern technologies have been practicing in removing toxic elements from drinking water. The water treatment technologies are briefly discussed here.

Membrane filtration technologies with different types of membranes show great promise for heavy metal removal for their high efficiency, easy operation and space saving. Ultra-filtration (UF) is a membrane technique working at low trans-membrane pressures for the removal of dissolved and colloidal material. To obtain high removal efficiency of metal ions, the micellar enhanced ultra-filtration (MEUF) and polymer enhanced ultra-filtration (PEUF) was proposed (Fenglian and Wang, 2011). But the costs of these techniques are comparatively high and gone beyond the capacity for most of the household use in developing countries. Thus an appropriate technology for water treatment is need for the household use in developing countries, which focuses on cost effective along with environmental and sustainability issues.

The adsorption process could be an effective and economic for removing heavy metal ions from contaminated water. It can remove heavy metal ions from various aqueous solutions even low metal ion concentrations. The efficiency of adsorption relies on the capability of the adsorbent to adsorb metal ions from the solutions onto its surfaces. Different naturally occurring adsorbents like activated carbon (Bailey, 1999; Brain *et al.*,

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1995; Koshima and Onishi, 1986; Wolfgang *et al.*, 1992), tea waste (Liang *et al.*, 1999), egg shells (Suyama *et al.*, 1995), mineral mixtures (Yuan *et al.*, 1999), rice husks (Khalid *et al.*, 1998) and brick kiln ash (Ghaffar, 2008), magnetite enriched sand-stone absorbent, iron-coated sand absorbent etc. are used as adsorbents in water treatment process. Adsorbents such as magnetite, iron filings, finely-chopped tin cans, aluminum oxide and treated clays, used for arsenic removal from arsenic contaminated water. A large proportion of the arsenic species in the water should also have been removed with the sediment forming in the precipitation tank, reducing the load on the adsorption bed.

Conventionally, a strong oxidant such as chlorine or potassium permanganate is used for oxidation of Mn (II) rather than oxygen alone (Hartmann, 2002). Mn (II) oxidation can lead to precipitation of Mn (III, IV) oxides which are in turn good adsorbents and oxidants (Hem, 1978). Some reports (BRTC-UNICEF, 2006; Hoque, 2006) revealed that Mn removal is significant in some types of community arsenic-iron removal plants currently being used in some arsenic affected areas, while Mn removal is insignificant in other removal plants. Adsorption of Mn on filter media and formation of Mn oxides coatings on the media are thought to be responsible for Mn removal and formation of Mn oxide coatings on filter media is a slow process and only limited information is available on factors affecting formation of such coatings, it is important of understand the chemistry of manganese oxidation and adsorption of the commonly used filter media. Many treatment technologies are available for arsenic remediation but none of them is found suitable for household use in developing countries due to technological and economic viewpoint. Adsorption process may be a useful tool for removing toxic elements from contaminated water due to low-cost and simple technology, which exhibit superior adsorption capacities and local availability.

A few reports (Ahmed *et al.*, 2002; BAMSAW, 2003; Chowdhury, 2004; Hossain, 1997; Mondal, 1998; Uddin, 1999) were found in the study area mainly focusing on arsenic contamination of groundwater and treatment process using indigenous materials. So far, the geochemistry of the groundwater in the Rajshahi City has not been studied. Since groundwater is intensively used for drinking purposes, an effort was made to reduce the literature research gaps, and to evaluate the quality indices of groundwater to understand the hydro-geochemical relationships of the water quality parameters for the suitability of groundwater resources.

Chapter Three

Materials and Methods

MATERIALS AND METHODS

The physico-chemical and microbial parameters of the groundwater samples were analyzed to understand the quality and water type in the study area. The analyses were done using several methods such as gravimetric, electrochemical, colorimetric and optical. Detailed analytical techniques of groundwater and aquifer soil samples, the data analysis and adsorption water treatment process of this study are discussed in this chapter.

3.1 Study area

Rajshahi City is located in the north-west of Bangladesh, which is the divisional headquarters as well as the administrative district (Figure 1). The study area covers approximately 93.34 km^2 and lies between latitudes 24°21'N and 24°25'N and longitudes 88°32' and 88°40' east. The City has a population of 7,63,952 with a density of 8,173 persons per km^2 (BBS, 2011). It consists of 30 wards and is situated on the northern banks of the river Padma (the downstream of the Ganges River in India). The climate of the City is generally marked by monsoons, high temperature, considerable humidity and moderate rainfall. It has a mean annual rainfall of below 1,524 mm compared to a national average of 2,540 mm (BBS, 2005).

The study area is situated in the Bengal Basin which has been formed primarily by the deposition of late Holocene to recent sediments carried by the Ganges (Haque *et al.*, 2012). The lithology of the area was found four types such as alluvial sand and silt, Barind clay residuum, and marsh clay and peat, and modified its character due to some post-depositional processes such as ploughing, bioturbation, and weathering (Alam *et al.*, 1990). Mineralogy of the sediments of the area was dominated by quartz with some plagioclase and potassium feldspar and volcanic, metamorphic, and sedimentary fragments (Uddin and Lundberg, 1998).

The subsoil is consisted of an external clayey layer with a thickness of approximately 18 meter and bellow this layer is fine sand of approximately 24 meter thick. Between 42 and 80 meter below ground level the subsoil consists very fine to medium associated with coarse sand and gravel; bellow this layer was fine sand layer down to 95 meter (AQUA,

1994). It is sharply demarcated the topography with an elevation from 18 meter mean sea level (MSL). The aquifer systems of the study area can be classified into two major classes such as the shallow and deep aquifers. The aquifers of the study area are generally multi-layered varying from unconfined to leaky-confined in the shallow alluvial deposits and confined in the deeper alluvial deposits (Ahmed *et al.*, 2004).
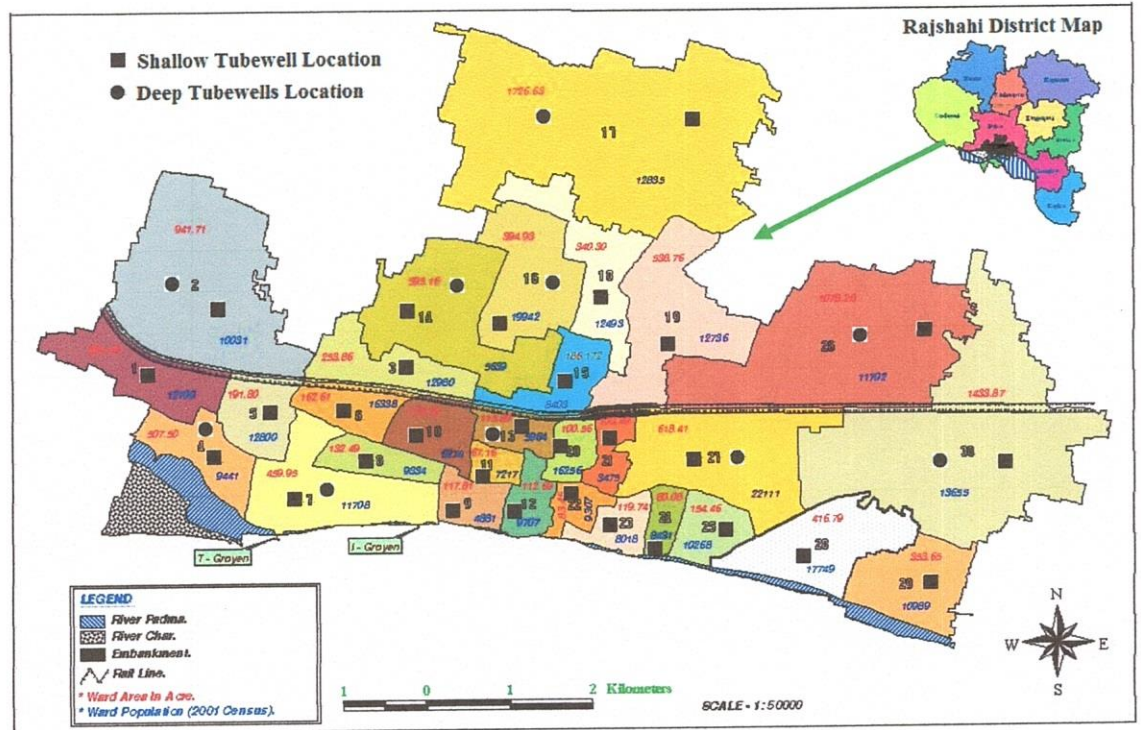
Figure 1. Groundwater sampling location map of Rajshahi City, Bangladesh.

3.2 Sample collection

3.2.1 Water sample collection

A total of 240 representatives groundwater (shallow and deep tubewells) samples were collected during pre-monsoon, monsoon and post-monsoon season covering two years to evaluate the seasonal variations, water quality, water type, geochemical process. 180 shallow tubewells water samples were collected from 30 locations and 60 deep tubewells water samples were collected from 10 locations in the study area. Detailed descriptions of sampling locations of shallow and deep tubewells are shown in Table 1.1 and Table 1.2, respectively in Appendix-1. The samples were collected in 1 liter plastic bottles, which were pre-washed with dilute HCl and rinsed three to four times with distilled water. The water samples were collected after 10 minutes pumping of each shallow and

deep tubewells to remove groundwater stored in the well. The Samples for trace metal analyses were acidified with HNO_3 and adjusted the pH<2, but the samples for analyzing physical parameters including pH, EC, total hardness (TH), total dissolved solids (TDS) and major anions were not acidified. Samples were labeled, sealed and transported to the laboratory and stored in a refrigerator at a temperature of about 4°C until the analysis was done. Bicarbonate and chloride were analyzed according to the standard procedures stated in American Public Health Association (APHA, 1995). For microbial analysis, water samples were collected in 250 ml capacity glass bottles, capped immediately and transported to the laboratory and stored in refrigerator at a temperature of about 4°C until the analysis was done.

3.2.2 Aquifer soil sample collection

A total of 30 aquifer soil samples were collected at depths (10-45 meter) from 30 locations during monsoon season in 2010 (Detailed descriptions of sampling locations are shown in Appendix-1, Table 1.3). The aquifer soil samples were collected from different wash borings. Then collected samples were stored in plastic bags and transported to the laboratory for physical and chemical analyses using extraction and digestion method.

3.3 Sample preparation

3.3.1 Water sample preparation

200 mL water sample was digested with 5 mL of di-acid mixture (HNO_3:$HClO_4$:: 9:4 ratio) on a hot plate and evaporated to one-fifth of its volume, and then it was allowed to cool. It was then filtered through Whatman No. 42 filter paper and made up to a volume of 50 mL by double distilled water.

3.3.2 Aquifer soil sample preparation

3.3.2.1 Extraction method

The aquifer soil samples were air dried for 24 hour, followed by grinding and sieving. To estimate the concentration of Na, Mg, K, Ca, HCO_3^-, Cl^-, NO_3^- and SO_4^{2-}, one part of air dried crushed soil was taken with 10 parts of neutral 1M ammonium acetate solution and shaken for 15 minutes. Then it was allowed to settle overnight. The supernatant was

filtered and analyzed for various parameters by AAS (Atomic Absorption Spectrophotometer) and UV-Spectrophotometer. For Mn analysis one part of air dried crushed soil was taken with 8 parts 0.5 M phosphoric acid and the extraction process was carried out by shaking for 10 minutes. Then it was allowed to settle overnight. The supernatant was filtered prior to analysis by AAS.

3.3.2.2 Digestion method

0.5g of dry soil sample was weighed and it was poured into a graduated test tube and mixed with 2 mL of aqua regia 1:3 (1 Conc. HCl: 3 Conc. HNO_3) for major heavy metal analyses such as Fe, Cu, Zn, As, Cd and Pb. The mixture was digested on a hot plate at 95°C for 1 hour and allowed to cool at room temperature. The sample was then diluted to 10 mL using double distilled water and allowed to settle overnight. The supernatman was filtered and analyzed using AAS as stated by Adams (1991).

3.4 Sample analysis

3.4.1 Water sample analysis

The collected groundwater samples were analyzed for the parameters including temperature, pH, EC, TH, TDS, TSS and the concentrations of major cations and anions. Temperature, pH and EC were determined immediately after collection of the samples to avoid further contamination. TDS, TH and chloride were determined by using evaporation, standard EDTA and $AgNO_3$ method, respectively. Samples for Na, Mg, K, Ca, Mn, Fe, Cu, Zn, As, Cd, and Pb ions analyzed using AAS (Simadzu AA-6800). NO_3^- and SO_4^{2-} were analyzed using UV-visible Spectrophotometer (Rowell, 1994). Microbial parameters such as total coliform (TC) and faecal coliform (FC) were determined by membrane filtration method. All experiments were conducted in triplicate to ensure accuracy and precision. All reagents used in this study were analytical grade chemicals.

i. Temperature, pH and EC

Temperature, pH and EC were measured by alcohol thermometer, pH meter and EC meter (EC-210, HANA, Italy), respectively.

ii. Total Dissolved Solids (TDS)

At first a (150ml) Pyrex beaker was taken and dried in an oven at 105° C for 24 hours and then allowed to cool. 100 mL of water sample was filtered through Whatman 42

filter in the above beaker and it was evaporated to dry in an oven at 105°C for 24 hours. Then the beaker was allowed to cool and weighed and the process was repeated until a constant weight was obtained.

$$\text{Total Dissolved Solids} = \frac{(A-B) \times 1000000}{V}$$

Where, A= Final weight of beaker (g)

B= Initial weight of beaker (g)

V = Volume (mL) of water sample taken = 100 mL

iii. Total Suspended Solids (TSS)

At first a Whatman 42 filter paper was taken and dried in an oven at 105°C for 24 hours and then allowed to cool. Then 100 mL of water sample was filtered through the oven dried Whatman 42 filter and it was evaporated to dry in an oven at 105°C for 24 hours. Then the filter paper was allowed to cool and weigh and the process was repeated until a constant weight was obtained.

$$\text{Total Suspended Solids (TSS, mg/L)} = \frac{(A-B) \times 100000}{V}$$

Where, A= Final weight of filter paper (after filtration) in gram

B= Initial weight of filter paper (before filtration) in gram

V = Volume (mL) of water sample taken = 100 mL

iv. Total Hardness (TH)

Total Hardness (TH) in water samples was determined by EDTA and the detailed of this method is given bellow:

A. Apparatus: Burette, pipette, stand, conical flask, volumetric flask.

B. Reagent: Erichrome Black T-indicator, NH_4Cl, NH_3, $Na_2B_4O_7.10H_2O$.

(a) Erichrome Black-T indicator: Erichrome Black-T indicator was prepared by weighed out exactly 0.5 g of Erichrome Black-T and 100 g of NaCl and it was mixed with 20 mL of distilled water in a 100 mL beaker by gradually warming. Finally, it was stored in a glass bottle for using 100 days.

(b) Ammonia Buffer: 20 g of borax ($Na_2B_4O_7.10H_2O$) was dissolved gradually in a 500 mL volumetric flask and made up to the volume 400 mL by distilled water. Again 5 g of NaOH and 2.5 g of sodium sulphide were dissolved in 50 mL distilled water and mixed with previous borax solution. Then the solution thoroughly mixed by shaking and finally it was made up to the mark of the volumetric flask (500 mL).

(c) Standard EDTA titrant, 0.01 M: 3.723 g analytical reagent grade EDTA di-sodium salt ($Na_2H_2C_{10}H_{12}O_8N_2$) was dissolved slowly in a 1000 mL volumetric flask and made up to the mark with distilled water gradually. It was standardized against standard calcium solution.

C. Procedure:

100 mL water sample was taken in a 250 mL conical flask and added 1 mL of ammonia buffer solution and 0.5 g Erichrome black-T indicator, subsequently. The standard EDTA titrant was slowly added, with continuous stirring until the color changed from wine red to blue. Noted the mL of 0.01 M EDTA titrant used for titration.

D. Calculation:

$$\text{Hardness (CaCO}_3\text{, mg/L)} = \frac{\text{Volume (mL) of EDTA used from burette}}{V} \times 100$$

$$\text{Where, } V = \text{Volume (mL) of sample taken} = 100 \text{ mL}$$

v. Sodium (Na)

The sodium ion in groundwater samples was determined using Atomic Absorption Spectrophotometric method, which describes as follows:

A. Apparatus: AAS wave length at 330.2 nm with 0.7 nm silt.

B. Reagent:

(a) 1000 mg/L standard solution: The standard solution of sodium ion was prepared by exactly taking 2.540 g of analytically pure (99%) NaCl in a 1000 mL volumetric flask and added distilled water slowly and shaken well and finally made up to the mark with distilled water.

b) Suppressing agent:

0.1% potassium: 5.20 g of KCl was dissolved in a 1000 mL volumetric flask and made up to the mark with distilled water gradually. Then 100 mL of 1% potassium ion solution was taken and diluted 1000 mL with distilled water to make the final concentrated of 0.1% K. To reduce percentage of relative standard deviation (RSD), 2 drops of 0.1% potassium solution was used for maintained in every standard and sample.

C. Procedure:

(a) Sample preparation: 100 mL water sample was taken in a beaker and added 2 mL concentrated HNO_3 and 3 mL concentration HCl. The beaker was heated 90-95°C on a hot plate until the volume of water was reached at 10-15 mL. Then, it was removed from hot plate and allowed to cool. Then samples were filtered through 0.45 μm pore membrane filter. Finally, the volume was made up to 100 mL with distilled water. Similar procedure was followed for the samples preparation of Mg, K, Ca, Mn, Fe, Cu, Zn, As, Cd and Pb.

(b) Standard curve: The proportions of 2, 5, 8 and 10 mL Na ion contained standard solutions were taken in four different 1000 mL volumetric flasks and distillated water was gradually added and thoroughly shaken and finally made up to the mark. Absorbance of the water samples were determined by AAS. A standard curve was made by plotting the absorbance against the concentration (Figure 2.1 in Appendix-2).

D. calculation:

Sodium (Na, mg/L) = Concentration of Na (mg/L) from standard curve × dilution factor

vi. Magnesium (Mg)

The magnesium ion in water samples was determined using Atomic Absorption Spectrophotometric method, which describes as follows:

A. Apparatus: AAS wave length at 285.21 nm with 0.7 nm silt.

B. Reagent:

(a) 1000 mg/L standard solution: The standard solution of magnesium ion was prepared by exactly taking 1.650 g of analytically pure (99%) MgO in a 1000 mL volumetric flask and added distilled water slowly and shaken well and finally made up to the mark with distilled water.

b) Suppressing agent:

0.1% Lanthanum solution: The solution of 1% lanthanum (La) was prepared by exactly taken 1 g of lanthanum chloride in a 100 mL volumetric flask and added to the 1.50 mL of 1M HCl. Then it was dissolved distilled water and finally, made up to the mark with distilled water gradually and shaken well. 10 mL of 1 % lanthanum was taken and diluted 100 mL with distilled water to make the final concentrated of 0.1% La. This solution was used for maintained in every standard and sample.

C. Standard curve: The proportions of 50, 100, 150 and 200 mL Mg ion contained standard solutions were taken in four different 1000 mL volumetric flasks and distillated water was gradually added and thoroughly shaken and finally made up to the mark with distilled water. Absorbance of the water samples were determined by AAS. A standard curve was made by plotting the absorbance against the concentration (Figure 2.2 in Appendix-2)

D. Calculation:

Magnesium (Mg, mg/L)

$$= (CmoL\ concentration\ of\ Mg\ from\ standard\ curve \times dilution\ factor) \times 1000$$

vii. Potassium (K)

The potassium ion in water samples was determined using Atomic Absorption Spectrophotometric method, which describes as follows:

A. Apparatus: AAS wave length at 766.49 nm with 0.7 nm silt.

B. Reagent:

(a) 1000 mg/L standard solution: The standard solution of potassium ion was prepared by exactly taking 1.910 g of analytically pure (99%) KCl in a 1000 mL volumetric flask and added distilled water slowly and shaken well and finally made up to the mark with distilled water.

(b) Suppressing agents:

0.1% potassium: 1 g of KCl was dissolved in a 100 mL volumetric flask and made up to the mark with distilled water gradually. To reduce percentage of relative standard deviation (RSD), 2 drops of 0.1% potassium solution was used for maintained in every standard and sample.

C. Standard curve: The proportions of 2, 8 and 10 mL K ion contained standard solutions were taken in three different 1000 mL volumetric flasks and distillated water was gradually added and thoroughly shaken and finally made up to the mark with distilled water. Absorbance of the water samples were determined by AAS. A standard curve was made by plotting the absorbance against the concentration (Figure 2.3 in Appendix-2).

D. Calculation:

Potassium (K, mg/L) = Concentration of K (mg/L) from standard curve

viii. Calcium (Ca)

The calcium ion in water samples was determined using Atomic Absorption Spectrophotometric method, which describes as follows:

A. Apparatus: AAS wave length at 422.7 nm with 0.7 nm silt.

B. Reagent:

(a) 1000 mg/L standard solution: The standard solution of calcium ion was prepared by exactly taking 0.250 g of analytically pure (99%) $CaCO_3$ in a 1000 mL volumetric flask

and added distilled water slowly and shaken well and finally made up to the mark with distilled water.

(b) Suppressing agents:

0.2% Lanthanum solution: The solution of 2% lanthanum was prepared by exactly taken 2 g of lanthanum chloride in a 100 mL volumetric flask and added to the 3 mL of 1M HCl. Again it was dissolved distilled water and finally, made up to the mark with distilled water gradually and shaken well. Then 10 mL of 2% lanthanum was taken and diluted 100 mL with distilled water to make the final concentrated of 0.2% lanthanum. That solution was used for maintained in every standard and sample.

C. Standard curve: The proportions of 0.5, 1 and 2 mL Ca ion contained standard solutions were taken in three different 1000 mL volumetric flasks and distillated water was gradually added and thoroughly shaken and finally made up to the mark with distilled water. Absorbance of the water samples were determined by AAS. A standard curve was made by plotting the absorbance against the concentration (Figure 2.4 in Appendix-2).

D. Calculation:

Calcium (Ca, mg/L) = Concentration of Ca (mg/L) from standard curve × dilution factor.

ix. Manganese (Mn)

The manganese ion in water samples was determined using Atomic Absorption Spectrophotometric method, which describes as follows:

A. Apparatus: AAS wave length at 279.48 nm with 0.2 nm silt.

B. Reagent:

(a) 1000 mg/l standard solution: The standard solution of manganese ion was prepared by exactly taking 3.070 g of analytically pure (99%) $MnSO_4.10H_2O$ in a 1000 mL volumetric flask and added distilled water slowly and shaken well and finally made up to the mark with distilled water.

b) Suppressing agent:

0.2% Calcium: The solution of 2% calcium was prepared by exactly taken 2 g of $CaCO_3$ in a 100 mL volumetric flask and added to the 3 mL of 1M HCl. Then it was dissolved distilled water and finally, made up to the mark with distilled water gradually and shaken well. Then 10 mL of 2% $CaCO_3$ solution was taken and diluted 100 ml with distilled water to make the final concentrated of 0.2% $CaCO_3$. This solution was used for maintained in every standard and sample.

C. Standard curve: The proportions of 1, 3 and 5 mL Mn ion contained standard solutions were taken in three different 1000 mL volumetric flasks and distillated water was gradually added and thoroughly shaken and finally made up to the mark with distilled water. Absorbance of the water samples were determined by AAS. A standard curve was made by plotting the absorbance against the concentration (Figure 2.5 in Appendix-2).

D. Calculation:

Manganese (Mn, mg/L) = Concentration of Mn (mg/L) from standard curve

x. Iron (Fe)

The iron ion in water samples was determined using Atomic Absorption Spectrophotometric method, which describes as follows:

A. Apparatus: AAS wave length at 248.3 nm with 0.7 nm silt.

B. Reagent:

1000 mg/L standard solution: The standard solution of iron ion was prepared by exactly taking 4.980 g of analytically pure (99%) $FeSO_4.7H_2O$ in a 1000 mL volumetric flask and added distilled water slowly and shaken well and finally made up to the mark with distilled water.

C. Standard curve: The proportions of 0.50, 1 and 2 mL Fe ion contained standard solutions were taken in three different 1000 mL volumetric flasks and distillated water was gradually added and thoroughly shaken and finally made up to the mark with

distilled water. Absorbance of the water samples were determined by AAS. A standard curve was made by plotting the absorbance against the concentration (Figure 2.6 in Appendix-2).

D. Calculation:

Iron (Fe, mg/L) = Concentration of Fe (mg/L) from standard curve) × dilution factor

xi. Copper (Cu)

The copper ion in water samples was determined using Atomic Absorption Spectrophotometric method, which describes as follows:

A. Apparatus: AAS wave length at 324.75 nm with 0.7 nm silt.

B. Reagent:

1000 mg/L standard solution: The standard solution of copper ion was prepared by exactly taking 3.930 g of analytically pure (99%) $CuSO_4.5H_2O$ in a 1000 mL volumetric flask and added distilled water slowly and shaken well and finally made up to the mark with distilled water.

C. Standard curve: The proportions of 0.5, 1 and 2 mL Cu ion contained standard solutions were taken in three different 1000 mL volumetric flasks and distillated water was gradually added and thoroughly shaken and finally made up to the mark with distilled water. Absorbance of the water samples were determined by AAS. A standard curve was made by plotting the absorbance against the concentration (Figure 2.7 in Appendix-2).

D. Calculation:

Copper (Cu, mg/L) = Concentration of Cu (mg/L) from standard curve

xii. Zinc (Zn)

The zinc ion in water samples was determined using Atomic Absorption Spectrophotometric method, which describes as follows:

A. Apparatus: AAS wave length at 213.86 nm with 0.7 nm silt.

B. Reagent:

1000 mg/L standard solution: The standard solution of zinc ion was prepared by exactly taking 4.980 g of analytically pure (99%) $ZnSO_4.7H_2O$ in a 1000 mL volumetric flask and added distilled water slowly and shaken well and finally made up to the mark with distilled water.

C. Standard curve: The proportions of 1, 3 and 5 mL Cu ion contained standard solutions were taken in three different 1000 mL volumetric flasks and distillated water was gradually added and thoroughly shaken and finally made up to the mark with distilled water. Absorbance of the water samples were determined by AAS. A standard curve was made by plotting the absorbance against the concentration (Figure 2.8 in Appendix-2).

D. Calculation:

Zinc (Zn, mg/L) = Concentration of Zn (mg/L) from standard curve

xiii. Arsenic (As)

The arsenic ion in water samples was determined using Atomic Absorption Spectrophotometric method by graphite furnace, which describes as follows:

A. Apparatus: AAS wave length at 193.70 nm with 0.7 nm silt.

B. Reagent:

1000 mg/L standard solution: The standard solution of arsenic ion was prepared by exactly taking 1.3203 g of analytically pure (99%) As_2O_3 in a 1000 mL volumetric flask and added distilled water slowly and shaken well and finally made up to the mark with distilled water.

C. Standard curve: The proportions of 4, 12 and 20 ppm As ion contained standard solutions were taken in three different 1000 mL volumetric flasks and distillated water was gradually added and thoroughly shaken and finally made up to the mark with

distilled water. Absorbance of the water samples were determined by AAS. A standard curve was made by plotting the absorbance against the concentration (Figure 2.9 in Appendix-2).

D. Calculation:

$$\text{Total inorganic Arsenic (As, mg/L)}$$

$$= \text{Concentration of As (µg/L) from standard curve} \times 1000$$

xiv. Cadmium (Cd)

The cadmium ion in water samples was determined using Atomic Absorption Spectrophotometric method, which describes as follows:

A. Apparatus: AAS wave length at 228.80 nm with 0.7 nm silt.

B. Reagent:

1000 mg/L standard solution: The standard solution of cadmium ion was prepared by exactly taking 2.282 g of analytically pure (99%) $3CdSO_4.8H_2O$ in a 1000 mL volumetric flask and added distilled water slowly and shaken well and finally made up to the mark with distilled water.

C. Standard curve: The proportions of 1, 2 and 4 mL Cd ion contained standard solutions were taken in three different 1000 mL volumetric flasks and distillated water was gradually added and thoroughly shaken and finally made up to the mark with distilled water. Absorbance of the water samples were determined by AAS. A standard curve was made by plotting the absorbance against the concentration (Figure 2.10 in Appendix-2).

D. Calculation:

Cadmium (Cd, mg/L) = Concentration of Cd (mg/L) from standard curve

xv. Lead (Pb)

The lead ion in water samples was determined using Atomic Absorption Spectrophotometric method, which describes as follows:

A. Apparatus: AAS wave length at 283.31 nm with 0.7 nm silt.

B. Reagent:

1000 mg/L standard solution: The standard solution of lead ion was prepared by exactly taking 1.599 g of analytically pure (99%) $Pb(NO)_3$ in a 1000 mL volumetric flask and added distilled water slowly and shaken well and finally made up to the mark with distilled water.

C. Standard curve: The proportions of 2.50, 5 and 10 mL contained Pb ion standard solutions were taken in three different 1000 mL volumetric flasks and distillated water was gradually added and thoroughly shaken and finally made up to the mark with distilled water. Absorbance of the water samples were determined by AAS. A standard curve was made by plotting the absorbance against the concentration (Figure 2.11 in Appendix-2).

D. Calculation:

Lead (Pb, mg/L) = Concentration of Pb (mg/L) from standard curve

xvi. Carbonate ion (CO_3^{2-}) and Bicarbonate ion (HCO_3^-)

The carbonate ion (CO_3^{2-}) and bicarbonate ion (HCO_3^-) in groundwater samples was determined using titration method, which describes as follows:

The alkalinity in water samples is caused due to the presence of carbonate ion (CO_3^{2-}), bicarbonate ion (HCO_3^-) and Hydroxide ion (OH^-). In this study CO_3^{2-} and HCO_3^- were determined.

A. Reagents: Phenolphthalein indicator, methyl orange indicator and 0.1 N HCl.

a) Preparation of phenolphthalein indicator: Phenolphthalein indicator was prepared by exactly taking 0.5 g phenolphthalein in a 100 mL volumetric flask and added 50% ethanol slowly and shaken well and finally made up to the mark with 50% ethanol. Then it was shaken well and finally stored in a glass bottle.

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b) Preparation of methyl orange indicator: Methyl orange indicator was prepared by exactly taking 0.5 g methyl orange in a 100 mL volumetric flask and added deionized water slowly and shaken well and finally made up to the mark with deionized water. Then it was shaken well and finally stored in a glass bottle.

B. Procedure:

Each of 100 mL of water sample was taken in two separate 250 mL conical flasks. 2 drops of phenolphthalein indicator were added to the first flask and no color was found indicated that phenolphthalein alkalinity (PA) was zero (0). So, CO_3^{2-} was absent in water sample. Then, 2 drops of methyl orange indicator were added to the 2nd conical flask and shaken gradually and color was detected. The sample containing 2nd flask was titrated with 0.1 N HCl until the color changed to orange indicating the end point. Hence, HCO_3^- was present in water sample and noted the volume (mL) of acid from the burette used for the titration.

C. Calculation:

$$\text{Total alkalinity (TA, } CaCO_3 \text{ mg/L)} = \frac{A \times N \times 1000 \times 50}{V}$$

Where, A= mL of HCl used for titration with methyl orange indicator

N=Normality of HCl=0.1 N HCl

V=Volume of water sample taken=100 mL

xvii. Chloride ion (Cl⁻)

The Chloride ion (Cl⁻) in water samples was determined using $AgNO_3$ titration method, which describes as follows:

A. Reagents: K_2CrO_4 indicator and 0.0141 N $AgNO_3$.

a. Preparation of 5% K_2CrO_4 (indicator): 5% K_2CrO_4 indicator was prepared by exactly taking 5 g $K_2Cr_2O_4$ in a 100 mL volumetric flask and it was dissolved by 50 mL distilled water. Then 0.0141 N $AgNO_3$ was dded drop wise in the $K_2Cr_2O_4$ containing volumetric flask until the first permanent red precipitate was produced. Filtered the solution and finally it diluted by distilled water slowly and finally made up to the mark with the distilled water.

b. *Preparation of 0.0141 N AgNO₃:* 2.397 g of $AgNO_3$ was weighed out, transferred to a 1000 mL volumetric flask and made up to the mark with distilled water gradually. The resulting solution was 0.0141 N. The solution was standardized against NaCl. Reagent-grade NaCl was dried overnight and cooled at a room temperature. 0.25 g portions of NaCl were weighed into Erlenmeyer flasks and it was dissolved by distilled water. Finally it was diluate up to the mark of 100 mL by distilled water. In order to adjust the pH of the solutions, small quantities of $NaHCO_3$ were added until effervescence ceased. About 2 mL of K_2CrO_4 was added and the solution was titrated to the first permanent appearance of red K_2CrO_4

B. Procedure:

At first 100 mL of water sample was filtered and taken in a 250 mL conical flask. 1 mL of K_2CrO_4 indicator was added to the flask and shaken slowly. Then sample was titrated with 0.0141 N $AgNO_3$ until the brick red color was arrived indicating the end point. Noted the mL of 0.0141 N $AgNO_3$ used for titration.

C. Calculation:

$$\text{Chloride (Cl}^-\text{, mg/L)} = \frac{(A \times N)}{V} \times 35450$$

Where, A= mL of 0.0141 N $AgNO_3$ used for titration from burette

N=Normality of $AgNO_3$=0.0141 N

V=Volume of water sample taken=100 mL

xviii. Nitrate ion (NO₃⁻)

The nitrate ion (NO_3^-) in water sample was determined using Ultraviolet (UV) Spectrophotometric method, which describes as follows:

A. Apparatus: Spectrophotometer wave length at 220 and 275 nm silt with matched silica cells of 1 cm.

B. Reagent:

(a) *Nitrate free water:* Double distilled water was used to prepare all solutions and dilutions.

(b) Stock nitrate solution: Potassium nitrate (KNO_3) was dried in an oven at 105°C for 24 hours. 0.7218 g KNO_3 was weighed out and it was transferred to a 1000 mL volumetric flask and made up to the mark with distilled water gradually, where 1 mL=100 µg NO_3^-N.

(c) Intermediate nitrate solution: 100 mL Stock nitrate solution was taken in a 1000mL volumetric flak and added distilled water gradually and finally made up to the mark where 1 mL=10 µg NO_3^-N. 2mL $CHCl_3$ was used per litter solution to preserve it for at least 6 months.

(d). 1 N Hydrochloric acid (HCl) solution: 83 mL of concentrated HCl was measued and transferred to in a 1000 mL volumetric flask and finally made up to the mark 1000 mL by distilled water gradually.

C. Procedure:

(a) Treatment of sample: 1 mL of 1 N HCl solution was mixed thoroughly in 50 mL clear sample and flitted.

(b) Preparation of standard curve: The proportions of 0.50, 1.0 and 2.0 mL intermediate nitrate solutions were taken in three different 1000 mL volumetric flasks and distillated water was gradually added and thoroughly shaken and finally made up to the mark with distilled water. Absorbance of the water samples were determined by AAS. A standard curve was made by plotting the absorbance against the concentration (Figure 2.12 in Appendix-2).

(c) Spectrophotometric measurement: The absorbance was read against distilled water set at zero absorbance. A wave length of 220 nm was used to obtain NO_3^- reading and a wave length of 275 nm used to determine interference due to dissolved organic matter.

D. Calculation:

The estimation of NO_3-N was measured using UV-Spectrophotometer at two wave lengths i.e., 275 and 220. The absorbance for samples and standard solutions were taken at two wave lengths and the absorbance reading at 275 nm was subtracted from the reading at 220 nm for each sample and standard solution.

$$\text{Nitrate-Nitrogen (NO}_3^- \text{-N mg/L)} = \frac{\mu g \, NO_3^- - N \text{ from standard curve}}{\text{Volume (mL) of sample taken}}$$

$$\text{Nitrate (NO}_3^-, \text{ mg/L)} = (NO_3^- - N) \times 4.429$$

xix. *Sulphate ions (SO_4^{2-})*

The sulphate ion (SO_4^{2-}) in water samples was determined using Ultraviolet (UV)-Spectrophotometric method, which describes as follows:

A. Apparatus: Spectrophotometer wave length at 420 nm silt.

B. Reagent:

(a) Buffer solution: The solution of buffer was prepared by taking exactly 30 g $MgCl_2.6H_2O$, 5 g sodium acetate ($CH_3COONa.3H_2O$), 0.111 g sodium sulphate (Na_2SO_4) and 20 mL acetic acid in a 1000 mL volumetric flask. Then it was dissolved with the distilled water and shaken well. Finally, it was made up to the mark with distilled water.

(b). Barium chloride: $BaCl_2$ crystal 20 to 30 mesh was used to made uniform turbidity.

(c) Standard sulphate solution: The standard sulphate solution was prepared by weighed out exactly 0.1479 g anhydrous Na_2SO_4 and it was taken in a 1000 mL volumetric flask. Then it was dissolved with the distilled water and finally, made up to the mark with distilled water, where 1 mL=100 µg sulphate (SO_4^{2-})

C. Procedure:

(a). Formation of barium sulphate turbidity: 100 mL water sample was taken in a 250 mL Erlenmeyer flask and 20 mL buffer solution was added and mixed with stirring apparatus. At the time of stirring a spoonful of $BaCl_2$ crystals was added and the solution was stirred for 1 minute.

(b) Measurement of turbidity: After stirring solution was poured in absorption cell of and turbidity was measured within 5 minutes.

(c) Preparation of standard curve: The proportions of 2, 4, 6, 8 and 10 mg/L of Na_2SO_4 solutions were taken in four different 1000 mL volumetric flasks and distillated water was gradually added and thoroughly shaken and finally made up to the mark with distilled water. Absorbance of the water samples were determined by AAS. A standard curve was made by plotting the absorbance against the concentration (Figure 2.13 in Appendix-2).

D. Calculation:

Sulphate (SO_4^{2-}, mg/L)

$$= \text{Concentration of } SO_4^{2-} \text{ (mg/L) from standard curve} \times \text{dilution factor}$$

xx. Total Coliform (TC)

The Total Coliform (TC) in water samples was determined using Membrane Filter procedure, which describes as follows:

A. Apparatus: 200 mL sample bottle, autoclave, culture dish, graduated membrane filter of 0.45 μm pore size and 47 mm diameter, filtration unit, hot plate, incubator, UV-disinfection chamber and Microscope.

B. Reagent: M-Endo Agar and ethanol.

C. Procedure:

(a) Preparation of culture medium: The culture media was prepared by exactly taking 51 g dehydrated M-Endo Agar in a 1000 mL volumetric flask and added distilled water slowly and shaken well and finally made up to the mark with distilled water. Then the solution was heated near to the boiling point to dissolve the agar medium. Then it was removed from heat and cooled to 50-45°C. 20 mL of 95% ethanol was added to the solution. 10 mL warm medium was dispensed to the sterilized petri dish.

(b) Sample preparation: All the Apparatus used for this experiment were sterilized by autoclaved. The water samples were collected in a 200 mL sterilized bottle and kept in refrigerator just after collection. 10 to 100 mL of water sample was taken in a beaker and diluted to 100 mL bacteria-free distilled water. Then, the solution was filtered through

0.45μm pore membrane filter in suction unit. The filter paper was removed carefully from filtration unit and placed on the culture media of the petri dishes.

(c) *Incubation:* The petri dishes were placed in the incubator where 35±0.5°C temperature was maintained for 24 hours.

(d) *Colony counting:* To determine colony counts on membrane filters, a low power binocular wide-field dissecting microscope, with a cool white florescent light was used. The typical coliform colony has a pink to dark-red color with a metallic (golden) seen.

D. Calculation:

Number of Total Coliform, TC (CFU/100 mL water)

$$= \text{Number of colonies on membrane filter} \times \text{dilution factor}$$

xxi. Faecal Coliform (FC)

The Faecal Coliform (FC) in water samples was determined using Membrane Filter procedure, which describes as follows:

A. Apparatus: 200 mL sample bottle, autoclave, culture dish, graduated membrane filter of 0.45 μm pore size and 47 mm diameter, filtration unit, hot plate, incubator, UV-disinfection chamber and Microscope.

B. Reagent: M-FC Agar, rosolic acid, NaOH and ethanol.

C. Procedure:

(a) *Preparation of culture medium:* The culture media was prepared by exactly taking 52.1 g dehydrated M-FC in a 1000 mL volumetric flask and added distilled water containing of 10 mL 1% rosolic acid in 0.2 N NaOH slowly and shaken well and finally made up to the mark with distilled water. The solution was heated near to the boiling point to dissolve the medium. Then it was removed from heat and cooled to 50-45°C. About 10 mL warm medium was dispensed to the sterilized petri dishes.

(b) *Sample preparation:* All the Apparatus used for this experiment were sterilized by autoclaved. The water samples were collected in a 200 mL sterilized bottle and kept in

refrigerator just after collection. 10 to 100 mL of water sample was taken in a beaker and diluted to 100 mL bacteria-free distilled water. Then the water sample was filtered with 0.45 μm pore membrane filter. The filter was removed carefully from filtration unit and placed on the culture media of the petri dish.

(c) Incubation: The petri dishes were placed in the incubator inversely where 44.5±0.2°C temperature was maintained for 24 hours.

(d) Colony counting: To determine colony counts on membrane filters, a low power binocular wide-field dissecting microscope, with a cool white florescent light was used. Colonies produced by faecal coliform bacteria on M-FC medium were various shades of blue. Non-faecal coliform are grey to cream-color. On M-FC medium very few non-faecal colonies were observed.

D. Calculation:

Number of Faecal Coliform, FC (CFU/100 mL water)

$$= \text{Number of colonies on membrane filter} \times \text{dilution factor}$$

3.4.2 Aquifer soil samples analysis

The aquifer soil samples were analyzed to determine the concentrations of heavy metals, major cations and anions.

i. Electrical Conductivity (EC)

5 mL distilled water was taken in a 50 mL conical flak and added exactly 1 g of air dry crushed aquifer soil. Then it was shaken for 30 minutes by potable shaker at 200 rpm. Then it was allowed to settle and the supernant was taken by pipette. The conductivity measured with a temperature-compensated probe of the supernant by EC meter, EC-210, HANA, Italy.

ii. Na, Mg, K, Ca, Mn, Fe, Zn, Cu, As, Cd and Pb ions

Atomic Absorption Method was to determine the concentration of Na, Mg, K, Ca, Mn, Fe, Cu, Zn, As, Cd and Pb ions in aquifer soil samples. The analytical procedures of the cations are already discussed above.

iii. HCO_3^-, Cl^-, NO_3^- and SO_4^{2-}

HCO_3^- and Cl^- in aquifer soil sample were determined using titration method. NO_3^- and SO_4^{2-} ions in aquifer soil sample were determined using UV-Spectrophotometric method. The analytical procedures of the anions are already discussed above

3.5 Water treatment process

3.5.1 Adsorption process

Adsorption experiments were carried out to remove or reduce contaminants metal ions such as Ca, Mn, Fe, As(total) and Pb from shallow tubewells water using indigenous material. Naturally occurring magnetite (Fe_3O_4), fine sand and stone chips were used as adsorbent to remove metal ions contaminants. Magnetite (Fe_3O_4) was collected from sand with the help of a magnet. The adsorbents were washed with distilled water and then allowed to air dried. All adsorbents were stored in polyethylene bags. Groundwater samples were collected from a shallow tubewells at the University of Rajshahi, Rajshahi, Bangladesh in October, 2010. The shallow tubewells water samples were spiked with Ca, Mn, Fe, As(total) and Pb ions to increase the initial concentration of the metal ions. In this way groundwater spiked with different initial concentrations of Ca, Mn, Fe, As(total) and Pb ions were prepared to operate batch and column adsorption processes.

3.5.2.1 Batch adsorption experiment

In the batch adsorption experiments, magnetite (Fe_3O_4) enriched sand were used as adsorbent. A portable bench top platform shaker was used to conduct the studies. 0.5-2 g of Fe_3O_4 (magnetite) and 10 g sand were taken in a 250 mL Erlenmeyer flask and added 50 mL spiked water. Then, it was shaken at 200 rpm at a room temperature ($30\pm2°C$). The samples from each flask were collected at time intervals of 15, 30, 60, 120, 240, 360 and 480 minutes and transferred to test tubes through 0.45µm porosity membrane filter paper and then metal ion concentration in the samples was determined by AAS.

3.5.2.2 Column adsorption experiment

In column adsorption studies were conducted in a glass column of 1 cm diameter with a height of 50 cm. The column was clamped vertically and a small piece of cotton wool

was used as a plug to support the adsorbent by a long glass rod to place the wool at the bottom of the column. Column was packed with each 10 cm layer filled from the bottom to top in the order of magnetite enriched sand, only sand and stone chips. Schematic diagram of experimental packed column is shown in Figure 2. Then added spiked groundwater from a fed bottle to top of the column and allowed it to percolate through the adsorbents bed at a flow rate of 5 mL/min. The treated water samples were collected from the bottom of the column and transferred to test tubes through 0.45µm porosity membrane filters and then metal ion concentrations of the samples were determined by AAS. A series of adsorption column experiments were carried out to optimizing the adsorption efficiency of different adsorption column packed with various amounts of magnetite (1-2g) enriched sand-stone and only sand-stone packed column.
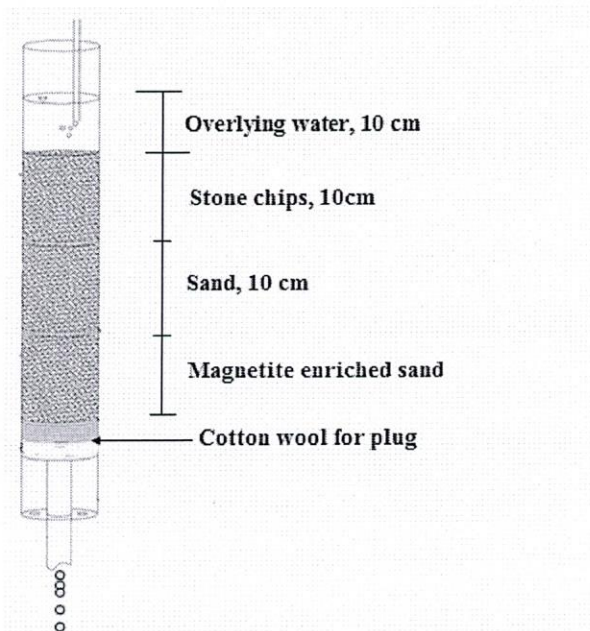
Figure 2. Schematic diagram of experimental packed column.

3.6 Data analysis

The experimental data were statistically analyzed using various software and the results were plot in figures to interpret the geochemical characteristics, water type and seasonal variation. Hydro-chemical facies and water type were illustrated using AQUCHEM software Version 5.1 which shows the relative concentrations of the different ions of analyzed water samples. The state of saturation of the groundwater with respect to the major carbonate mineral species was assessed in order to investigate the controls on the

composition of the groundwater and the approximate degree to which the groundwater has equilibrated with the various carbonate mineral phases. The Saturation Indices (SI) was determined using AQUCHEM software Version 5.1 (Parkhurst and Appelo, 1999). Positive values of SI indicate precipitation or a stable condition for minerals, zero value indicates that the solution is in equilibrium with a mineral and negative values indicate dissolution of a mineral (Lee and Gilkes, 2005). Chloro Alkaline Indices (CAI) were determined in order to identify the hydro-geochemical processes (ion exchange and reverse ion exchange). Principal component analysis (PCA) of R-mode factor was determined using SPSS 15 software packages to reveal the relationship among the parameters, and the data were standardized according to criteria presented by Davis (2002). In order to conclusively determine the main controls on the geochemistry, Gibb's ratios were calculated for cations and anions using equation developed by Gibbs (1970). Finally, the analyzed results of shallow and deep tubewells water compared to the WHO and Bangladesh Drinking Water Standard (BD-DWS) for evaluation the water quality.

Chapter Four
Results and Discussion

RESULTS AND DISCUSSION

Groundwater derives its mineral character essentially from reactions between rainwater and the host rock over a time scale of days, months, or years during percolation. Modification of water chemistry in groundwater can occur through physical, chemical, and biological processes. Anthropogenic activities through excessive use of agrochemicals, release of septic tank effluent, and domestic waste also have considerable effect on groundwater quality. In addition, the quality of water may be affected by the mixing of freshwater with mineralized water from the deeper parts of the aquifer and/ or from underlying formations. The current study focused on the factors controlling the groundwater composition, soil chemistry, water type and also tried to remove contaminants using adsorption process from the water.

4.1 Physico-chemical parameters of aquifer soil and groundwater

4.1.1 Physico-chemical parameters of aquifer soil

A total of 30 aquifer soil samples were collected from 30 locations at depths (10-45 meter) during monsoon 2010 to know the physico-chemical parameters of aquifer soil (details results in Appendix 3). The statistical summary results of analyzed shallow aquifer soil samples in monsoon season in 2010 are shown in Table 1. The highest and lowest concentrations of EC were found in sample number ASS 26 and 09 (Aquifer Soil Sample), respectively and the values for maximum, minimum and mean were 2928, 1040 and 1800.18 μS/cm (Table 1). The concentration of Ca^{2+} in aquifer soil was found highest among cations and its mean and standard deviation were 166.08$\pm$30.30 mg/kg (Table 1). Among metal ions, Cd^{2+} concentration was found lowest and its mean and standard deviation were 0.133$\pm$0.119 mg/kg (Table 1). Among anions, HCO_3^- and NO_3^- showed the highest and lowest concentrations and their concentrations were 580 mg/kg in ASS 2 and 3.87 mg/kg in ASS 27, respectively.

The analyzed results of the study showed that the mean concentrations of cations and anions were followed in the order: $Ca^{2+}> Mg^{2+}> Na^+> K^+> Fe^{3+}> Mn^{2+}> Zn^{2+}> Cu^{2+}> Pb^{2+}> As$ (total)$> Cd^{2+}$ and $HCO_3^-> Cl^-> SO_4^{2-}> NO_3^-$, respectively (Table 1). It is well established that natural metal loadings to groundwater reflect the chemical composition

of local bedrock (Piispanen and Nykyri, 1997; Loukola-Ruskeeniemi *et al.*, 2003). In general water composition mostly depends on the aquifer soil/materials with the reaction of rainwater during percolating through the soil strata.

Table 1

Characteristics of shallow aquifer soil samples in monsoon season, 2010

Parameters	Minimum	Maximum	Mean ± SD	Count, N
EC	1040.00	2928.00	1800.18±460.80	30
Na	38.76	81.01	54.91±10.03	30
Mg	6.39	166.80	86.75±34.90	30
K	7.23	20.44	13.46±4.21	30
Ca	109.36	220.00	166.08±30.30	30
Mn	2.200	11.430	6.347±2.458	30
Fe	5.930	11.860	8.789±1.638	30
Cu	0.120	1.600	0.750±0.401	30
Zn	0.080	1.600	0.756±0.397	30
As	0.058	0.850	0.350±0.240	30
Cd	0.020	0.380	0.133±0.119	30
Pb	0.090	4.010	0.733±1.054	30
HCO_3^-	187.31	580.00	325.52±97.00	30
Cl^-	36.04	121.78	76.78±19.54	30
NO_3^-	3.87	13.65	8.74±2.49	30
SO_4^{2-}	38.73	89.60	55.22±11.12	30

Unit: All units are in mg/kg except EC in µS/cm

4.1.2 Seasonal variation of physico-chemical and microbial parameters of groundwater

A total of 240 representative groundwater (180 shallow and 60 deep tubewells) samples were collected during pre-monsoon, monsoon and post-monsoon season covering two years of 2009 and 2010 to analyze various physico-chemical parameters (detailed results in Appendix 4-5)

4.1.2.1 Variation in physical parameters in groundwater

i. Temperature

The highest mean temperature of shallow tubewells was observed 28.44°C in pre-monsoon 2010 and the lowest was 26.03°C in post-monsoon 2009 during the study

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period (Table 2). The highest mean temperature of deep tubewells was to be observed 27.75°C in pre-monsoon 2009 and the lowest was 26.05°C in post-monsoon 2010 during the same period (Table 3).The results indicate that the groundwater temperature was slightly varies with seasonal temperature. Jinwal and Dixit (2008) supported the present finding where the groundwater temperature recorded in pre-monsoon in Bhopal, India was higher than the post-monsoon. Water temperature of both shallow and deep tubewells in the study area followed in the order: pre-monsoon>monsoon>post-monsoon.

Table 2

Physical parameters of shallow tubewells water samples in the pre-monsoon, monsoon and post-monsoon seasons

Para-meters	Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Temp.	28.03±0.96	28.44±0.61	28.12±1.45	27.60±2.20	26.03±0.62	26.13±0.81
pH	7.50±0.29	7.45±0.18	6.22±0.44	6.07±0.44	7.09±0.24	7.09±0.28
EC	444.90±223.5	337.34±144.5	341.88±86.9	342.57±78.8	668.03±129.9	537.97±178.8
TDS	319.05±169.4	226.86±112.6	199.51±67.97	188.61±72.8	472.36±141.3	378.17±122.7
TSS	158±66.67	132.67±49.40	173.33±30.32	183.67±49.16	173.33±82.77	163.33±69.84
TH	379.50±79.80	385.73±57.51	179.01±33.65	200.28±37.7	333.33±66.60	347.57±61.19

Unit: All units are in mg/L except Temperature in °C and EC in µS/cm and pH

ii. pH

The highest mean pH of shallow tubewells measured was 7.50 in pre-monsoon 2009 and the lowest was 6.09 in monsoon 2010 during the study period (Table 2). The highest mean pH of deep tubewells was 7.74 in pre-monsoon 2009 and the lowest was 6.33 in monsoon 2010 during the same period (Table 3). The results indicate that the groundwater pH was nearly neutral and slightly varies with seasons. Sundar and Saseetharan (2008) supported the present finding where the groundwater pH measured in pre-monsoon in Tamil Nadu in India was higher than the post-monsoon. pH was weakly acidic during monsoon season due to increase the groundwater volume. Then pH was increased in post-monsoon from slightly acidic to slightly alkaline could be due to the

being steadily enriched up to high overall mineralization. Higher pH in water during pre-monsoon was more than other seasons due to decrease the volume of water. The water pH of both shallow and deep tubewells in the study area followed in the order: pre-monsoon>post-monsoon>monsoon.

iii. Electrical conductivity (EC)

The highest mean values of EC were 668.03 and 737.50 µS/cm for the shallow and deep tubewells, respectively in post-monsoon 2009 (Table 2 and Table 3) could be leaching and subsequent infiltration as the groundwater table was nearer to the surface, which apparently suggests the enhancement of solute enrich in the aquifer. The lowest mean values of EC were measured 337.34 in pre-monsoon 2010 and 351.20 µS/cm in the monsoon 2010 for the shallow and deep tubewells, respectively (Table 2 and Table 3). Deshmukh (2011) supported the present finding where the groundwater EC measured in post-monsoon in Sangamner in India was higher than the pre-monsoon. EC of both the shallow and deep tubewells water samples in the study area followed: post-monsoon>pre-monsoon>monsoon.

Table 3

Physical parameters of deep tubewells water samples in the pre-monsoon, monsoon and post-monsoon seasons

Para-meters	Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Temp.	27.75±0.54	27.13±1.40	26.90±1.30	27.50±1.41	26.47±0.76	26.05±0.90
pH	7.74±0.13	7.67±0.10	6.34±0.28	6.33±0.35	7.02±0.20	7.03±0.19
EC	371.40±43.38	385.50±43.00	353.20±74.75	351.20±74.62	737.50±162.3	555.80±134.9
TDS	264.00±30.62	276.00±30.62	186.88±60.00	185.96±61.00	266.00±30.98	276.09±30.74
TSS	140.0±51.63	158.0±50.29	172.0±67.13	121.0±36.65	221±101.16	206.0±59.85
TH	274.00±50.98	284.00±51.98	168.31±27.53	172.58±29.79	449.00±142.6	444.10±138.2

Unit: All units are in mg/L except Temperature in °C, EC in C µS/cm and pH

iv. Total Dissolved Solids (TDS)

The highest mean values of TDS of shallow tubewells was measured 472.36 mg/L in post-monsoon 2009 and the lowest was 188.61 mg/L in monsoon 2010 during the study period (Table 2). The highest mean values of TDS of deep tubewells was found to be 276 mg/L in post-monsoon 2010 and the lowest was 185.96 mg/L in monsoon 2010 in the same period (Table 3). During post-monsoon season groundwater is evaporated and water table falls that increase TDS in the post-monsoon season. TDS of both the groundwater in the study area were followed: post-monsoon>pre-monsoon>monsoon.

v. Total Suspended Solids (TSS)

The highest mean values of TSS of shallow tubewells water was measured 183.67 mg/L in monsoon 2010 and the lowest was 132.67 mg/L in pre-monsoon 2010 during the study period (Table 2). The highest mean values of TSS of deep tubewells water was found to be 221 mg/L in post-monsoon 2009 and the lowest was 121 mg/L in monsoon 2010 in the same period (Table 3). During post-monsoon season groundwater is evaporated and water table falls that increase TSS in the post-monsoon season. TSS of water of the shallow tubewells in the study area was in the order: pre-monsoon>post-monsoon>monsoon and that of deep tubewells was followed: post-monsoon>pre-monsoon>monsoon.

vi. Total hardness (TH)

The highest mean value of TH was found to be 385.73 mg/L in pre-monsoon 2010 and the lowest mean value was found to be 179.01 mg/L in monsoon 2009 for shallow tubewells during the study period (Table 2). Ravichandan and Jayaprakash (2011) supported the present finding where the shallow tubewells water TH measured in pre-monsoon in north Chennai in India was higher than the post-monsoon. The highest mean value of TH for deep tubewells was measured 449 mg/L in post-monsoon 2009 and the lowest was 168.31 mg/L in monsoon 2009 during the study period (Table 3). A similar observation was made by Shende *et al.,* (2013). The analysis results of TH illustrate that the both samples for the pre and post-monsoons were hard to very hard types whilst hard category in monsoon. TH of water of the shallow tubewells in the study area was in the order: pre-monsoon>post-monsoon>monsoon and that of deep tubewells was in the order: post-monsoon>pre-monsoon>monsoon.

4.1.2.2 Variation of major anionic parameters in groundwater

i. Bicarbonate ion (HCO$_3^-$)

The highest mean value of HCO$_3^-$ of shallow tubewells water was 366.53 mg/L in pre-monsoon 2010 and the lowest was 171.82 mg/L in post-monsoon 2009 during the study period (Table 4). The highest mean value of HCO$_3^-$ of deep tubewells was 235.17 mg/L in pre-monsoon 2010 and the lowest was 148.50 mg/L in post-monsoon 2009 during the same period (Table 5). Mishra *et al.*, (2011) supported the present finding where the HCO$_3^-$ in groundwater samples in Maddhya Pradesh, India was higher in the pre-monsoon than the post-monsoon. Lowering of HCO$_3^-$ values in post-monsoon could be the dilution effect of rainwater infiltration during the monsoon season leading to higher groundwater level. Due to the origin of HCO$_3^-$ related to the aquifer lithology and the concentration effect which increase its concentration in pre-monsoon season. HCO$_3^-$ in water of both the shallow and deep tubewells in the study area was followed: pre-monsoon>monsoon>post-monsoon (Table 4 and 5).

Table 4

Major anionic parameters of shallow tubewells water samples in the pre-monsoon, monsoon and post-monsoon seasons

Para-meters, mg/L	Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
HCO$_3^-$	366.53±36.0	363.03±44.48	176.76±40.56	198.93±59.51	171.82±36.0	191.72±44.50
Cl$^-$	58.25±22.13	58.10±19.63	33.60±7.32	38.91±8.73	74.27±28.45	67.58±18.54
NO$_3^-$	1.33±0.77	1.23±0.34	1.39±0.40	1.42±0.73	2.41±1.81	1.81±0.83
SO$_4^2$	40.21±10.97	38.36±10.10	36.59±9.08	32.73±6.23	43.65±11.31	42.46±11.20

ii. Chloride ion (Cl$^-$)

The highest mean value of Cl$^-$ concentration of shallow tubewells was found 74.27 mg/L in post-monsoon 2009 and the lowest was 33.60 mg/L in monsoon 2009 during the study period (Table 4). The significant increased of Cl$^-$ in the post-monsoon rather than pre-monsoon and monsoon for shallow tubewells due to substantiate the high leaching of salt with percolating rain water and anthropogenic sources of chloride include fertilizers, and human and animal waste. Deshmukh (2011) supported the present finding where the Cl$^-$

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in groundwater samples in Sangamner in India was higher in the post-monsoon than the pre-monsoon.

The highest mean value of Cl^- concentration of deep tubewells was found to be 60.53 mg/L in pre-monsoon 2010 and the lowest was 35.31 mg/L in monsoon 2010 during the same period (Table 5). A similar observation was found by Mishra *et al.*, (2011) and Ravichandan and Jayaprakash (2011). Cl^- concentration was increased in the pre-monsoon of deep tubewells water may be caused of decreasing water volume compare to that of the monsoon. Cl^- concentration of water of the shallow tubewells in the study area followed in the order: post-monsoon>pre-monsoon>monsoon and that of the deep tubewells was in the order: pre-monsoon>post-monsoon>monsoon.

Table 5

Major anionic parameters of deep tubewells water samples in the pre-monsoon, monsoon and post-monsoon seasons

Para-meters, mg/L	Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
HCO_3^-	201.48±65.56	235.17±78.62	165.67±56.09	182.20±56.13	148.50±55.51	189.05±87.7
Cl^-	59.47±16.89	60.53±17.69	37.23±8.14	35.31±9.10	41.64±17.63	41.18±15.18
NO_3^-	1.25±0.84	1.33±0.74	1.84±0.88	1.85±0.91	2.07±1.13	2.01±0.97
SO_4^{2-}	37.95±6.05	40.17±5.74	32.25±2.59	31.19±2.66	42.89±10.69	41.12±9.53

iii. Nitrate ion (NO_3^-)

The highest mean value of NO_3^- concentration of shallow tubewells was determined 2.41 mg/L in post-monsoon 2009 and the lowest was 1.23 mg/L in pre-monsoon 2010 during the study period (Table 4). The highest mean value of NO_3^- concentration of deep tubewells was found to be 2.07 mg/L in post-monsoon 2009 and the lowest was 1.25 mg/L in pre-monsoon 2009 during the same period (Table 5). Deshmukh (2011) showed a similar observation. The results show that NO_3^- concentration in water samples was not significantly changed with seasons (Table 5). Moreover, the NO_3^- concentrations in both the water samples were found lowest among anions (Table 4 and Table 5). In natural conditions, the concentration of NO_3^- does not exceed 10 mg/L in the water (Cushing *et al.*, 1973). The NO_3^- concentrations of both shallow and deep tubewells water samples in the study area was in the order: post-monsoon>monsoon>pre-monsoon.

iv. Sulphate ion (SO₄²⁺)

iv. Sulphate ion (SO$_4^{2+}$)

The highest mean value of SO$_4^{2+}$ concentration of shallow tubewells was measured 43.65 mg/L in post-monsoon 2009 and the lowest was 32.73 mg/L in monsoon 2010 during the study period (Table 4). The highest mean SO$_4^{2+}$ concentration of deep tubewells was measured to be 42.89 mg/L in post-monsoon 2009 and the lowest was 31.19 mg/L in monsoon 2010 during the same period (Table 5). Deshmukh (2011) supported the present finding where the SO$_4^{2-}$ in groundwater samples in Sangamner in India was higher in the post-monsoon than the pre-monsoon. The change in SO$_4^{2-}$ concentration in water samples was negligible with respect to seasons although slightly increase was noticed in the post-monsoon season and it may be due to the action of leaching and anthropogenic activities. The SO$_4^{2-}$ concentrations of water of both shallow and deep tubewells water samples in the study area followed in the order: post-monsoon>pre-monsoon>monsoon.

4.1.2.3 Variation of major cataonic parameters in groundwater

i. Sodium ion (Na⁺)

i. Sodium ion (Na$^+$)

The highest mean value of Na$^+$ concentration of shallow tubewells was found to be 24.46 mg/L in post-monsoon and the lowest was 21.61 mg/L in monsoon during the study period and same year 2010 (Table 6). The highest mean value of Na$^+$ concentration of deep tubewells was measured to be 29.52 mg/L in post-monsoon 2009 and the lowest was 18.88 mg/L in monsoon 2009 during the same period (Table 7). But the concentrations of Na$^+$ were nearly same in pre-monsoon and post-monsoon. Venugopal *et al.*, (2009) and Singh *et al.*, (2011) illustrated a similar observation of Na$^+$ concentrations in groundwater samples in Chennai and Noida Metropolitan City in Uttar Pradesh in India. The Na$^+$ concentration of both the shallow and deep tubewells water samples in the study area followed in the order: post-monsoon>pre-monsoon>monsoon.

ii. Magnesium ion (Mg²⁺)

ii. Magnesium ion (Mg^{2+})

The highest mean value of Mg^{2+} concentration of shallow tubewells was measured 29.86 mg/L in post-monsoon 2010 and the lowest was 25.23 mg/L in monsoon 2009 during the study period (Table 6). The highest mean value of Mg^{2+} concentration of deep tubewells was found to be 29.66 mg/L in post-monsoon 2010 and the lowest was 24.23 mg/L in

monsoon 2010 during the same period (Table 7). There was a little increase in the concentration of Mg^{2+} during the post-monsoon than pre-monsoon and monsoon for both tubewells. Similar results of Mg^{2+} concentration in groundwater samples were reported (Kuldip-Singh *et al.*, 2011; Ravichandan and Jayaprakash, 2011 and Shende *et al.*, 2013). In monsoon season, the concentrations of Mg^{2+} were slightly lower than pre and post-monsoon due to rainwater recharge. The Mg^{2+} concentration of both shallow and deep tubewells water samples in the study area was in the order: post-monsoon>pre-monsoon>monsoon.

Table 6

Major cationic parameters of shallow tubewells water samples in the pre-monsoon, monsoon and post-monsoon seasons

Para-meters, mg/L	Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Na	24.29±4.21	23.39±2.75	21.88±3.27	21.61±4.93	23.07±3.33	24.46±4.57
Mg	26.84±5.07	27.39±4.60	25.23±2.77	26.48±3.75	26.31±4.02	29.86±3.75
K	7.68±1.41	5.61±2.32	3.00±0.26	3.19±0.73	8.02±1.24	6.65±1.97
Ca	93.05±14.01	91.88±15.15	59.70±11.43	58.52±12.61	82.55±23.31	84.42±22.35

iii. Potassium ion (K⁺)

The highest mean value of K^+ concentration of shallow tubewells was measured to be 8.02 mg/L in post-monsoon 2009 and the lowest was 3 mg/L in monsoon 2009 during the study period (Table 6). The highest mean value of K^+ concentration of deep tubewells was found to be 8.29 mg/L in post-monsoon 2009 and the lowest was 3.41 mg/L in monsoon 2010 during the same period (Table 7). The results show that the concentrations of K^+ were nearly the same in pre and post-monsoon. Kuldip-Singh *et al.*, (2011) reported that the K^+ concentrations in groundwater samples in Bathinda district of Punjab, northwest India was found higher in the post-monsoon than the pre-monsoon, and the results supported the present study findings. The analysis results show that K^+ concentration was found almost half in monsoon compare to the other seasons due to dilution effect of rainwater infiltration. The K^+ concentration of both shallow and deep

tubewells water samples in the study area was in the order: post-monsoon>pre-monsoon>monsoon.

Table 7

Major cationic parameters of deep tubewells water samples in the pre-monsoon, monsoon and post-monsoon seasons

Para-meters, mg/L	Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010
	Mean ± SD	Mean± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Na	22.57±3.46	20.26±2.79	18.88±1.46	18.97±1.48	29.52±6.37	26.94±3.50
Mg	25.07±4.08	25.77±3.73	24.34±0.97	24.23±0.94	29.66±2.76	29.03±3.60
K	5.57±1.98	5.68±1.52	3.44±1.05	3.41±1.04	8.29±1.41	7.03±1.31
Ca	86.07±18.80	83.51±17.5	66.47±19.75	65.04±17.21	87.30±17.62	88.36±18.27

iv. Calcium ion (Ca^{2+})

The highest mean value of Ca^{2+} concentration of shallow tubewells water was determined to be 93.05 mg/L in pre-monsoon 2009 and the lowest was 58.52 mg/L in monsoon 2010 during the study period (Table 6). A report showed by Kuldip-Singh *et al.,* (2011) on Ca^{2+} concentrations in shallow tubewells water in Bathinda district of Punjab in India that the ionic concentration in pre-monsoon water samples was higher than the post-monsoon season. The highest mean value of Ca^{2+} concentration of deep tubewells was found to be 88.36 mg/L in post-monsoon 2010 and the lowest was 65.04 mg/L in monsoon 2010 during the same period (Table 7). Ca^{2+} concentration of the shallow and deep tubewells water samples in the study area followed in the order: pre-monsoon> post-monsoon> monsoon and post-monsoon> pre-monsoon> monsoon, respectively.

4.1.2.4 Variation of heavy metals in groundwater

Heavy metals are the elements having atomic weights between 63.5 and 200.6, and in this study, 7 heavy metals namely Mn, Fe, Cu, Zn, As, Cd and Pb ions of the shallow and deep tubewells water samples were analyzed during pre-monsoon, monsoon and post-monsoon seasons in 2009 and 2010. The analyzed results of shallow and deep tubewells water samples are illustrated in Table 8 and Table 9, respectively.

i. Manganese ion (Mn^{2+})

The highest mean value of Mn^{2+} concentration of shallow tubewells was obtained to be 1.749 mg/L in post-monsoon 2009 and the lowest was 1.129 mg/L in monsoon 2009 during the study period (Table 8). The highest mean value of Mn ion concentration of deep tubewells was found to be 2.70 mg/L in post-monsoon 2010 and the lowest was 1.123 mg/L in monsoon 2010 during the same period (Table 9). Mn^{2+} concentrations in both the water samples were found higher in post-monsoon season compared to the pre-monsoon and monsoon seasons due to leaching action of Mn ion. The results show that Mn ion concentration of both the groundwater samples in the area followed in the order: post-monsoon>monsoon>pre-monsoon and post-monsoon>monsoon>pre-monsoon for the deep tubewells water.

Table 8

Heavy metals concentration of shallow tubewells water samples in the pre-monsoon, monsoon and post-monsoon seasons

Para-meters, mg/L	Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Mn	1.472±0.848	1.426±0.964	1.129±0.895	1.734±1.311	1.749±1.262	1.302±0.882
Fe	3.56±1.57	3.40±1.49	0.85±0.28	1.18±1.11	4.89±1.49	3.91±1.18
Cu	0.065±0.109	0.100±0.131	0.023±0.040	0.024±0.016	0.107±0.137	0.135±0.197
Zn	0.196±0.189	0.180±0.148	0.056±0.055	0.048±0.037	0.313±0.231	0.337±0.173
As	0.025±0.022	0.017±0.013	0.014±0.016	0.010±0.009	0.018±0.016	0.020±0.020
Cd	0.009±0.015	0.016±0.021	0.017±0.003	0.024±0.007	0.007±0.006	0.008±0.006
Pb	0.012±0.007	0.028±0.061	0.205±0.056	0.202±0.066	3.340±0.550	3.218±0.519

ii. Iron (Fe)

The highest mean value of Fe ion concentration of shallow tubewells was obtained to be 4.89 mg/L in post-monsoon 2009 and the lowest was 0.85 mg/L in monsoon 2009 during the study period (Table 8). The highest mean value of Fe ion concentration of deep tubewells was measured 4.62 mg/L in post-monsoon 2009 and the lowest was 0.82 mg/L

in monsoon 2009 during the same period (Table 9). Raju (2006a) supported the present finding where the Fe) ion concentration in groundwater samples in Tirumala-Tirupati environs in India was higher in the post-monsoon than the pre-monsoon. In the monsoon season iron from biotite mica and laterites are leached into solution in ferrous state under reducing condition and its concentration was comparatively low due to dilution (Kumar, 2010). After monsoon season, Fe ion concentration was increased due to volume of water decrease in the aquifer zone. Applin and Zhao (1989), and White *et al.*, (1991) reported that concentration of Fe ion in groundwater may be higher under more reducing conditions due to bacteriological degradation of organic matter which leads to the formation of various humic and fluvic compounds. The Fe ion concentration of water of both shallow and deep tubewells water samples in the study area followed in the order: post-monsoon>pre-monsoon>monsoon.

iii. Copper ion (Cu²⁺)

The highest mean value of Cu^{2+} concentration of shallow tubewells was found 0.135 mg/L in post-monsoon 2010 and the lowest was 0.023 mg/L in monsoon 2009 during the study period (Table 8). The highest mean value of Cu^{2+} concentration of deep tubewells was found to be 0.583 mg/L in pre-monsoon 2009 and the lowest was 0.021 mg/L in monsoon 2009 during the same period (Table 9). Cu^{2+} concentration of both shallow and deep tubewells water samples in the study area followed in the order: post-monsoon>pre-monsoon>monsoon.

iii. Zinc ion (Zn²⁺)

The highest mean value of Zn^{2+} concentration of shallow tubewells was measured 0.337 mg/L in post-monsoon 2010 and the lowest was 0.048 mg/L in monsoon 2010 during the study period (Table 8). The highest mean value of Zn^{2+} concentration of deep tubewells was to be measured 0.273 mg/L in pre-monsoon 2010 and the lowest was 0.041 mg/L in monsoon 2009 during the same period (Table 9). Zn^{2+} concentration of both shallow and deep tubewells water samples in the study area followed: post-monsoon>pre-monsoon>monsoon.

Table 9

Heavy metals concentration of deep tubewells water samples in the pre-monsoon, monsoon and post-monsoon seasons

Para-meters, mg/L	Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Mn	1.299±0.887	1.123±0.796	2.415±1.145	2.603±1.349	2.700±1.566	2.609±1.215
Fe	2.05±0.69	1.84±1.06	0.82±0.50	0.84±0.55	4.62±1.20	3.53±1.02
Cu	0.355±0.234	0.370±0.202	0.021±0.015	0.024±0.026	0.583±1.239	1.003±1.509
Zn	0.188±0.068	0.273±0.096	0.041±0.017	0.043±0.021	0.254±0.219	0.271±0.224
As	0.009±0.004	0.016±0.015	0.007±0.005	0.009±0.003	0.010±0.008	0.018±0.015
Cd	0.007±0.006	0.013±0.007	0.034±0.008	0.032±0.006	0.009±0.009	0.011±0.010
Pb	0.019±0.006	0.028±0.012	0.161±0.059	0.161±0.059	3.121±0.503	3.212±0.470

iv. Arsenic (As)

The highest mean value of As (total) concentration in the shallow tubewells water was measured to be 0.025 mg/L in pre-monsoon 2009 and the lowest was 0.010 mg/L in monsoon 2010 during the study period (Table 8). The highest mean value of As(total) concentration of deep tubewells was found to be 0.018 mg/L in post-monsoon 2010 and the lowest was 0.007 mg/L in monsoon 2009 during the same period (Table 9 and details in Appendix 5.7). The results show that the seasonal variation in concentrations of arsenic was observed may be due to infiltration rain water. A similar observation was illustrated by Ali *et al.*, (2012) for the shallow groundwater of Ballia District in Uttar Pradesh in India. The arsenic concentration of the shallow tubewells in the study area was in the order: pre-monsoon>post-monsoon>monsoon and that of deep tubewells was in the order: post-monsoon>pre-monsoon>monsoon.

vi. Cadmium ion (Cd^{2+})

The highest mean value of Cd^{2+} concentration of shallow tubewells was obtained 0.024 mg/L in monsoon 2010 and the lowest was 0.007 mg/L in post-monsoon 2009 during the study period (Table 8). The highest mean value of Cd^{2+} concentration of deep tubewells was found to be measured 0.034 mg/L in monsoon 2009 and the lowest was 0.007 mg/L

in post-monsoon 2009 during the same period (Table 9). Cd^{2+} concentration of both shallow and deep tubewells water samples in the study area was in the order: monsoon>pre-monsoon>post-monsoon.

vii. Lead ion (Pb^{2+})

The highest mean value of Pb^{2+} concentration of shallow tubewells was found 3.340 mg/L in post-monsoon 2009 and the lowest was 0.012 mg/L in pre-monsoon 2009 during the study period (Table 8). A similar report was found by Singh *et al.*, (2011) in shallow tubewells water samples in Uttar Pradesh in India. The highest mean value of Pb^{2+} concentration of deep tubewells was to be determined 3.212 mg/L in post-monsoon 2010 and the lowest was 0.019 mg/L in pre-monsoon 2009 during the same period (Table 9). Pb^{2+} concentration range 0.090 to 4.014 mg/kg in aquifer soil (Appendix-3) with an average 0.733 mg/kg (Table 1) in monsoon season whereas concentration of Pb^{2+} in shallow tubewells water samples was 0.001 to 0.313 mg/L in the same season in 2010 (Appendix 4.7) which indicated that the Pb^{2+} concentration in groundwater in the study area was the natural source. However, the Pb^{2+} concentration of both groundwater samples in post-monsoon season was found higher due to dissolution of Pb ores and anthropogenic activities. Pb^{2+} concentration of groundwater samples in the area was in the order: post-monsoon>monsoon>pre-monsoon.

4.2 Comparison between shallow and deep tubewells water quality

Average water quality parameters of shallow and deep tubewells in two years of Rajshahi City and compared with World Health organization (WHO, 2008) and Bangladesh Drinking Water Standard (BD-DWS) which are shown in Table 10-14.

The overall mean temperature of shallow and deep tubewells water samples were nearly the same (Table 10). But the samples of shallow tubewells temperature were slightly higher than deep tubewells as expected because in general the water temperature decreases with depth. A similar observation was found for the groundwater in Warangal City in India by Shende *et al.*, (2013). Table 10 shows that the temperature for the both the tubewells water were below the permissible limit of WHO and Bangladesh Drinking Water Standards (BD-DWS).

The average pH of the analyzed shallow and deep tubewells water samples were 6.905 and 6.979 (Table 10). Deep tubewells water sample pH was slightly higher than shallow tubewells due to mineralization during percolation of rainwater. The overall results of pH of the study indicate that the groundwater was slightly acidic to neutral nature. The low pH of the groundwater of the study area may be related to the wide distribution of lateritic soil (CESS, 1984). Most of the groundwater samples pH were within the permissible limit as prescribed by WHO (2008) and BD-DWS. The results also show that a few of samples in the monsoon season were found bellow the standards. A low pH (below 6.5) can cause corrosion of water carrying metal pipes, thereby releasing toxic metals such as zinc, lead, cadmium, copper etc (Trivedy and Goel, 1986). Furthermore, low pH values in groundwater can cause gastrointestinal disorders like hyper acidity, ulcers, and stomach pain with burning sensation (Rajesh *et al.*, 2001). Though pH has no direct effect on human health, but it shows close relations with some other chemical constituents of water (Pitt *et al.*, 1999). Since, pH of maximum groundwater samples were within the permissible limit, so there was no chance to damages mucous membrane present in nose, mouth, eye, abdomen, anus in human beings.

Table 10

Statistical summary of physical parameters in the groundwater of Rajshahi City and comparison with standards

Parameters	Shallow tubewells	Deep tubewells	BD DWS	WHO DWS, 2008
	Mean ± SD	Mean ± SD		
Temperature, °C	27.390 ± 0.676	27.187 ± 0.535	-	NGL
pH	6.905 ± 0.179	6.979 ± 0.136	6.5-8.5	6.5-8.5
EC, µS/cm	445.44 ± 49.407	454.98 ± 52.469	-	1400
TDS, mg/L	297.435 ± 49.696	241.648 ± 21.691	-	NGL
TH, mg/L	304.238 ± 29.752	302.281 ± 54.485	200- 500	200
TSS, mg/L	164.11 ± 22.32	149.50±22.01	10	-

*NGL-No Guide Line

The mean value of Electrical conductivity (EC) of shallow tubewells water samples was lower than the deep tubewells water (Table 10). A similar observation was found by Garfias *et al.*, (2010) and Shende *et al.*, (2013). In general, the EC of deep aquifer water

was greater than the shallow aquifer because the deep aquifer system is a vertically continuous sequence of rocks with undefined thickness and contains water with high concentrations of various elements (Ca^{2+}, Mg^{2+}, HCO_3^- and Cl^-) generally increasing with depth. As the maximum allowable limit for EC in drinking water is 1,400 µS/cm (WHO, 2008), thus most of the groundwater samples were within the maximum limit.

Mean value of TDS concentration of the shallow tubewells (297.435 mg/L) which was greater than the deep tubewells (241.648 mg/L) (Table 10). Garfias *et al.*, (2010) reported on TDS of shallow and deep tubewells water that the results were similar to the present study. There is no guide line value for TDS by WHO (2008). On the basis of TDS, Davis and DeWiest (1966) classified of groundwater up to 500 mg/L (desirable for drinking); 500-1,000 mg/L (permissible for drinking) and up to 3,000 mg/L (useful for agricultural purposes). Based on this classification, it was observed that most of the samples were desirable for drinking purpose. On the other hand, as per the TDS classification (Fetter, 1990), the collected all groundwater samples of pre-monsoon, monsoon and post-monsoon periods belong to fresh type (TDS<1,000 mg/L).
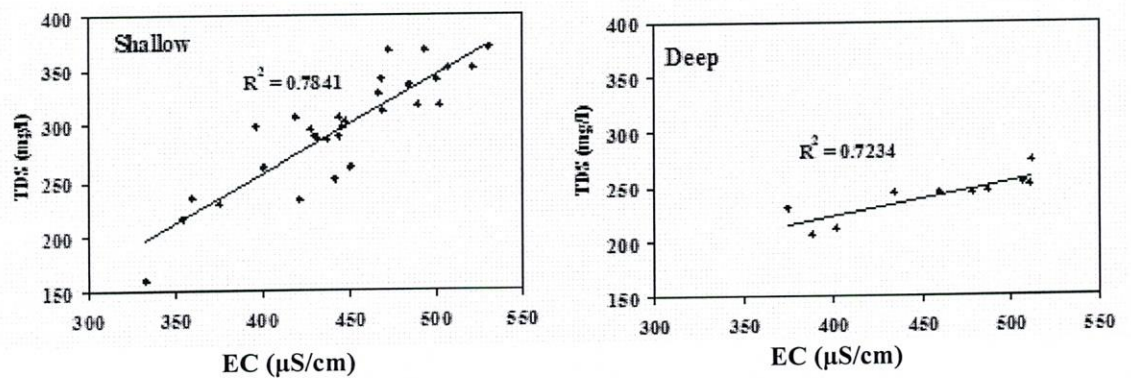
Figure 3. EC versus TDS shows positive R^2 confirming the linear relationship of two parameters and the efficacy of the field measurements.

A plot of EC versus TDS in the shallow and deep tubewells water samples are shown in Figure 3, which illustrates good positive correlations and the coefficients values are 0.7841 and 0.7234 for shallow and deep tubewells, respectively. The results indicate that the linear relationship between EC and TDS conforms to the efficiency and accuracy of the field measurements.

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Mean value of TSS concentration of the shallow tubewells (164.11 mg/L) which was greater than the deep tubewells (149.50 mg/L) (Table 10). The results show that all the all groundwater samples exceeded the permissible limit of BD-DWS for TSS (Table 10, Appendix 4, Table 4.2 and Appendix 5, Table 5.2).

Overall mean concentrations of total hardness (TH) of shallow and deep tubewells were nearly the same (Table 10). On the basis of Sawyer and McCarty (1967), hardness in water can be classified into soft (>75 mg/L), moderately hard (75-150 mg/L), hard (150-300 mg/L) and very hard (>300 mg/L) categories. Based on TH, Dufor and Becker (1964) classified water as 0-60 mg/L, soft; 61-120 mg/L, moderately hard; 121-180 mg/L, hard and >180 mg/L very hard water. Based on these classification about 90% of samples belongs to very hard type and rest to hard type water (Appendix 4, Table 4.2 and Appendix 5, Table 5.2). About 80% of groundwater samples had TH more than total alkalinity (TA), which indicated that the groundwater was characterized by carbonated hardness (Chow, 1964). Such hardness can be removed easily from the waters by simple boiling or adding lime.

Hardness is very important property of water from its domestic and industrial application point of view. The acceptable limit of total hardness (as $CaCO_3$) is 200 mg/L, which can be extended up to 600 mg/L in case of non-availability of any alternate water source (WHO, 2008). The hardness value 150-300 mg/L and above may cause kidney problems and kidney stone formation (Jain, 1998), as it causes unpleasant taste and reduce ability of soap to produce lather. Groundwater in the area exceeded the limit of 300 mg/L as $CaCO_3$ was considered to be hard as per classification by Sawyer and McCarthy (2003) and the probable source of it might be due to geology of the rocks, industrial discharge, and sewage effluent.

The data indicated that TH values of all samples were lower than 500 mg/L, which was the maximum permissible limit of Bangladesh standard. Hardness has no adverse effect on health, but it can prevent formation of lather with soap and increases the boiling point of the water. The high TH concentration may cause encrustation on water supply distribution systems, water heater, boilers and cooking utensils in Rajshahi City area. There was some suggestive evidence that long term consumption of extremely hard water might lead to an increased incidence of urolithiasis and cardiovascular disorders

(Durvey *et al.*, 1991). The very hard water requires softening for household or commercial use.

Mean concentration of HCO_3^- of most of the shallow tubewells water samples were much greater than deep tubewells (Table 11). In general, more carbonate mineral dissolution takes place in shallow aquifer than deep aquifer. A similar observation was found by Garfias *et al.*, (2010) that near the water table the rainwater can easily infiltrate and the leaching water break down the calcite and produce more HCO_3^- in shallow aquifer than deep aquifer. The chemical data show that the concentration of HCO_3^- (68 to 510 mg/L) and most of the shallow tubewells water samples exceeded the desirable limit of 300 mg/L (Appendix-4, Table 4.3). Bicarbonates may be derived mainly from the neutralization of CO_2, originated either by adsorption from the atmosphere or from the decomposition of organic matter in the recharge area. Reaction of carbonic acid with the carbonate and/or silicate minerals may also release bicarbonates in the solution. So, the elevated concentration of HCO_3^- suggested that the groundwater system is open to soil CO_2, resulting from the decay of organic matter and root respiration, which in turn, combines with rainwater to form bicarbonate (Matthess and Harvey, 1982). Bicarbonate is a major element in human body, which is necessary for digestion. It should not exceed 300 mg/L in the potable water, as it may lead to kidney stones in the presence of higher concentration of Ca, especially in dry climatic regions.

Table 11

Statistical summary of major anions in the groundwater of Rajshahi City and comparison with standards

Parameters, mg/L	Shallow tubewells	Deep tubewells	BD DWS	WHO DWS, 2008
	Mean ± SD	Mean ± SD		
HCO_3^-	245.301 ± 29.592	188.362 ± 22.279	300	100
Cl^-	55.315 ± 9.900	44.901 ± 9.703	150-600	250
NO_3^-	1.598 ± 0.482	1.665 ± 0.513	10	50
SO_4^{2-}	38.756 ± 5.204	36.604±2.915	400	250

The overall average concentration of Cl^- for shallow and deep tubewells water were 55.315 and 44.901 mg/L, respectively (Table 11). This was the second highest ionic

concentrations, after HCO_3^- (Table 11). Cl^- concentration was lower due to the study area might be attributed to mainly natural geochemical activities. Cl^- in water imparts a salty taste and some times higher consumption causes the crucial for the development of essential hypertension, risk for stroke, left ventricular hypertension, osteoporosis, renal stones and asthma in human beings (McCarthy, 2004). Although, the Cl^- plays an important role in balancing level of electrolyte in blood plasma, but higher concentration can produce some physical disorders. All samples of both groundwater water contain Cl^- concentration below the WHO and BD-DWS. So, health risk due to Cl^- was not significant in the area.

The overall mean concentration of SO_4^{2-} for shallow tubewells water was higher than the deep (Table 11). However, the concentrations of SO_4^{2-} for both groundwater samples were lower than HCO_3^- and Cl^-. It may be happened as sulphate does not appear to be directly related to other solute concentrations (Garfias *et al.*, (2010). In general, the presence of SO_4^{2-} concentration in shallow aquifer water may higher than deep aquifer water due to dissolved oxygen concentration is higher in shallow aquifer than deep aquifer. Garfias *et al.*, (2010) suggested that the deep tubewells are probably under anaerobic conditions. The lower SO_4^{2-} content indicated that the study area was not a densely industrial City because high content of SO_4^{2-} contributed due to bio-chemical, anthropogenic sources and industrial process etc. The SO_4^{2-} was one of the most important anions present in groundwater produce catharsis, dehydration and gastrointestinal irritation effect upon human beings when it is present in excess of 150 mg/L (Ramesh and Vennila, 2012). SO_4^{2-} concentration of both tubewells water was bellow the WHO and BD-DWS (Table 11). It is mainly derived from gypsum on oxidation of pyrites.

The mean value of NO_3^- concentration of deep tubewells water samples was found slightly higher compared to the shallow tubewells water and both the groundwater NO_3^- concentration were bellow the standards. In natural conditions, the concentration of NO_3^- does not exceed 10 mg/L in the water (Cushing *et al.*, 1973). Thus the results of the study indicate that the main source of NO_3^- in groundwater aquifer was lithological.

Average value of Na^+ concentration was nearly the same for both the shallow and deep tubewells (Table 12) as expected in general. The primary source of sodium in natural

water is from the release of the soluble products during the weathering of plagioclase feldspars. The Na^+ concentration in drinking water more than 50 mg/L makes the water unsuitable for domestic use because it causes severe health problems like hypertension (Patnaik et al., 2002). Therefore, sodium restricted diet is suggested to the patients, who suffer from the heart diseases and also from the kidney problems. The higher concentration of Na^+ may pose a risk to a persons suffering from cardiac, renal and circulatory diseases (Haritash et al., 2008). Groundwater of the area is safe for drinking with reference to the concentration of Na^+, which is less than 250 mg/L. So, there is no change for the any kind of disease due to the excessive concentration of Na^+ in groundwater in Rajshahi. The study suggests that Na^+ may derived from weathering of halaite, feldspar rocks sources in this area due to low concentration as 250 mg/L.

Overall mean value of Mg^{2+} concentration of shallow and deep tubewells were found nearly same and the ionic concentrations were lower compared to Ca^{2+} due to the fact that the dissolution of magnesium rich minerals is a slow process and that of calcium is more abundant in the earth's crust. All the samples not exceeded the permissible limit of both standards. The Mg^{2+} derived from dissolution of magnesium calcite, gypsum and dolomite from source rocks. Mg^{2+} is an essential ion for functioning of cells in enzyme activation, but at higher concentration, it is considered as laxative agent (Garg et al., 2009), while deficiency may cause structural and functional changes in human beings.

Table 12

Statistical summary of major cations in the groundwater of Rajshahi City and comparison with standards

Parameters, mg/L	Shallow tubewells Mean ± SD	Deep tubewells Mean ± SD	BD DWS	WHO DWS, 2008
Na	23.117 ± 1.957	22.766 ± 2.240	200	200
Mg	27.017 ± 2.130	26.220 ± 1.661	35	30
K	5.660 ± 0.566	5.626 ± 0.521	12	-
Ca	78.354 ± 7.599	78.541 ± 0.378	75	-

Overall mean value of K^+ concentration shallow and deep tubewells water were nearly same for the study area groundwater (Table 12). A research report on the hydrochemistry

and origins of mineralized waters in the Puebla aquifer system in Mexico by Garfias *et al.*, (2010) stated a similar observation. The natural source of K^+ in water usually originates from the chemical weathering and subsequent dissolution of minerals of local igneous rocks such as feldspars (orthoclase and microcline), mica and sedimentary rocks as well as silicate and clay minerals (Howari and Banat, 2002). K^+ in groundwater less than 10 mg/L due to greater resistance of K^+ source (potassium silicate, K-feldsfer) to weathering. The study result indicates that all most all groundwater samples not exceeded the permissible limit of K^+ concentration in the water and it was about one third of Na^+ concentration. The low contribution of K^+ may be due to the greater resistance of K^+ to weathering and its fixation in the formation of clay minerals of the alluvial soils of major-ion chemistry of the Ganga-Brahmaputra by Sarin *et al.*, (1989).

Overall average value of Ca^{2+} concentration of shallow tubewells water was found slightly lower than deep tubewells (Table. 12) and the result was supported by Garfias *et al.*, (2010) may be caused of possible mineralization in deeper aquifer. According to the BD-DWS the permissible limit Ca^{2+} is 75 mg/L in drinking water. But there is no guideline for Ca^{2+} in drinking water (WHO, 2008). However, researchers suggested that a minimum of 20 mg/L (Novikov *et al.*, 1983) and an optimum of about 50 (40-80) mg/L (Rachmanin *et al.*, 1990; Kozisek, 1992) Ca^{2+} present in drinking water may be the most suitable for human consumption. Kozisek (2006) showed that there was a higher risk of gall stones, kidney stones, urinary stones, arthrosis and arthropathies in populations supplied with water of hardness higher than 300 mg/L. The study results show that about 70% of groundwater samples exceeded the maximum permissible BD-DWS limit.

Mn^{2+} concentration was found higher in deep tubewells than the shallow tubewells (Table 13). About 100% samples exceed the permissible limit of Mn^{2+} of BD-DWS and WHO's standard (Appendix-4, Table 4.5 and Appendix-5, Table 5.5). The National Hydro-geochemical Survey conducted by the BGS and DPHE (2001) showed that 39% of shallow tubewells and 2% of deep tubewells exceeded the WHO guideline value. It also found that three quarters of the 3,534 wells surveyed in 61 out of 64 districts exceeded the Bangladesh drinking water standard (0.1 mg/L) for manganese. The study show that most of the shallow and deep tubewells water samples exceeded BD-DWS which confirmed that the Mn minerals present in the Brahmaputra and Ganges floodplains. Mn^{2+} may deposit within pipes and break off as black particles that give

water an unpleasant appearance and taste. High intakes of Mn^{2+} through both inhalational exposures and drinking water have been shown to be toxic (Calne *et al.*, 1994). High intake Mn^{2+} have adverse neurotoxic health effect and WHO recommends guideline value of 0.4 mg/L (WHO, 2008) to protect against neurological damage. It is associated with a characteristic syndrome called Manganism, which involves both psychiatric symptoms and Parkinsonian features (IMFNB, 2002; Dobson *et al.*, 2004; Yamada *et al.*, 1986).

Average concentrations of Fe ion in shallow and deep tubewells were 3.093 and 2.225 mg/L, respectively (Table 13). About 90% samples exceeded the permissible limit for Fe ion in water in the study area of BD-DWS and WHO' standard. A study carried on design parameters for rural water supplies in Bangladesh by Ahmed (1981), and Hossain and Huda (1997) stated that in Rajshahi district people use tubewells water having Fe ion concentration 4.0 mg/L, which is consonance the present research findings. The shallow aquifer Fe ion content was higher than the deep aquifer may be due to the bacteriological degradation of organic matter which leads to the formation of various humic and fluvic compounds. Another study carried out on iron content in groundwater in Bangladesh by Hossain and Huda (1997), and they suggested that Fe ion concentration in groundwater was independent of the depth of aquifer in any location. So, it can be conclude that Fe ion content in groundwater depends on various geological, geo-hydrological and physical factors of the aquifers and rather than depth.

The results show that the shallow tubewells water samples contained high amount of Fe ion, which was 10.31 and 7.41 times higher than WHO's and BD-DWS, respectively, (Table 4.6 in Appendix-4) and the deep tubewells water samples also contained 3.093 and 2.66 times higher than WHO and BD-DWS, respectively (Table 5.6 in Appendix-5). A similar study carried on Tirumala-Tirupati environs in India reported by Raju (2006a) where iron concentration was high as the study area. About 90% of groundwater samples exceeded the permissible limit of the drinking water standard for Fe ion standard (WHO, 2008). According to Singhal and Gupta (1999), Fe ion content in groundwater was mainly due to the dissolution of iron oxides.

The study observe that sampling area may be primarily covered with laterites, leaching of iron under the existing anoxic condition, which may be attributed to the high concentration of Fe ion in groundwater. Hem (1991) illustrated that high Fe ion concentrations in groundwater may be due to presence of iron minerals in the soils and/or weathered materials favorable for reduction of ferric iron into ferrous iron in the circulating groundwater. In this study, discharges of waste effluents on land and weathering of rock and are generally considered the main source of Fe ion in groundwater. High concentration of Fe ion may lead to liver disease called as haermosiderosis (Rajgopal, 1984). Iron contained water makes the teeth and nail black and weak, stickiness of hair, roughness of skin, which are very common in the study area. Soap also didn't response well due presence of iron in water (Hossain and Huda, 1997).

Table 13

Statistical summary of heavy metal ions in the groundwater of Rajshahi City and comparison with standards

Parameters, mg/L	Shallow tubewells Mean ± SD	Deep tubewells Mean ± SD	BD-DWS	WHO DWS, 2008
Mn	1.468 ± 0.781	2.198 ± 0.741	0.1	0.4
Fe	3.093 ± 0.638	2.225 ± 5.722	0.3-1	0.3
Zn	0.188 ± 0.071	0.176 ± 0.083	5	NGL
Cu	0.076 ± 0.058	0.393 ± 0.417	1	2
As	0.017 ± 0.008	0.012 ± 0.004	0.05	0.01
Cd	0.014 ± 0.005	0.016 ± 0.006	-	0.03
Pb	1.167±0.140	1.122±0.126	0.05	0.01

Zn^{2+} concentration of shallow tubewells water was higher than the deep tubewells but in case of Cu^{2+} and Cd^{2+} concentration found opposite trend to Zn^+ (Table 13). Zn^{2+}, Cu^{2+} and Cd^{2+} were found to have low concentrations in three seasons and did not exceed the WHO (2008) and BD-DWS indicating low content in the aquifer soil in the study area. The results show that the highly toxic metal Cd^{2+} was found within the prescribed limits for both the shallow and deep tubewells water samples.

Overall As (total) concentration was higher in the shallow tubewells water than the deep tubewells indicating deeper aquifer water is safer than shallow. The study illustrates that the shallow tubewells contained arsenic concentrations low to moderately high may be due to the oxidation of arsenopyrite in the soil. A number of researches reported that the water of many shallow tubewells in Bangladesh and West Bengal, India have the As (total) concentration exceeded the WHO's permissible limit due to arsenopyrite exposed to air and water as in weathering reactions. Oxidation of pyrite and arsenopyrite may be expressed by equations (1) and (2), respectively (Benony *et al.*, 2008).

$$FeS_2 + 3.5O_2 + H2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

$$FeAsS + 3.5O_2 + 1.5 H_2O = Fe^{2+} + AsO_4^{3-} + SO_4^{2-} + 3H^+ \dots\dots\dots\dots\dots\dots(2)$$
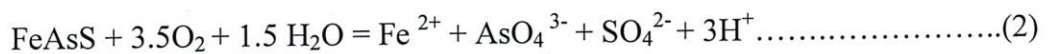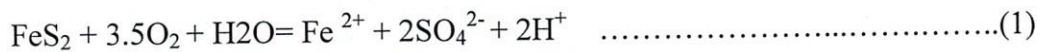
The study results show that the arsenic concentration of most of the shallow tubewells water samples exceeded the WHO's permissible limits of 0.01 mg/L during pre- and post-monsoon seasons (Table 4.7 in Appendix-4). Overall about 40% samples exceeded the permissible limit of arsenic prescribed WHO (2008). But only about 15% samples exceeded the BD-DWS permissible limit (0.05 mg/L). The arsenic concentrations for most of the shallow and deep tubewells water samples were found bellow the permissible limit. Acute exposure of arsenic can cause nausea, vomiting, diarrhea, muscle cramps, salivation, sensory disturbances, liver injury, renal failure and kidney disease and long-term exposure to inorganic arsenic may cause darkening of the skin and the appearance of small warts on the palms, soles and torso. Ingesting arsenic increases the risk of skin cancer and tumors of the bladder, kidney, liver and lung (Smith *et al.*, 1992).

Pb^{2+} in groundwater in the study area was found slightly higher in shallow tubewells than the deep tubewells (Table 13). A similar observation was made by Ravichandan and Jayaprakash (2011) in groundwater in Chenni in India. In general, Pb^{2+} is usually found in low concentration in natural waters because Pb containing minerals are less soluble in water. Concentration of lead in natural water increases mainly through anthropogenic activities. The results show that average Pb^{2+} concentrations was found to be above the maximum permissible limit (0.01 mg/L) of WHO's standard for drinking water quality in the study area (Table 13). The results also show that 100% samples in monsoon and post-monsoon seasons of both tubewells water contained Pb^{2+} concentrations above the maximum permissible limit (0.05 mg/L) of BD-DWS (Table 4.7 in Appendix-4 and

Table 5.4 in Appendix-5). Pb^{2+} is toxic and also considered a probable human carcinogen. The report showed that Pb^{2+} intake via drinking water involved a potential health hazard. Pb^{2+} inhibits several key enzymes involved in the overall process of haemosynthesis, whereby metabolic intermediate accumulates (Verrma, 1995). The study illustrates that lithological and anthropogenic activities such as corrosion of distribution systems, plumbing materials, municipal wastes, lead-acid storage batteries, electroplating, dyes, paints, glassware, roofing and gasoline may be the main cause of abundance of lead ion in both the water samples.

The maximum number of total coliform (TC) and faecal coliform (FC) bacteria were found 16 and 6, respectively at Upashahor (STW-14) for shallow tubewells water samples (Table 4.8 in Appendix-4). The highest number TC and FC bacteria of deep tubewells water samples were found 3 at Rajshahi University Campus (DTW-10) and 1, respectively (Table 5.8 in Appendix-5). The results illustrate that the mean values of total coliform (TC) and faecal coliform (FC) bacteria were found higher in shallow tubewells water than the deep tubewells due to anthropogenic causes and both the bacteria exceeded the prescribed permissible limits (Table 14) indicated not suitable for drinking purpose.

Table 14

Statistical summary of microbial parameters in the groundwater of Rajshahi City in post-monsoon season and comparison with standards

Parameters, CFU/100mL	Shallow tubewells			Deep tubewells			BD -DWS	WHO DWS, 2008
	Minimum	Maximum	Mean ± SD	Minimum	Maximum	Mean ± SD		
TC	0	16	6.20±4.31	0	3	1.20±1.22	0	0
FC	0	6	0.80±1.4	0	1	0.30±0.4		

4.3 Hydro-geochemical facies and water types

In order to understand the hydro-chemical facies and water types of groundwater in the study area, the concentrations of major cations and anions were plotted in the Piper tri-linear diagram using AQUACHEM software Version 5.1 (Figure 4). In the Piper diagram, overall average major cations and anions are plotted in the two base triangles, and the overall information from the two triangles was combined together on a

quadrilateral (Piper, 1944). The ternary anion diagram relating HCO_3^-, SO_4^{2-} and Cl^- shows that most of the groundwater samples contain a high amount of HCO_3^- and plotted points cluster toward the alkalinity apex with secondary trends toward Cl^- and SO_4^{2-}. The cation diagram (Figure 4) show that the majority of groundwater samples contained $Ca^{2+}+Mg^{2+}$ higher than Na^++K^+. The diagram shows that HCO_3^- and Ca^{2+} were the dominant ions in groundwater samples. Therefore, most of the analyzed shallow and deep tubewells water samples fall in the field of Ca^{2+}-HCO_3^- type in the quadrilateral diagram during the pre, post-monsoon and monsoon (Figure 4). Sadashivaiah *et al.*, (2008) illustrated the same water type of shallow tubewells water in Tumkur Taluk, Karnataka State in India.
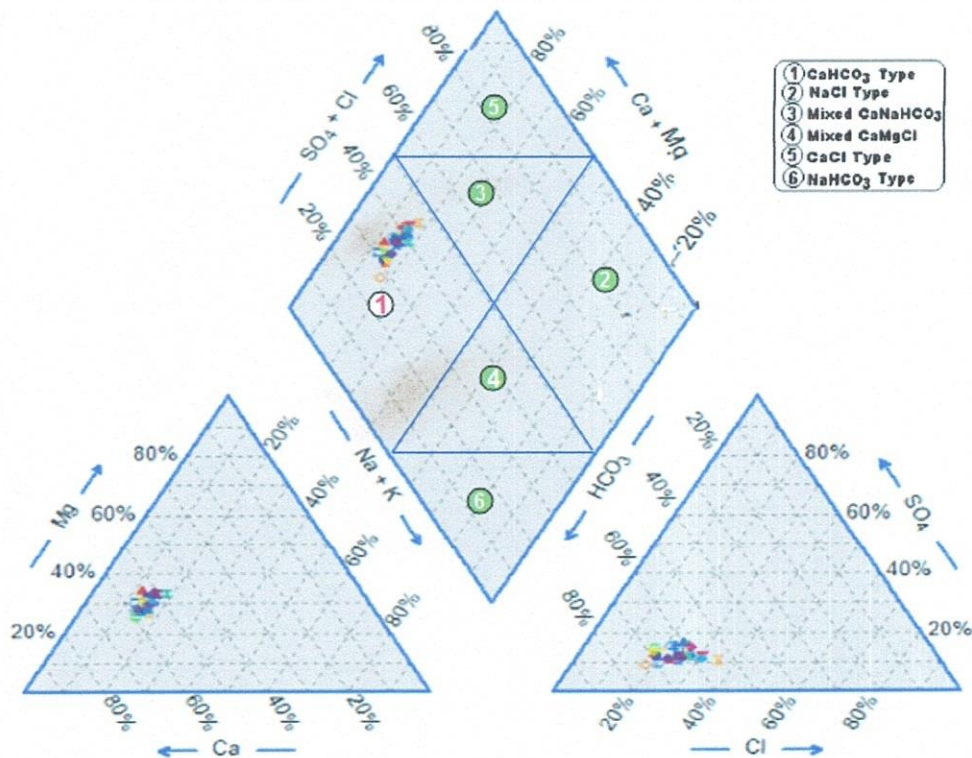
Figure 4. Hydro-chemical facies of groundwater in Rajshahi City in Piper diagram constructed using AQUCHEM software Version 5.1 (water type: Ca^{2+}-HCO_3^-).

Hydro-chemical facies and water types can also be determined by Chadha (1999) diagram. The diagram was a modification of Hill Piper diagram with a view to extend its applicability in representing water analysis in the simplest possible way. In the diagram (Figure 5), the difference in milli-equivalent percentage between alkaline earths (Ca^{2+} + Mg^{2+}) and alkali metals (Na^+ + K^+) was plotted on the X-axis, and the difference in milli-

equivalent percentage between weak acidic anions (CO_3^{2-} + HCO_3^-) and strong acidic anions (Cl^- + SO_4^{2-}) was plotted on the Y-axis. The rectangular field of the plot describe the primary character of the water including the permanent and temporary hardness domain for that the rectangular field was divided into eight sub-fields, each of which represents a water type and hardness domain (Figure 5). Overall distribution of the analyzed mean data on the plot suggest that the majority of shallow tubewells water samples in the study area fall under the subfield of alkaline earths and weak acidic anions that exceed both alkali metals and strong acidic anions (Ca^{2+}-Mg^{2+}-HCO_3^- type); such water exhibited temporary hardness (Figure 5). A few number of shallow tubewells water samples fall under the subfield of alkaline earths exceeding alkali metals and strong acidic anions exceeding weak acidic anions (Ca^{2+}-Mg^{2+}-Cl^- type), such waters have permanent hardness (Figure 5). All water samples of deep tubewells of the study area fall under the subfield of alkaline earths and weak acidic anions that exceed both alkali metals and strong acidic anions (Ca^{2+}-Mg^{2+}-HCO_3^- type) for three seasons (Figure 5). A similar observation was found by Raju (2006b) in the groundwater of the upper Gunjanaeru River basin, Andra Pradesh District in India.
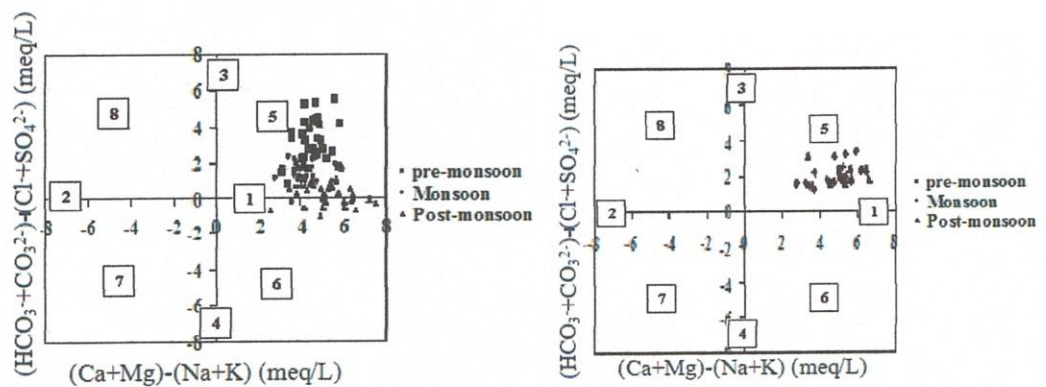
Figure 5. Chadha Diagram showing geochemical classification and hydro-chemical parameters of groundwater of the study.

So, there was a similarity between the Piper (Ca^{2+}-HCO_3^- type) and Chadha (Ca^{2+}-Mg^{2+}-HCO_3^- type) diagram. As the Mg^{2+} concentration in water samples was lower compared to the Ca^{2+} concentration, thus the results suggests that the water type of this area was considered to be Ca^{2+}- HCO_3^-. The obtained water type may be the cause of weathering of silicate and dissolution of carbonate minerals in the aquifer zone of the study area.

4.4 Geo-chemistry of groundwater

4.4.1 Geochemical processes of groundwater

The rock-water interaction generally includes chemical weathering of rock forming minerals, dissolution-precipitation of carbonates, and ion exchange between water and clay minerals. The abundance and distribution of elemental ions such as Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-} and Cl^- in the water are dependent on erosion and chemical weathering of the rocks in the source area. Interaction between groundwater and its surrounding minerals in the alluvium may be the main process for the observed chemical characteristics of groundwater in the study area.

4.4.1.1 Silicate weathering

Silicate weathering can be understood by estimating the ratio between $Na^+ + K^+$ and the total cations (TZ^+). The results show that the majority of the groundwater samples were much above the $Na^+ + K^+ = 0.5TZ^+$ line (Figure 6) indicating the silicate weathering was not involvement in the geochemical processes.
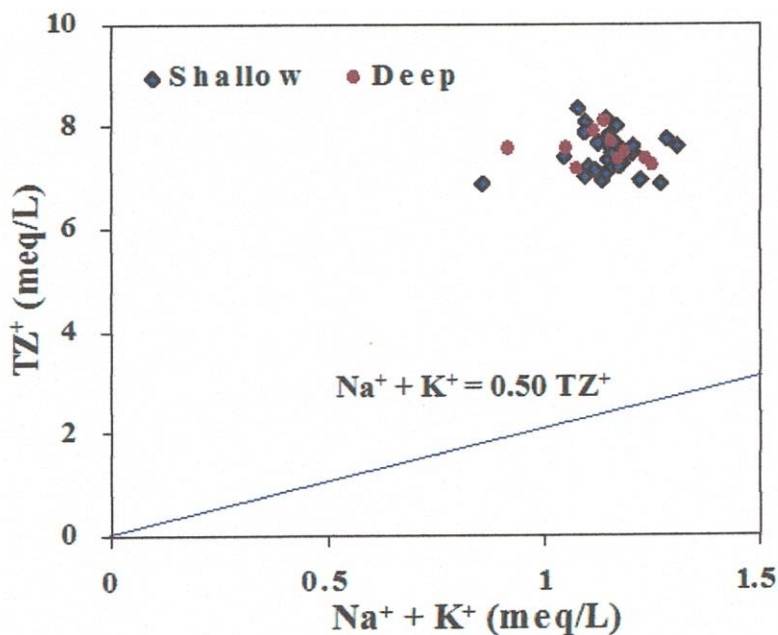
Figure 6. Scatter diagram of ($Na^+ + K^+$) versus total cations (TZ^+).

Stallard and Edmond (1983) reported that the plotted samples were near the $Na^+ + K^+ = 0.5TZ^+$ line indicated the involvement of silicate weathering in the geochemical

processes of the Amazan, which contributed mainly Na^+ and K^+ to the groundwater. Weathering of soda feldspar and potash feldspars may contribute Na^+ and K^+ ions to the groundwater. In Rajshahi City groundwater samples of K^+ was not as abundant as that of Na^+ and it may due to the potassium minerals were less susceptible for weathering than sodium minerals. A similar observation was made by Sharma *et al.,* (1998) where the Na^+ in groundwater was higher than the K^+ of Muktsar in India.

Further, $(Ca^{2+} + Mg^{2+})$ versus total cations (TZ^+) plot of groundwater samples have a linear spread between 1: 0.5 $(Ca^{2+} + Mg^{2+} = 0.5TZ^+)$ line and most of the sample fall above the 1:1 equiline indicate that $(Ca^{2+} + Mg^{2+})$ was not resulted from the weathering of silicate minerals (Figure 7). Magdy *et al.,* (2012) stated that the relation of $Ca^{2+} + Mg^{2+}$ versus total cations (TZ^+) plot of groundwater samples were fallen along 1:1 equiline indicated that ions $(Ca^{2+} + Mg^{2+})$ was resulted from the weathering of silicate minerals. So, silicate weathering was not involved in the study area may be due to most of the silicate comprise rocks did not react readily with the groundwater.
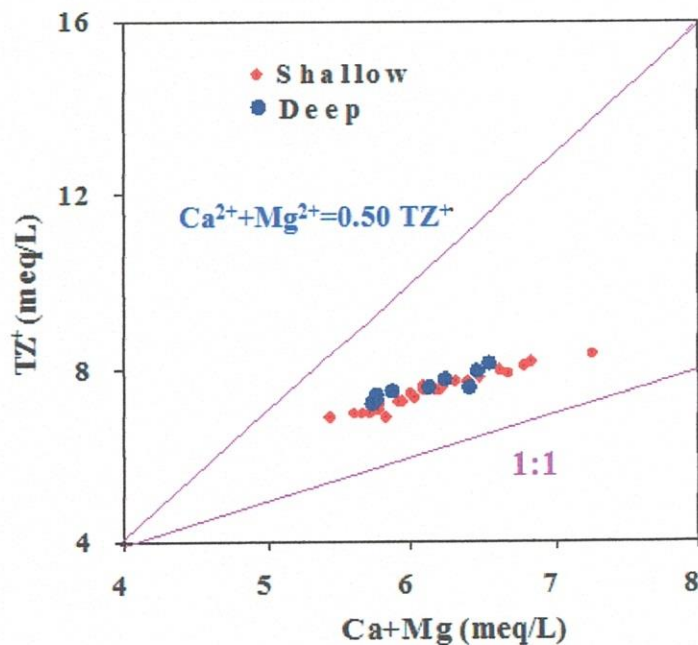
Figure 7. Scatter diagram of $(Ca^{2+} + Mg^{2+})$ versus total cations (TZ^+).

4.4.1.2 Carbonate weathering

Carbonate may the main source from the crystalline limestone, dolomitic limestone and calcareous nodules (the lime rich weathered mantle overlies carbonate rocks) in the

sedimentary rock formed area. Ca^{2+} was the dominant cations to the total cations in the pre, post-monsoon and monsoon. While among anions HCO_3^- was the most dominant to the total anions in three seasons. The carbonates from these sources may dissolve and added to the groundwater system with recharging water during rainfall, leaching and mixing processes.

The study results show that most of the groundwater samples found below the ratio line 2 and above 1.5. Maya and Loucks (1995) suggested that the dolomite dominance of the dissolution that present in alluvium, when the molar ratio of Ca^{2+}/Mg^{2+} is equal to 1, the calcite that present in the alluvium, where the ratio of Ca^{2+}/Mg^{2+} is greater than 1, and the silicate weathering present when the Ca^{2+}/Mg^{2+} molar ratio become higher than 2. According the above classification, the results illustrate that the calcite weathering was suggested in the study area (Figure 8). However, only a few samples that lied above the ratio line 2 indicate the effect of silicate minerals but extent was very less. By and large the chemical composition of the groundwater resulted from the calcite weathering in the study area.
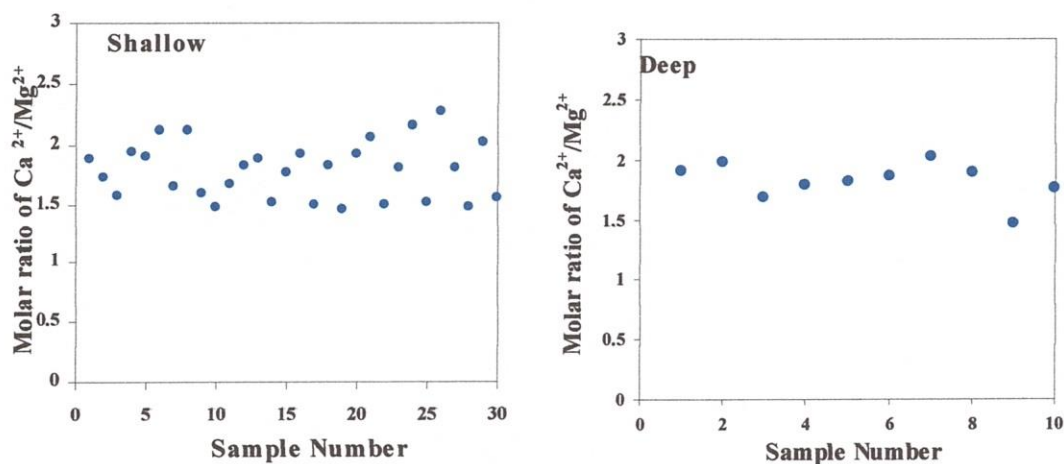
Figure 8. Scatter diagram of Ca^{2+}/Mg^{2+} molar ratio of shallow and deep tubewells water samples in the study area.

In the Ca^{2+} versus HCO_3^- scatter diagram showed that both the shallow and deep tubewells water samples fall below the 1:2 line and there was no samples fall along and above the 1:4 line (Figure 9). Garrels and Mackenzie (1971) reported that if calcite weathering geochemical process, then the samples falls below the 1:2 Ca^{2+} versus HCO_3^- line and for the dolomite weathering it would be 1:4. A report made by Jalali (2007b)

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that the average molar ratio of Ca^{2+}/HCO_3^- measured in the Famenin groundwater in western Iran of (0.43) was close to the suggested value of 0.50 and indicated that calcite was the main source of Ca^{2+}.
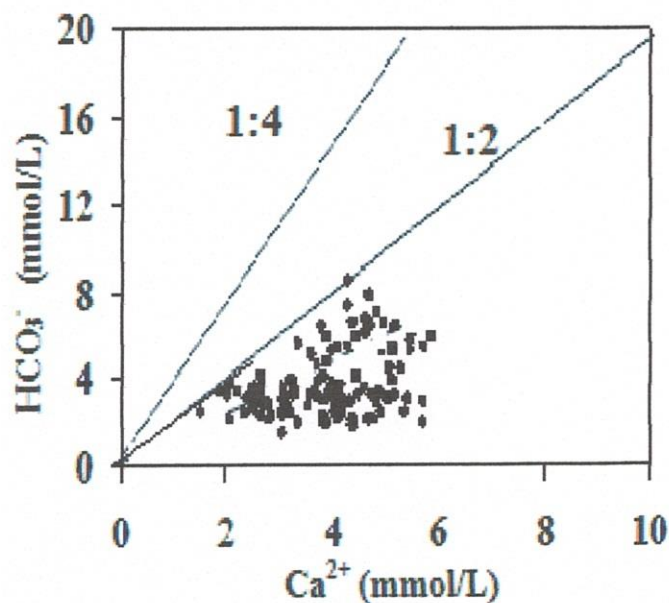
Figure 9. Scatter diagram of Ca^{2+} versus HCO_3^-.

The sources of Ca^{2+} and Mg^{2+} in groundwater also can be deduced from the (Mg^{2+} + Ca^{2+}) versus HCO_3^- relationship (Figure 10). As this ratio also does not increase with salinity (Figure 10 and 11). Mg^{2+} and Ca^{2+} are added to solution at a lesser rate than HCO_3^- ratio which was evident from the all groundwater samples of the study area which fall under the line 1:1. The results show that the ratio of m(Ca^{2+} + Mg^{2+})/mHCO_3^- was around 0.5 (Figure 10), which indicate that Ca^{2+} and Mg^{2+} originate solely from the dissolution of calcite in the aquifer. A similar report was made by Sami (1992) where the ratio was 0.5 of the groundwater in Eastern Cape in South Africa. Another similar result was found by Sharma *et al.*, (1998) of groundwater quality assessment in Muktsar in India, where the abundance of Ca^{2+} + Mg^{2+} was the dominant cations species.
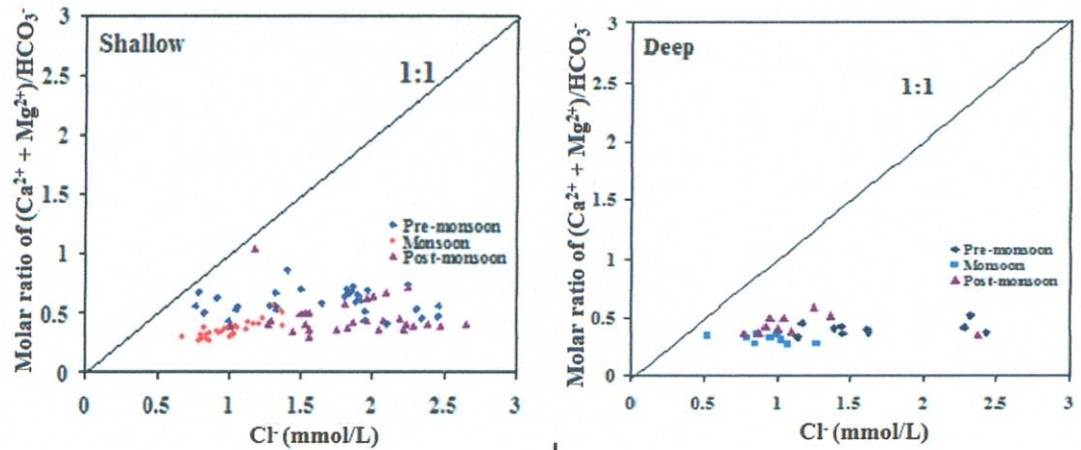
Figure 10. Scatter diagram of $m(Ca^{2+} + Mg^{2+})/mHCO_3^-$ versus Cl^- of shallow and deep tubewells water samples of the study area.

From the earlier discussion it is evident that the calcite weathering was the major geochemical process and it may enhance by the carbonic acid and/or sulfuric acid.

The possibility of calcite weathering by sulfuric acid can be identified by Ca^{2+} and SO_4^{2-} ratio. In the Ca^{2+} versus SO_4^{2-} scatter diagram showed that both the shallow and deep tubewells water samples fall below the 1:2 line, and there was no samples fall above the 1:1 equiline ($Ca^{2+} = SO_4^{2-}$) (Figure 11). Das and Kaur (2001) reported that if sulfuric acid was the weathering agent, then the $Ca^{2+}:SO_4^{2-}$ ratio would be almost 1:1. According to the above statement and the Figure 11 illustrate that sulfuric acid was not the weathering agent of calcite.
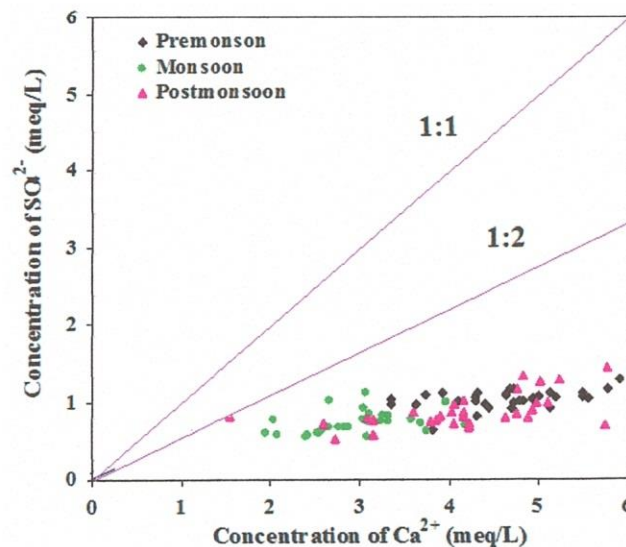
Figure 11. Scatter diagram of Ca^{2+} versus SO_4^{2-} of the groundwater samples of the study area.

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The overall mean C-ratio ($HCO_3^-/HCO_3^- + SO_4^{2-}$) of shallow tubewells and deep tubewells water were 0.86 and 0.84, respectively (Table 15). Brown *et al.*, (1996) proposed estimating the C-ratio ($HCO_3^-/HCO_3^- + SO_4^{2-}$) to characterize the relative importance of two major proton producing reactions carbonation and oxidation of sulphides. The C-ratio 1.0 indicates carbonation reactions involving pure dissolution and acid hydrolysis, consuming protons from atmospheric CO_2. Conversely a C-ratio of 0.5 suggests coupled reactions involving the weathering of carbonates by protons derived from sulphide oxidation. Since the overall average C-ratio of groundwater was 0.85 in the area suggests coupled reactions, involving mainly pure dissolution and may protons derived sulfuric acid. But protons derived were not exclusively from the oxidation of sulphides. A similar result was found by Raju *et al.*, (2011) in the groundwater of Varanasi, Uttar Pradesh in India where the C-ratio was 0.87.

Table 15

The overall mean C-ratio ($HCO_3^-/HCO_3^- + SO_4^{2-}$) of groundwater in Rajshahi City

Parameters	Shallow tubewells	Deep tubewells	Average
HCO_3^-, ppm	245.30	188.37	216.84
SO_4^{2-}, ppm	38.76	36.60	37.68
$HCO_3^-/(HCO_3^- + SO_4^{2-})$	0.86	0.84	0.85

The HCO_3^- may come from the dissolution of carbonate minerals, root soil CO_2 or from the bacterial degradation of organic contamination. The dissolution of carbonate is an equilibrium process, which is controlled by CO_2 partial pressure. The statistical parameters of the computed P_{CO_2} values for the water samples are shown in Table 16.

Table 16

Partial pressure of CO_2 determine by the AQUACHEM software Version 5.1

P_{CO_2}, atm	Shallow tubewells			Deep tubewells			Atmospheric CO_2
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	
	0.0112	0.0518	0.0866	0.0041	0.0459	0.0130	0.0003

The computed result illustrate that P_{CO_2} was found higher than that of the atmospheric 0.0003 (atm) for both the shallow and deep tubewells water samples in three seasons. The elevated P_{CO_2} values indicate that the groundwater system was open to soil CO_2 enhancing the possibility of calcite dissolutions. This suggests that the groundwater was supersaturated with respect to carbonate minerals. The main mechanism for the dissolution of calcite may be as follows:

$$CaCO_3 + CO_2 \text{ (g)} + H_2O = Ca^{2+} + 2HCO_3^- \dots\dots\dots\dots\dots\dots\dots (3)$$

This reaction includes the following step:

$$CO_2 \text{ (g)} + H_2O = H^+ + HCO_3^- \dots\dots\dots\dots\dots\dots\dots\dots (4)$$

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \dots\dots\dots\dots\dots\dots\dots\dots (5)$$

A certain amount of CO_2 may be the result of the hydration of urea that reached the unsaturated zone:

$$CO(NH_2)_2 + H_2O = NH_4^+ + 2OH^- + CO_2 \dots\dots\dots\dots\dots\dots (6)$$

High concentration of Ca^{2+} and HCO_3^- attributed to weathering of calcite and it was enhanced by the carbonic acid and the possible source of calcite may be calcareous nodules because the study area was formed by sedimentary rock and it was composed of calcareous nodules (the lime rich weathered mantle overlies carbonate rocks). Zaheeruddin and Khurshid (2004) stated that the Gangetic alluvial deposited area was the main source of calcareous nodules in the clay and fine sands.

4.4.2 Identification of hydro-geochemical process

The hydro-geochemical data subjected to various conventional graphical plots in order to identify the hydro-geochemical processes and mechanisms in the aquifer of the study area. All the possible identified processes are explained below in details.

4.4.2.1 Ion exchange and cation exchange

Ion exchange is one of the important processes that responsible for the concentration of ions in groundwater during its travel through underground. Control on the dissolution of undesirable constituents in waters is impossible during the subsurface run off but it is essential to know the various changes undergone by waters during the

travel (Johnson, 1979). It can be understood by studying the Chloro Alkaline Indices. Chloro Alkaline Indices were categorized into two indices such as CAI 1 and CAI 2, and the value of CAI 1 and CAI 2 were calculated using by the equation 7 and 8.

$$CAI\ 1 = Cl^- - (Na^+ + K^+)/Cl^- \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(7)}$$

$$CAI\ 2 = Cl^- - (Na^+ + K^+)/(SO_4^{2-} + HCO_3^- + Cl^- + CO_3^{2-}) \dots\dots\dots \text{(8)}$$

(All values are expressed in meq/L).

Schoeller (1965) stated that the important of CAI values in determine the ion exchange mechanism. When there was an exchange between Na^+ or K^+ with Mg^{2+} or Ca^{2+} in the groundwater, both the above indices will be positive and if there was reverse ion exchange prevalent then both these indices will be negative. Figure 12 shows that the shallow groundwater samples of study area exhibited both exchange reaction processes on the seasonal basis. The reverse ion-exchange reaction process was dominant in the pre-monsoon season, while ion-exchange reaction process was dominant in the post-monsoon and monsoon for the shallow tubewells water samples (Figure 12).
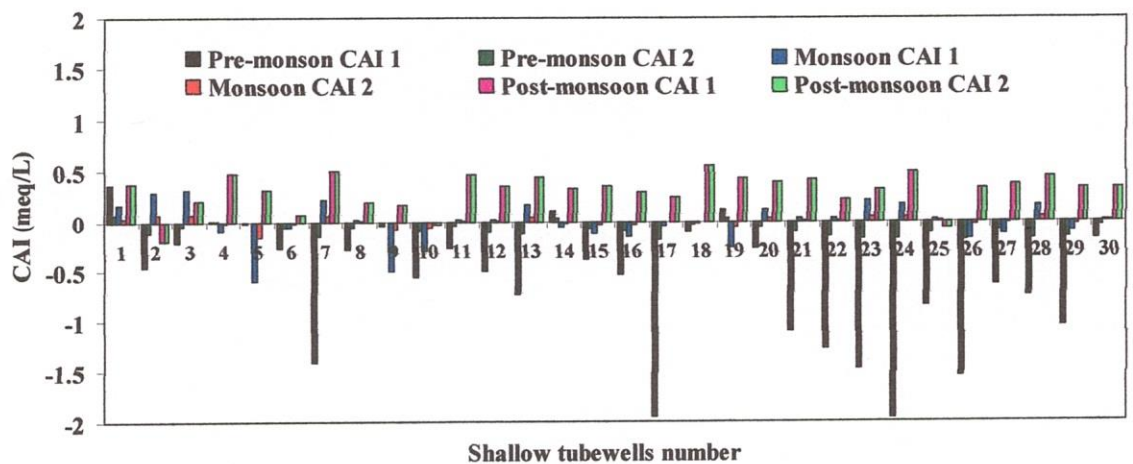
Figure 12. Bar diagram of Chloro Alkaline Indices (CAI) 1 and (CAI) 2 for pre, post-monsoon and monsoon season for the shallow tubewells water samples.

Similarly, it can be illustrate that the ion-exchange reaction process was dominant in pre-monsoon while reverse ion-exchange reaction process was dominant in post-monsoon and monsoon with the exceptions of few samples for the deep tubewells (Figure 13).
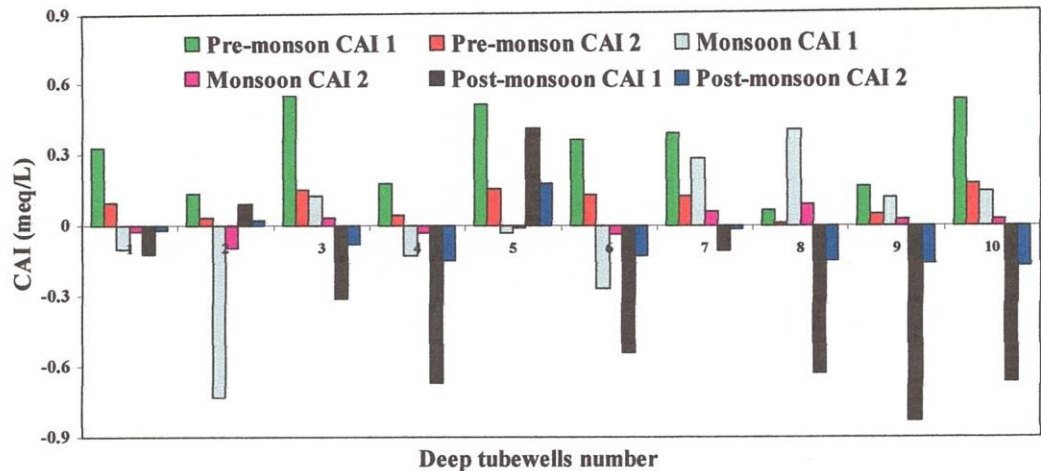
Figure 13. Bar diagram of Chloro Alkaline Indices (CAI) 1 and (CAI) 2 for pre, post-monsoon and monsoon season for the deep tubewells water samples.

Overall results indicate that reverse ion exchange process was dominant. Although, ion exchange process was observed but the extent was less. It could be ensured from the relation between $(SO_4^{2-} + HCO_3^-)$ and $(Ca^{2+} + Mg^{2+})$.

The relation between $(SO_4^{2-} + HCO_3^-)$ and $(Ca^{2+} + Mg^{2+})$ show that most of the shallow and deep tubewells water samples found above the ratio line 1:1. Cerling *et al.*, (1989), and Fisher and Mulican (1997) suggested that the reverse ion exchange would be to be dominant, when the samples fall above the equline (1:1) in the figure $(SO_4^{2-} + HCO_3^-)$ versus $(Ca^{2+} + Mg^{2+})$, and the ion exchange would be dominant, when the samples fall below the equline. According to the above statement, the results illustrate that the most of the shallow and deep tubewells water samples belong to reverse ion exchange process (Figure 14).
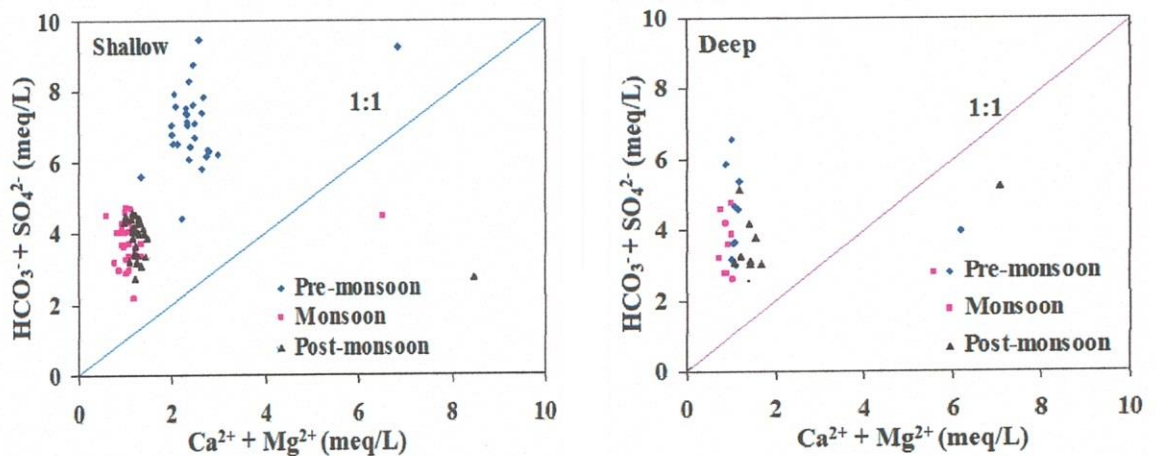
Figure 14. Scatter plot $SO_4^{2-} + HCO_3^-$ versus $Ca^{2+} + Mg^{2+}$.

The plot of $(Ca^{2+} + Mg^{2+})$ versus (Cl^-) (Figure 15) illustrates that the total concentration of Ca^{2+} and Mg^{2+} did not increase with increasing salinity which could be the indication of reverse ion exchange in the clay/weathered layer except few samples of groundwater in the post-monsoon. This observation is in consonance with the results of Figure 14.
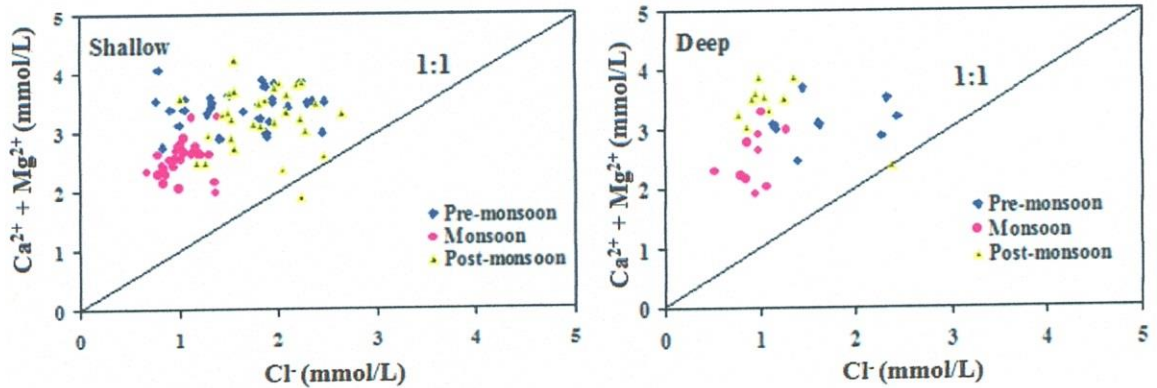
Figure 15. Relation between $(Ca^{2+} + Mg^{2+})$ and Cl^-.

4.4.3 Saturation Indices (SI)

The saturation indices (SI) are indicators of the saturation state of a mineral with respect to a given water composition. The saturation index is defined as: SI = log10 (IAP/Ksp), IAP is the ion-activity product, and Ksp is the solubility product constant for the mineral. If SI < 0; the mineral is under-saturated with respect to the solution and the mineral can dissolve. If SI > 0, the mineral is over-saturated and it can precipitate, but not dissolve, and if SI is close to zero (0), the mineral may be not reacting at all or may be reacting reversibly.

Table 17

Overall mean Saturation Indices (SI) for calcite of the analyzed shallow and deep tubewells water samples using AQUACHEM software Version 5.1

SI	Shallow tubewells			Deep tubewells		
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon
Calcite	0.635	-1.518	0.074	0.641	-1.435	0.010

Table 17 shows the results of Saturation Indices (SI) of the calcite reactive mineral in the study area. It was noticeable that the groundwater (shallow and deep tubewells) was

significantly under-saturated with respect to calcite in monsoon season. However, the groundwater samples were slightly oversaturated with calcite in the post-monsoon season and oversaturated during the pre-monsoon season (Table 17). A report illustrated by Jalali (2007b) that the higher HCO_3^- and Ca^{2+} concentrations would cause a greater calcite over-saturation, which could eventually induce their precipitation. Hence, the study results suggest that the calcite dissolution was the controlling process, which increased Ca^{2+} and/ or HCO_3^- in the shallow and deep tubewells water in the area.

4.4.4 Principal component analysis

The overall chemical parameters of shallow and deep tubewells water samples in Rajshahi City were correlated by the principal component analysis (PCA). The number of significant principal components was selected on the basis of the Kaiser criterion. To get a better insight into the latent structure of the data, the principal component extracted correlation matrix was subjected to varimax orthogonal rotation i. e. factor analysis. Factor analysis is used to reduce the complex data to an easily interpretable form (Davis, 2002). In this work, R-mode factor analysis was chosen which provides several positive features that allow interpretation of the data set more scientifically. In order to evaluate the variables belonging to a specific chemical process and also to find out the dominance and contribution of the major elements in terms of the total data set, Factor loadings and eigenvalues were examined (Table 18). The components eigenvalues higher than one is the most significant (Miller and Miller, 2000). According to this criterion, the first three principal components were considered due to eigenvalues higher than one. Hence, reduced dimensionality of the descriptor space is three. The first three factors which accounts for about 44.865% and 67.510% of variance for the shallow and deep tubewells, respectively with eigenvalues >1 have been extracted from the principal factor matrix after varimax rotation using SPSS 15 software (Table 18).

Table 18

Principal component loadings and explained variance for the three components with varimax normalized rotation in Rajshahi City

Parameters	Shallow tubewells			Deep tubewells		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Na	0.077	**0.766**	-0.134	0.161	0.181	**0.806**
Mg	0.023	-0.085	**-0.679**	-0.129	**0.884**	0.113
K	-0.251	**-0.634**	0.121	0.008	0.065	-0.027
Ca	**0.880**	-0.052	-0.043	-0.075	0.337	**-0.797**
Mn	-0.414	0.093	0.134	**0.513**	-0.256	-0.047
Fe	0.020	**0.569**	0.059	-0.090	-0.141	**0.713**
Cu	-0.152	-0.145	**0.780**	**0.939**	-0.180	0.041
Zn	-0.058	0.185	0.472	-0.398	**0.770**	-0.263
As	0.062	**-0.549**	0.196	0.410	**0.878**	0.043
Cd	**0.606**	0.148	0.102	-0.394	**0.847**	-0.006
Pb	0.057	-0.133	0.364	**-0.686**	-0.007	0.440
HCO_3^-	**0.826**	-0.090	-0.262	0.061	**0.707**	**-0.615**
Cl^-	-0.175	0.496	0.077	**0.828**	0.154	-0.038
NO_3^-	-0.086	-0.289	**0.668**	-0.726	-0.012	-0.477
SO_4^{2-}	**0.537**	0.367	0.236	**0.544**	-0.006	0.351
Eigenvalues	2.424	2.200	2.105	3.665	3.665	2.806
% variance explained	16.163	14.667	14.035	24.236	24.368	18.707
% cumulative variance	16.163	30.830	44.865	24.236	48.803	67.510

Shallow tubewells water

Factor 1 has the highest positive loadings of Ca^{2+}, Cd^{2+}, HCO_3^-, SO_4^{2-} and low factor loadings for the remaining parameters (Table 18). Factor 1, which has strong positive loadings on Ca^{2+} and HCO_3^-, explains 16.163% of the total variance. Factor 1 is possibly the result of the water-rock interaction, interpreted as relating to the weathering of calcite. The natural recharge process would have induced bicarbonate to the groundwater was rich in CO_2. The dissolution of the CO_2 in the adjacent aquifers due to precipitation would have increased the concentration of Ca^{2+} and HCO_3^- in the water bodies. So, Factor 1 may represent a lithological factor. Factor 2 has the highest (positive) factor loadings of Na^+, Fe ion, and the highest (negative) loading of K^+ and As(total) ion can be considered as geogenic (lithological) factor (Table 18). Factor 3 has the highest

(positive) loadings of Cu^{2+}, NO_3^- and highest (negative) value Mg^{2+} (Table 18 andit also could be defined as geogenic (lithological) factor. So, three principal factors could be considered to be a lithogenic component, as the variability of the elements seems to be controlled by the rocks.

Deep tubewells water

Factor 1 has the highest factor loadings (positive) of Mn^{2+}, Cu^{2+}, Cl^-, SO_4^{2-}, and the highest (negative) Pb^{2+}, and low factor loading for the remaining parameters (Table 18). This association suggests that Factor 1 may represent a lithogenic along with anthropogenic factor. Factor 2 has the highest (positive) factor loadings of Mg^{2+}, HCO_3^-, Zn^{2+}, As (total) and Cd^{2+} and low factor loadings for the remaining parameters can be considered as geogenic factor (Table 18). Factor 3 has the highest (positive) factor loadings of Na^+ and Fe ion, and highest (negative) Ca^{2+} and HCO_3^- factor loadings (Table 18). Factor 3 also may considered the result of the water-rock interaction, interpreted as relating to the weathering of calcite, and Na and Fe ions related minerals and this factor considered as geogenic factor. Thus, Factor 1 can be defined as a mixture of geogenic and anthropogenic component due to the presence of high Pb^{2+} levels in groundwater. Factor 2 and Factor 3 can be considered to be a lithogenic component, as the variability of the elements seems to be controlled by the rocks.

From the above observation of the extracted three factors (Factor 1, 2 and 3), the groundwater in the study area was mainly controlled by the rock/minerals dissolution. A similar report was made by Chan (2001) and Laurent *et al.*, (2010) where the main contributors for changing the geochemical composition of the groundwater was the weathering processes.

4.4.5 Mechanism of controlling groundwater chemistry

The weathering of minerals is of prime importance in controlling groundwater chemistry. Various processes are involving in the controlling groundwater chemistry includes rock-water interaction, salinization, evaporation, rainfall and precipitation. Gibbs diagrams (Gibbs, 1970) are widely employed to assess the functional sources of dissolved chemical constituents. The diagram is divided into zones based on the contribution of recharging precipitation, rock weathering and evaporation on the hydrochemistry. Gibb's

ratios for both cations and anions were calculated in order to conclusively determine the main controls on the geochemistry using the following equation 9 and 10, respectively.

$$\text{Gibbs Ratio I} = Cl^- / (Cl^- + HCO_3^-) \dots\dots\dots\dots\dots\dots\dots\dots\dots(9)$$

$$\text{Gibbs Ratio II} = (Na^+)/(Na^+ + Ca^{2+}) \dots\dots\dots\dots\dots\dots\dots (10)$$

Where, the concentrations of the ions are in meq/L.
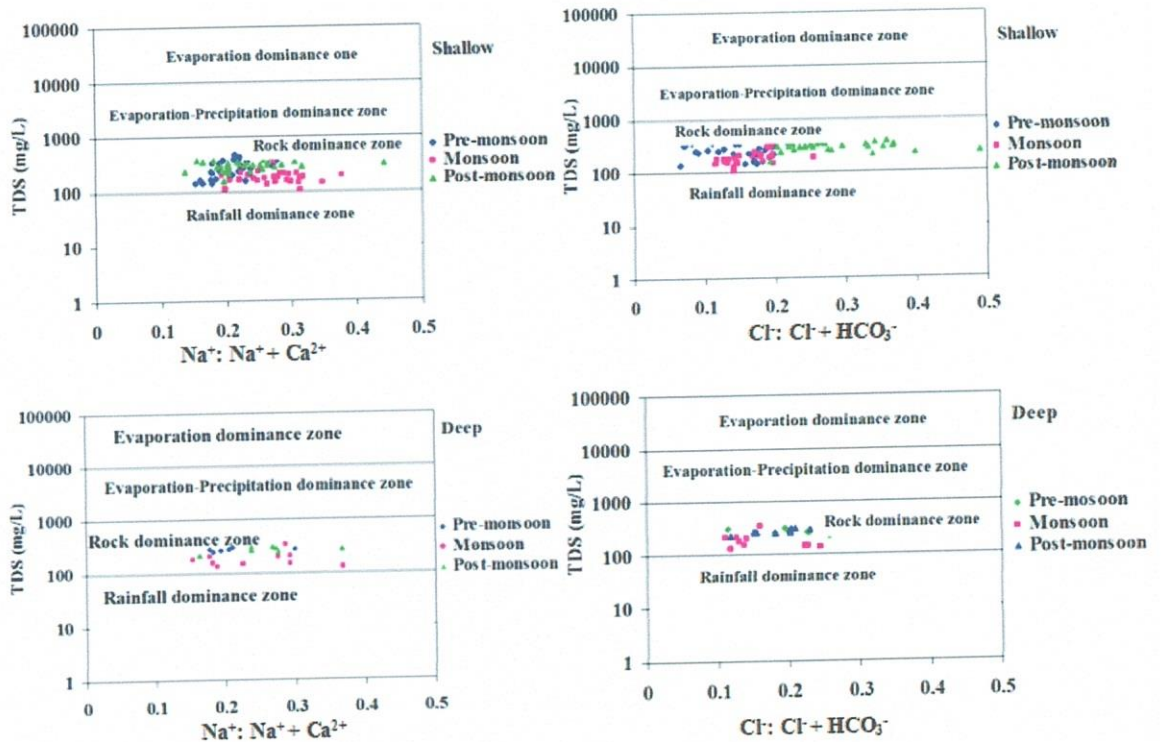
Figure 16. Gibbs diagram showing the positions of controlling mechanisms of groundwater chemistry in the study area.

The Gibbs ratios were plotted against TDS, on the semi log axes as shown in Figure 16. The distribution of sample points in Gibb's diagram show that the ratio of cations, $Na^+/(Na^+ + Ca^{2+})$ and anions, $Cl^-/(Cl^- + HCO_3^-)$ were fallen in the rock domain zone for shallow and deep tubewells water samples (Figure 16). The results suggest that rock weathering was the main causative factor in the evolution of chemical composition of groundwater in the study area.

Stiff diagrams (Stiff, 1951) were generated for the arithmetic averages of the measures of the physico-chemical parameters used in this study. The study result showed that the shallow aquifer soil samples anions and cations were much higher than the shallow tubewells water samples (Figure 17), which indicates that variuous elemelntal

concentrations came from the soil disolution in the study area. This is in consonance with the results of Figure 16 and Table 18. So, rock-water interaction appeared to be the main cause of influencing the geochemistry of groundwater in the study area.

Shallow tubewells

Deep tubewells
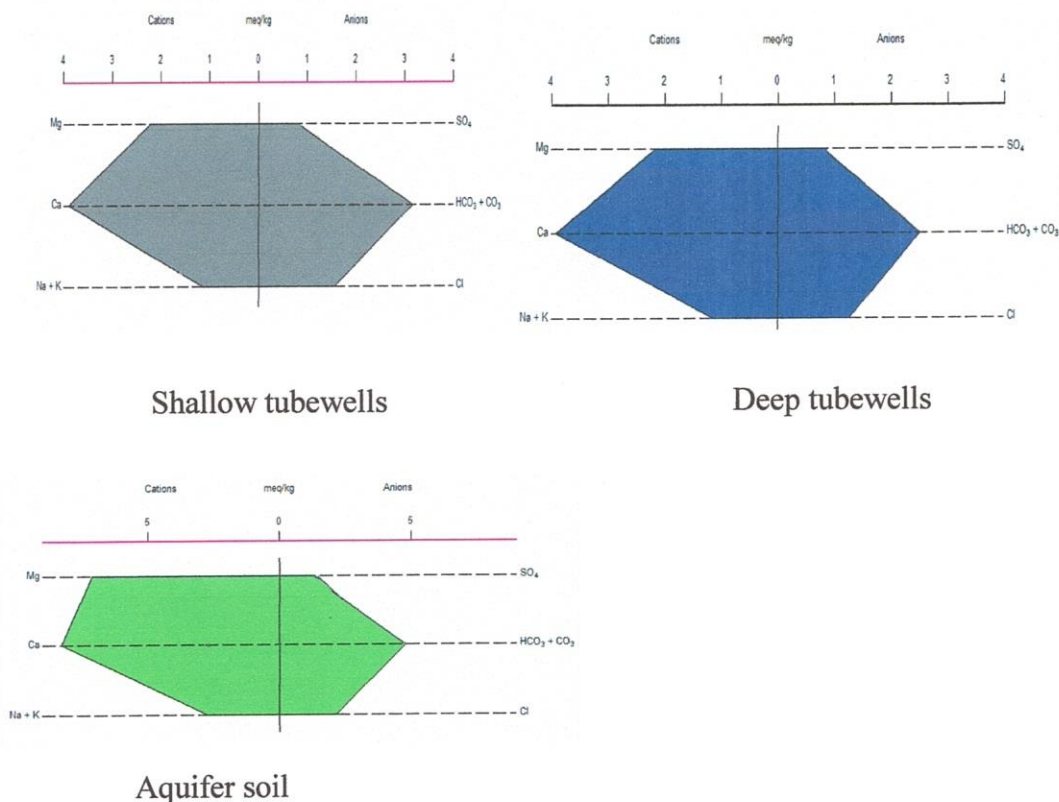
Aquifer soil

Figure 17. Stiff diagrams from the statistical summaries of the major ions of shallow aquifer soil, shallow tubewells and deep tubewells water samples.

4.5 Groundwater Quality

The quality of groundwater is important because it determines the suitability of water for drinking, domestic, agricultural and industrial purposes (Tatawat and Chandel, 2008). The high concentration of heavy metals in the groundwater has serious environmental significance. The concentrations of some heavy metals i.e. Mn^{2+}, Fe, As(total) and Pb^{2+} present in most of the water samples exceeded the permissible levels recommended for drinking by the BD-DWS and WHO (2008) standards. Mn, Fe and Pb ions were found the principal contaminant in almost all of the analyzed samples. The study observes that these ions presence in water samples may be due to rock, air and water interaction and in addition to anthropogenic activities. The analysis results suggest that the higher

concentration of TH, HCO_3, Ca, Mn, Fe, Pb ions in water were the cause of weathering of aquifer materials. TC and FC were presence in higher concentration in the shallow tubewells water than the deep tubewells. So, groundwater in Rajshahi City area shows a wide range of characteristics in terms of physical, chemical and microbial parameters during three seasons. The groundwater shows a higher amount of heavy metals may be due to rock dissolution associated with natural drains, sewage canals and industrial units. The study observes that the quality of groundwater was not suitable for drinking purpose in the study area. Hence, adequate treatment is required to remove excessive contaminant metal ions especially for Ca, Mn, Fe, As(total) and Pb ions in the study area water to meet the requirements of safe drinking water.

4.6 Treatment

Safe water is vital for improving the health and quality of life of people and eventually alleviates poverty. The provision of safe water for public consumption starts with knowledge of the quantity and quality of the source water followed by designing and development of appropriate technology to deal with the contaminants. Presently about 97% of the total drinking water production in Rajshahi City is from groundwater source (R WASA, 2013). A perusal of the general groundwater quality data of Rajshahi City indicates that the quality of groundwater is deteriorating in the study area. This situation the study focused on collecting shallow and deep tubewells water samples, analyze and gather information on the levels of various physico-chemical and microbial parameters of groundwater in Rajshahi City. The overall observation of the study that excessive concentration of Ca, Mn, Fe, As(total) and Pb is imperative to remove of these ions due to these metal ion can posses potential human health hazards and/ or aesthetic problems. The study investigated the removal of Ca, Mn, Fe, As(total) and Pb ions from the groundwater using batch and column adsorbent experiments. A series of batch and column adsorption experiments were conducted using sand and sand-stone enriched with varying ionic strength of spiked water (Details methodology of the adsorption process is stated in the previous chapter).

4.6.1 Batch adsorption experiments

Removal of manganese

Figure 18 shows the adsorption of Mn^{2+} on the adsorbent surfaces for the initial concentration containing 3.0 mg/L Mn^{2+} spiked groundwater. The graph line for the sand adsorbent shows that the removal percentage of manganese increased very rapidly during the first 120 min and then decreased rapidly with time. The similar observation was made for both 1 g and 2 g magnetite (Fe_3O_4) enriched sand adsorbents. The maximum Mn^{2+} removal percentage achieved to be about 92, 67 and 44 % for sand, 1 g and 2 g Fe_3O_4 enriched sand adsorbent, respectively from the initial concentration containing 3.0 mg/L Mn^{2+} spiked groundwater (Figure 18). The results suggest that sand adsorbent showed the best Mn^{2+} removal performance among the Fe_3O_4 enriched sand adsorbents. A report made by Tasneem and Ali (2010) where Mn^{2+} removal was most effective sand adsorbent than iron-coated sand absorbent.
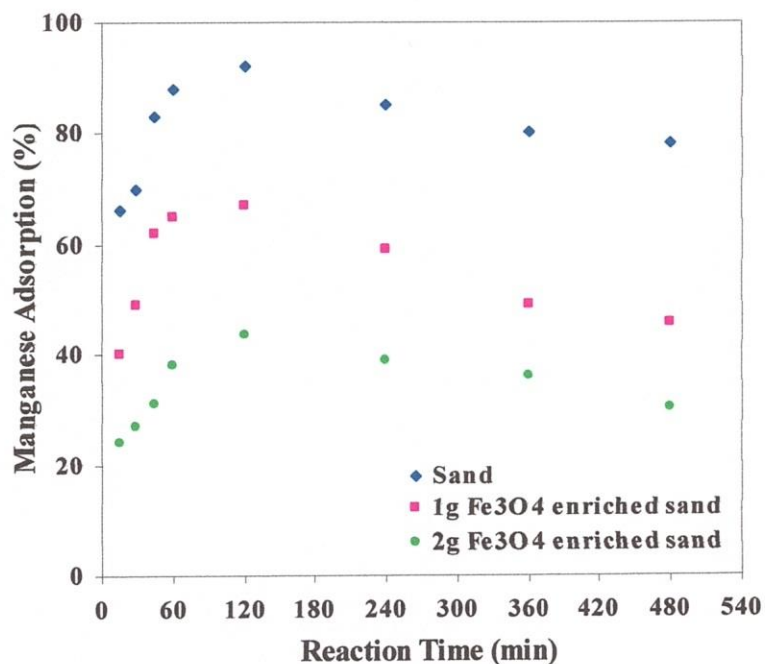
Figure 18. Adsorption of Mn^{2+} as a function of time for the 3.0 mg/L initial Mn^{2+} concentration spiked groundwater.

Removal of arsenic

The adsorption of As(total) on the adsorbent surfaces for the 0.50 mg/L initial As(total) concentration is shown in Figure 19. The graph line for 2 g Fe_3O_4 enriched sand adsorbent shows that the removal percentage of As(total) increased very rapidly during the first 120 min and then increased slowly and it continued for 360 min and finally decreased with time. The graph line for 1 g Fe_3O_4 enriched sand adsorbent shows that the removal percentage of As(total) increased very rapidly during the first 120 min and then increased slowly for 240 min and then decreased with time. Similar observation was made for only sand adsorbent. The maximum removal percentage obtained about 97, 94 and 56% for the 2 g, 1 g Fe_3O_4 enriched sand and sand adsorbent, respectively from the initial concentration containing 0.50 mg/L As(total) spiked groundwater. The results suggest that 2 g Fe_3O_4 enriched sand adsorbent show the best removal performance among the adsorbents.
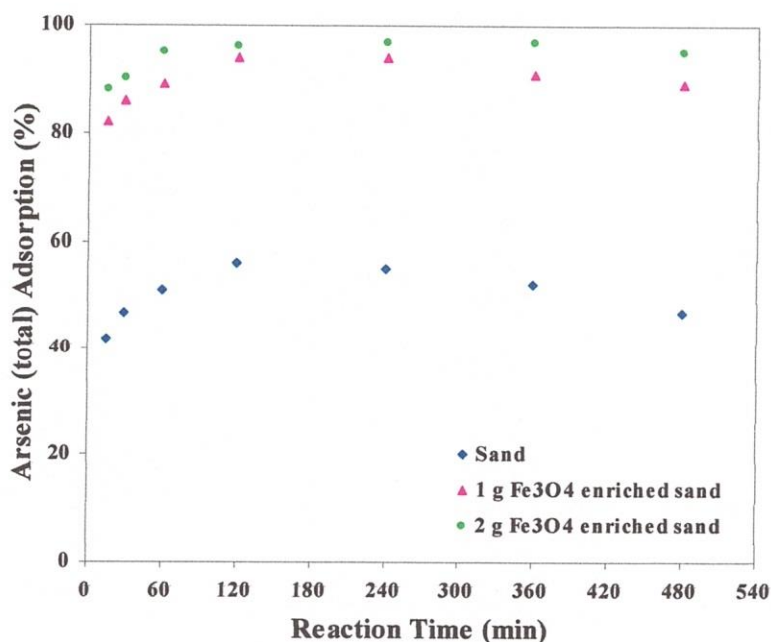
Figure 19. Adsorption of As(total) as a function of time for the 0.5 mg/L initial As(total) concentration spiked groundwater.

The adsorption of As(total) on the adsorbent surfaces for 1.0 mg/L initial As(total) is shown in Figure 20. The graph line for sand adsorbent shows that the removal percentage of As(total) increased very rapidly during the first 60 min and then decreased with time.

The graph line for 1 g Fe_3O_4 enriched sand adsorbent shows that the removal percentage of As(total) increased very rapidly during the first 120 min and then increased slowly and it continued for 360 min and finally decreased with time. The graph line for 2g Fe_3O_4 enriched sand adsorbent shows that the removal percentage of As(total) increased very rapidly during the first 120 min and then decreased with time. The maximum removal percentage achieved about 61, 88 and 99% for sand, 1 g Fe_3O_4 enriched sand and 2 g Fe_3O_4 enriched sand adsorbent, respectively from the initial concentration containing 1.0 mg/L As(total) spiked groundwater.
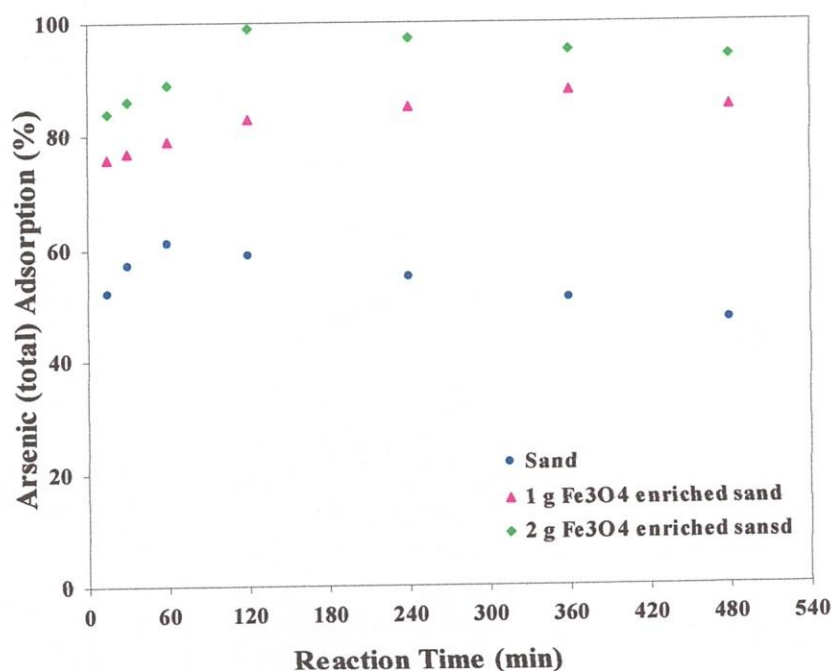
Figure 20. Adsorption of As(total) as a function of time for the 1.0 mg/L initial As(total) concentration spiked groundwater.

The results suggest that 2 g Fe_3O_4 enriched sand adsorbent showed the best removal performance among the adsorbents for the 0.50 and 1.0 mg/L initial concentration containing of As(total) spiked groundwater.

Removal of lead ion (Pb^{2+})

Figure 21 shows the adsorption of lead on the adsorbent surfaces for 3.0 mg/L initial Pb^{2+} concentration spiked water. The graph line for 2 g Fe_3O_4 enriched sand adsorbent shows that the removal percentage of Pb^{2+} increased very rapidly during the first 120 min

and then increased slowly and it continued for 240 min and finally decreased sharply with time. The graph line for 1.5 g Fe_3O_4 enriched sand adsorbent shows that the Pb^{2+} removal percentage increased very rapidly first 240 min and then increased slowly with increased time. For 1 g Fe_3O_4 enriched sand adsorbent shows that the removal percentage of lead increased very rapidly during the first 120 min and then slowly increased up to 360 min and finally decreased sharply with time. Pb^{2+} removal percentage of lead increased very rapidly during the first 120 min and then increased slowly and it continued for with time. The maximum removal percentage achieved to be 83, 80, 72 and 38% for the 2 g, 1.5 g, 1 g Fe_3O_4 enriched sand and sand adsorbent, respectively from the initial concentration containing 3.0 mg/L Pb^{2+} spiked groundwater. The results suggest that 2 g Fe_3O_4 enriched sand adsorbent showed the best Pb^{2+} removal performance among the adsorbents.
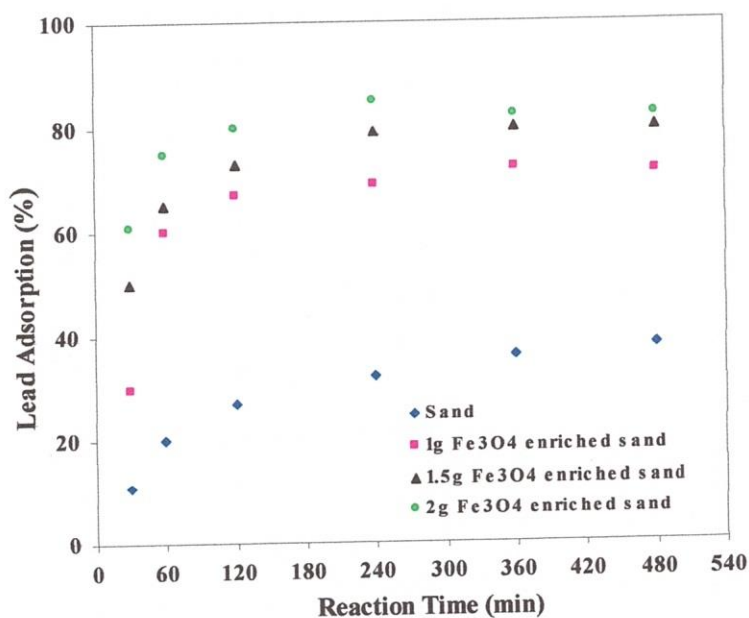
Figure 21. Adsorption of Pb^{2+} as a function of time for the 3.0 mg/L initial Pb^{2+} concentration spiked groundwater.

4.6.2 Column adsorption experiments

Removal of calcium (Ca^{2+})

In order to assess the Ca^{2+} removal efficiency of 100 and 200 mg/L initial concentrations of Ca^{2+} spiked groundwater, column experiments were conducted by sand-stone, 1 g and 2 g Fe_3O_4 enriched sand-stone adsorbents. Ca^{2+} in groundwater could be removed up to

about 56, 67 and 77% for the sand-stone, 1g Fe_3O_4 and 2g Fe_3O_4 enriched sand stone adsorbents, respectively from the initial concentration containing 100 mg/L Ca^{2+} spiked groundwater (Table 19) whilst they were about 37, 46 and 63% for the sand-stone, 1g Fe_3O_4 and 2g Fe_3O_4 enriched sand stone adsorbents, respectively from the initial concentration containing 200 mg/L Ca^{2+} spiked groundwater (Table 19). The experiment results show that the Ca^{2+} removal efficiency increased with the increasing the amount of Fe_3O_4 in the sand-stone adsorbent. The efficiency was dropped from 77 to 63% for the higher initial concentration spiked groundwater (Table 20). Only, 2g Fe_3O_4 enriched sand stone adsorbents could obtained for permissible limit of BD-WDS (75 mg/L) however, all adsorbent could fulfilled the BD-WDS for the initial concentration of 200 mg/L of Ca^{2+} spiked water (Table 19).

Table 19

Concentrations of Ca^{2+} in column adsorbents treated water

Adsorbents	Initial concentration, mg/L	Treated water concentration, mg/L	Removal Efficiency, (%)	WHO (2008), mg/L	BD DWS, mg/L
Sand-stone	100	43.75	56	-	75
1g Fe_3O_4 sand-stone		32.74	67		
2g Fe_3O_4 sand-stone		23.42	77		
Sand-stone	200	125.24	37		
1g Fe_3O_4 sand-stone		108.48	46		
2g Fe_3O_4 sand-stone		73.42	63		

Removal of iron (Fe ion)

In order to assess the Fe ion removal efficiency of 3.0 and 5.0 mg/L initial concentrations of calcium spiked groundwater, column experiments were conducted by sand-stone, 1g and 2g magnetite enriched sand-stone adsorbents. The maximum Fe ion in groundwater could be removed up to 51, 58 and 70% for the sand-stone, 1g Fe_3O_4 and 2g Fe_3O_4 enriched sand stone adsorbents, respectively from the initial concentration containing 3.0 mg/L Fe ion spiked groundwater (Table 20). For the initial concentration of 5.0 mg/L Fe ion contained spiked water, the maximum Fe ion removal percentages were 55, 68 and 81% for the sand-stone, 1g Fe_3O_4 and 2g Fe_3O_4 enriched sand stone adsorbents, respectively from the initial concentration containing 5 mg/L Fe ion spiked groundwater (Table 20). Only for the 2g Fe_3O_4 enriched sand column treated water of both initial

concentration fulfilled the quality of BD-DWS (0.3-1.0 mg/L) (Table 20). The experiment results show that the Fe ion removal efficiency increasing with increasing the amount of Fe_3O_4 in sand-stone adsorbent.

Table 20

Concentrations of Fe ion in column adsorbents treated water

Absorbents	Initial concentration, mg/L	Treated water concentration, mg/L	Removal Efficiency (%)	WHO DWS, mg/L	BD-DWS, mg/L
Sand-stone		1.47	51		
1g Fe_3O_4 sand-stone	3.0	1.25	58		
2g Fe_3O_4 sand-stone		0.88	70	0.30	0.30-1.0
Sand-stone		2.27	55		
1g Fe_3O_4 sand-stone	5.0	1.59	68		
2g Fe_3O_4 sand-stone		0.96	81		

2g magnetite enriched sand adsorbent showed the best removal efficiencies among the adsorbents. However, the maximum removal efficiency of Mn^{2+} was obtained using only sand adsorbent. In the column experiment, 2g magnetite enriched sand-stone adsorbent also showed the best removal efficiencies among the adsorbents for removal Ca and Fe ion from spiked groundwater. The magnetite enriched sand-stone adsorbent reduced the minerals efficiently and thus the treated water contained minerals were within the permissible limits of WHO and BD-DWS. Hence, the sand-stone enriched with magnetite could be used as a potential adsorbent for treating Ca, Fe, As (total) and Pb ions containing drinking water. The sand-stone column showed the maximum adsorption efficiency for Mn ion removal but the magnetite enriched sand adsorbent showed better removal efficiency for the other minerals. The study suggests that a column will be packed with adsorbent from top to bottom in order of sand, magnetite enriched sand and stone chips to get the maximum adsorption capacity due to adsorption behaviors of the adsorbents.

Conclusion

CONCLUSION

A total of 180 shallow and 60 deep tubewells water samples were collected from 30 and 10 locations, respectively during pre, post-monsoon and monsoon season covering two years. Also a total of 30 aquifer soil samples were collected at depths (10-45 meter) from 30 locations during monsoon season in 2010 to determine the contaminants potential. The experimental data were statistically analyzed using various software and the results were plot in figures to interpret the geochemical characteristics, water type, seasonal variations and water quality. The study was attempted to understand the geochemistry of groundwater in Rajshahi City and also tried to reduce harmful parameters from the water in order to improve its quality for drinking purpose.

The concentrations of Ca^{2+} and Cd^{2+} were found in aquifer soil in the highest and lowest quantities among cations, respectively and their mean and standard deviation were 166.08 ± 30.30 and 0.133 ± 0.119 mg/kg, respectively. Among anions, HCO_3^- and NO_3^- showed in the highest and lowest concentrations and their concentrations were 580 and 3.87 mg/kg, respectively. The results of the analyses showed that the mean concentrations of cations and anions were followed the order: $Ca^{2+} > Mg^{2+} > Na^+ > K^+ > Fe^{3+} > Mn^{2+} > Zn^{2+} > Cu^{2+} > Pb^{2+} > As(total) > Cd^{2+}$ and $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$, respectively. These ionic parameters would dissolve in water under different geo-chemical processes and increase concentration of different ions in groundwater.

The analysis results of the hydro-chemical composition of the shallow and deep tubewells water in the Rajshahi City showed that the groundwater of the study area was slightly acidic to neutral pH, hard to very hard and fresh category. Ca^{2+} was the dominant ionic species among the cations of the shallow tubewells water samples, with an average of 78.354 mg/L (range 28.31-121.35 mg/L) whilst the other determined cations were Na (11.71-39.67 mg/L), Mg (11.52-35.75 mg/L), K (0.22-11.78 mg/L, Mn (0.052-4.269 mg/L), Fe (0.14- 8.04 mg/L), Cu (0.001-0.770 mg/L), Zn (0.002-0.982 mg/L), As (0.001-0.081 mg/L), Cd (0.001-0.081 mg/L) and Pb (0.001-4.014 mg/L). For the deep tubewells, Ca^{2+} was also the dominant ionic species among the cations with an average of 78.541 mg/L (range 37.70-110.54 mg/L) whilst the other determined cations were Na (11.19-39.67 mg/L), Mg (18.58-35.55 mg/L), K (1.96-10.75 mg/L), Mn (0.037-4.943

mg/L), Fe (0.25-7.01 mg/L), Cu (0.001-4.077 mg/L), Zn (0.013-0.750 mg/L), As (0.001-0.056 mg/L), Cd (0.001-0.051 mg/L) and Pb (0.009-3.936 mg/L). The catonic order of the groundwater were: $Ca^{2+}> Mg^{2+}> Na^{+}> K^{+}> Fe^{3+}> Mn^{2+}> Pb^{2+}> Zn^{2+}> Cu^{2+}>$ As(total)$> Cd^{2+}$. Among the anions, HCO_3^- was the dominant species with an average of 245.301 mg/L (range 60-510 mg/L) whilst the concentrations of Cl^-, SO_4^{2-} and NO_3^- ranged from 17.43 to 110.99, 16.54 to 71.81 and 0.10 to 7.27 mg/L, respectively in the shallow tubewells water. HCO_3^- was the dominant species among the anions of deep tubewells water with an average of 188.362 mg/L (68-421.50 mg/L) whilst the concentrations of Cl^-, SO_4^{2-} and NO_3^- ranged from 15.59 to 88.98, 23.20 to 67.50 mg/L, and 0.10 to 4.60, respectively. The major anions of the shallow and deep tubewells water were followed the order of $HCO_3^-> Cl^-> SO_4^{2-}> NO_3^-$. So, Ca^{2+} and HCO_3^- were the dominant cation and anion, respectively among the ionic parameters in the groundwater samples.

Elevated level of TH, HCO_3, Ca, Mn, Fe, As(total) and Pb ions were found in the groundwater samples of the study area that exceeded the limits of WHO and BD-DWS. The possible source of Fe and As(total) ions in the study area might be the pirite and arsenopyrite in the aquifer soil. The study show that most of the samples exceeded BD-DWS limits for Mn mineral present in the Brahmaputra and Ganges floodplains. The Pb^{2+} presence in water samples may be due to rock, water and air interaction, and in addition to anthropogenic activities. The ionic parameters in groundwater were lower compared to the ions present in the aquifer soil. So, the comparison study between the analyzed aquifer soil and the groundwater samples reveals that the aquifer soil was the main source of ionic constitutes in the groundwater in the study area. The microbial analysis of the water samples illustrate that the mean value of total coliform (TC) and faecal coliform (FC) exceeded the permissible limits of WHO and BD-DWS for drinking purpose.

The concentrations of major cations and anions were plotted in the Piper tri-linear diagram using AQUACHEM Version: 5.1 software and the diagram illustrates that the water type of both the groundwater samples was Ca^{2+}- HCO_3^-. A plot of $m(Ca^{2+} + Mg^{2+})/mHCO_3^-$ against Cl^- diagram indicated that the presence of high concentration of Ca^{2+} and HCO_3^- in water was the cause of calcite weathering as the molar ratio of Ca^{2+}/Mg^{2+} was found higher than one (1). The C-ratio ($HCO_3^-/ HCO_3^- + SO_4^{2-}$) analysis

of the groundwater samples suggested that carbonic acid was the weathering agent of calcite. The mean values of P_{CO_2} in the shallow and deep tubewells water were 0.0499 and 0.0210 atm, respectively which were greater than the normal P_{CO_2} in atmosphere (0.0003 atm) indicated that the groundwater became charged with CO_2 during infiltration process. The Saturation Indices shows that Ca^{2+} and HCO_3^- in groundwater were mostly dissolving from calcite in monsoon and precipitating in pre and post-monsoon seasons. Negative values of Chloro Alkaline Indices suggest that the reverse ion exchange process was the major chemical reaction controlling the chemistry of the groundwater. From the above discussion, it may be concluded that the calcite dissolution was the controlling process, which increased Ca^{2+} and/ or HCO_3^- in the groundwater in the area. The experimental data analyses using Gibbs plots, Saturation Indices, Stiff diagram and Factor analysis describe that the presence of various elements in groundwater was the cause of rock/mineral-water interaction. The groundwater of Rajshahi City shows a wide range of characteristics in terms of physical, chemical and microbial parameters during the three seasons.

The results show significant amounts of metal ions, e.g. Ca, Mn, Fe, As(total) and Pb ions present in the shallow and deep tubewells water samples in all seasons. About 70, 100, 90, 25 and 90% groundwater samples exceeded the WHO and BD DWS limits for Ca, Mn, Fe, As (total) and Pb ions, respectively in the study area. Thus the quality of groundwater of the area was not suitable for drinking purpose. Excessive intake of these metals ions via drinking water pose a potential health threat and they may cause several diseases such as urolithiasis, cardiovascular disorders, haermosiderosis, psychiatric symptoms, parkinsonian features, cancer of the skin, urinary bladder, kidney, lung, haemosynthesis, and disorders of the circulatory and nervous system. Thus it is imperative to treat the groundwater before using as portable water in order to improve water quality and ensure safe water in the area.

The study also investigated the removal of Ca, Mn, Fe, As(total) and Pb ions from the groundwater using batch and column adsorbent experiments. A series of batch and adsorption experiments were conducted using sand, stone and magnetite (Fe_3O_4) enriched sand adsorbents. 2g magnetite enriched sand adsorbent showed the best removal efficiencies among the adsorbents and the removal percentage were about 97

and 83% for As(total) and Pb^{2+} from the initial concentration containing 0.50 mg/L As(total) and 3 mg/L Pb^{2+} spiked groundwater, respectively in batch adsorption process. However, the maximum removal efficiency of Mn^{2+} was 92% obtained using only sand adsorbent from the initial concentration containing 3.0 mg/L Mn^{2+} spiked water. In the column experiment, 2g magnetite enriched sand-stone adsorbent also showed the best removal efficiencies among the adsorbents and the removal percentage were about 77 and 70% Ca^{2+} and Fe ion from the initial concentration containing 100 mg/L Ca^{2+} and 3.0 mg/L Fe ion spiked groundwater, respectively. The magnetite enriched sand-stone adsorbent reduced the minerals efficiently and thus the treated water contained minerals were within the permissible limits of WHO and BD-DWS. Hence, the sand-stone enriched with magnetite could be used as a potential adsorbent for treating Ca, Fe, As (total) and Pb ions containing drinking water.

The sand-stone column showed the maximum adsorption efficiency for Mn ion removal but the magnetite enriched sand adsorbent showed better removal efficiency for the other minerals. The study suggests that a column will be packed with adsorbent from top to bottom in order of sand, magnetite enriched sand and stone chips, to get the maximum adsorption capacity due to adsorption behaviors of the adsorbents. Moreover, a detailed study on kinetics and mechanism of sand-stone enriched magnetite adsorbent would be considered for further development of the adsorbent process. Finally, the magnetic enriched sand-stone adsorbent could be considered as economically suitable indigenous materials for removing contaminants from water.

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Appendices

Appendix-1: Detailed descriptions of different sampling locations

Table 1.1 Detailed descriptions of sampling locations of shallow tubewells of Rajshahi City

Sampling locations	Ward No.	Sample No.
Kasiadanga Bazar, Rajpara	1	STW-1
Horogram Colony, Rajpara	2	STW-2
New Bisimla, Kadirgonj, Rajpara	3	STW-3
Bulonpukur, Rajpara	4	STW-4
Vatapara, Helenabad Colony, Rajpara	5	STW-5
Bhohorampur (Near Rail Line), Rajpara	6	STW-6
Srirampur, Rajpara	7	STW-7
Kazihata, Boalia-Rajpara	8	STW-8
Hosnigonj, Boalia-Rajpara	9	STW-9
WAPDA colony (Kolabagan), Rajpara	10	STW-10
Malopara, Boalia	11	STW-11
Ranibazar, Boalia	12	STW-12
Dorokhorbona (West side of Rail Line), Boalia	13	STW-13
Uposhahor, Boalia	14	STW-14
Rajshahi Polytechnique Institute, Boalia	15	STW-15
Supura Industrial Region, Boalia	16	STW-16
Islami Bank Medical College Campus, Naudapara Shah Makdum	17	STW-17
Shalbagan (Near Forest Office), Boalia	18	STW-18
Sotobangram Colony, Boalia	19	STW-19
Sultanabad, Boyalia	20	STW-20
Near Siroil High School, Boalia	21	STW-21
Sagorpara, Boalia	22	STW-22
Shekhartek, Boalia	23	STW-23
Kazla Hilful Fuzul Mosque, Matihar	24	STW-24
Raninagra, Boalia	25	STW-25
Nomovaddra, Boalia	26	STW-26
RUET Campus, Matihar	27	STW-27
Dorumpur Lichutola, Matihar	28	STW-28
Shampur, Dhasmari, Matihar	29	STW-29
Rajshahi University Campus (In front of Library), Matihar	30	STW-30

* STW-Shallow Tubewells Water

Table 1.2 Detailed descriptions of sampling locations of deep tubewells in Rajshahi City

Sampling locations	Ward No.	Sample No.
Horogram Muncipara, Rajpara	1	DTW-1
Horogram Nutonpara, Rajpara	2	DTW-2
Rajshahi Medical College Campus, Laxmipur	7	DTW-3
Hetemkha, Rajpara	11	DTW-4
Kadirgonj, Gorhanga, Boalia	13	DTW-5
Sopura Cantonment, Boalia	16	DTW-6
Islami Bank Medical College Campus, Naudapara, Shah Makdum	17	DTW-7
Mehercondi, Boalia	26	DTW-8
RUET Campus, Matihar	27	DTW-9
Rajshahi University Campus (Near Stadium), Matihar	30	DTW-10

* **DTW-Deep Tubewells Water**

Table 1.3 Detailed descriptions of sampling locations of shallow aquifer soil samples in Rajshahi City during monsoon season in 2010

Sampling locations	Depth, meter	Ward No.	Sample No.
Horogram, Muncipara, Rajpara	21	1	ASS-1
Horogram, Ranidigi, Rajpara	34	2	ASS-2
Laxmipur, Dinggadoba (Near Rail line), Rajpara	36	3	ASS-3
Goyalpara, Rajpara	23	4	ASS-4
Mohisbathan, Rajpara	29	5	ASS-5
Bilsimla (Near Rail Line), Rajpara	38	6	ASS-6
Chandipur, Rajpara	35	7	ASS-7
Shipaipara, Boalia-Rajpara	21	8	ASS-8
Dorgapara, Boalia-Rajpara	43	9	ASS-9
Hetamkha, Boalia	21	10	ASS-10
Kadirgonj (Near Gorshthan), Boalia	35	11	ASS-11
Ranibazar, Boalia	38	12	ASS-12
Shostitola, Kadirgonj, Boalia	24	13	ASS-13
Tarokhadia, Rajpara	40	14	ASS-14
Shazipara, Sopura, Boalia	27	15	ASS-15
Near BADC Office, Sopura, Boalia	37	16	ASS-16
Naudapara Bazar, Shah Makdum	36	17	ASS-17
Asam Colony, Boalia	41	18	ASS-18
Cotobangram Bazar, Boalia	29	19	ASS-19
Sultanabad, Boalia	43	20	ASS-20
Siroil, Boalia	23	21	ASS-21
Goramara, Boalia	34	22	ASS-22
Ramchadrapur, Raninagar, Boalia	41	23	ASS-23
Ahmedpur, Ramchdrapur, Boalia	37	24	ASS-24
Talimari, Matihar	29	25	ASS-25
Meherchandi, Boalia	35	26	ASS-26
Debishigpara, Matihar	43	27	ASS-27
Dorumpur, Matihar	38	28	ASS-28
Khozapur, Matihar	41	29	ASS-29
Rajshahi University Campus (Near Binodpur Gate), Matihar	32	30	ASS-30

* ASS-Aquifer Soil Sample

Appendix-2: Standard curves for various chemical parameters

y = 0.0139x + 0.0013
r= 0.9999
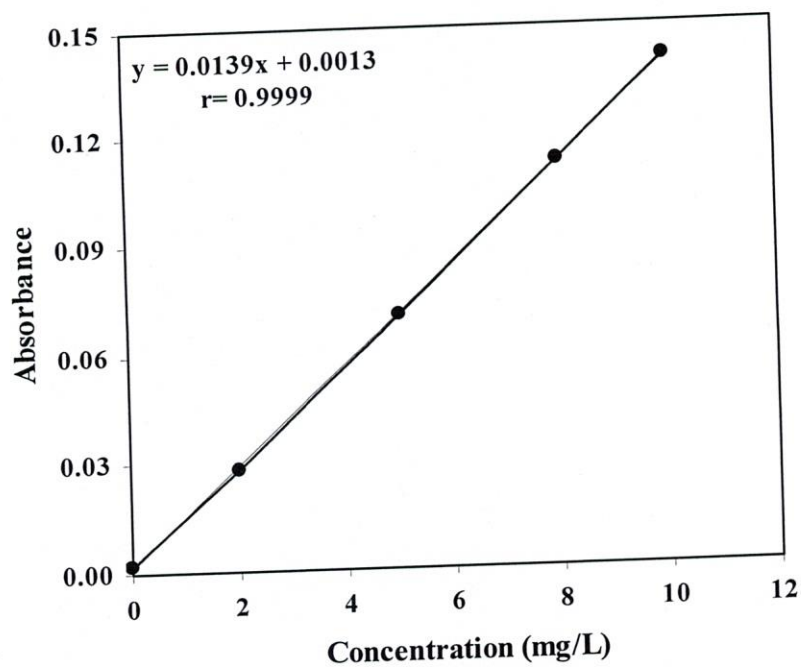
Figure 2.1. Standard curve of sodium (Na).

y = 48.19x + 0.0294
r= 0.9988
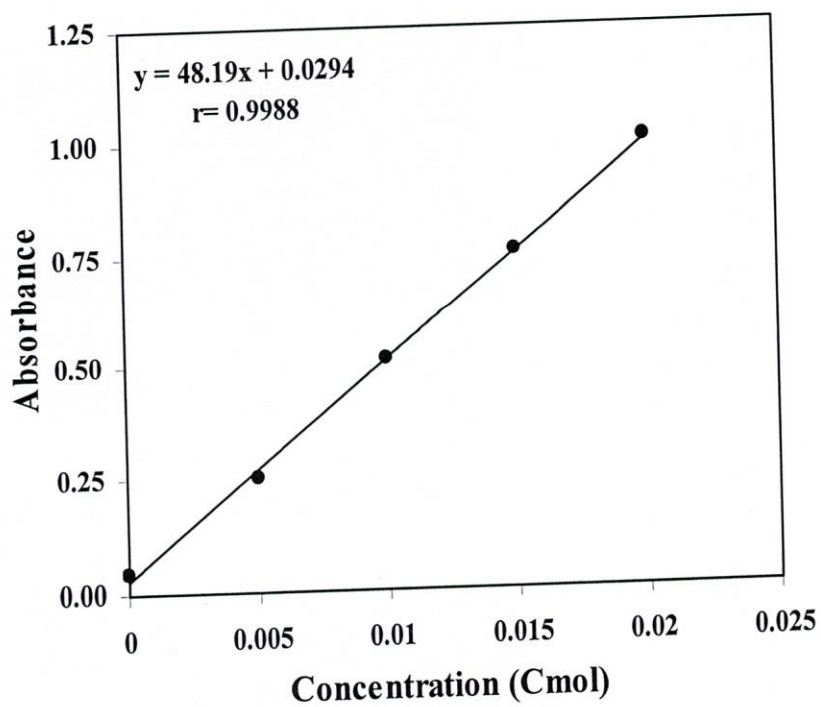
Figure 2.2. Standard curve of magnesium (Mg).
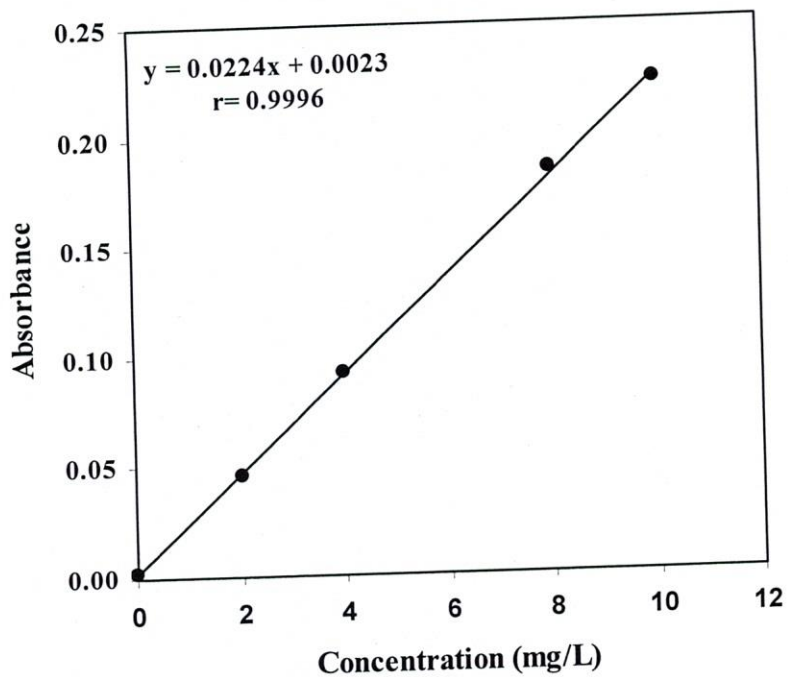
Figure 2.3. Standard curve of potassium (K).
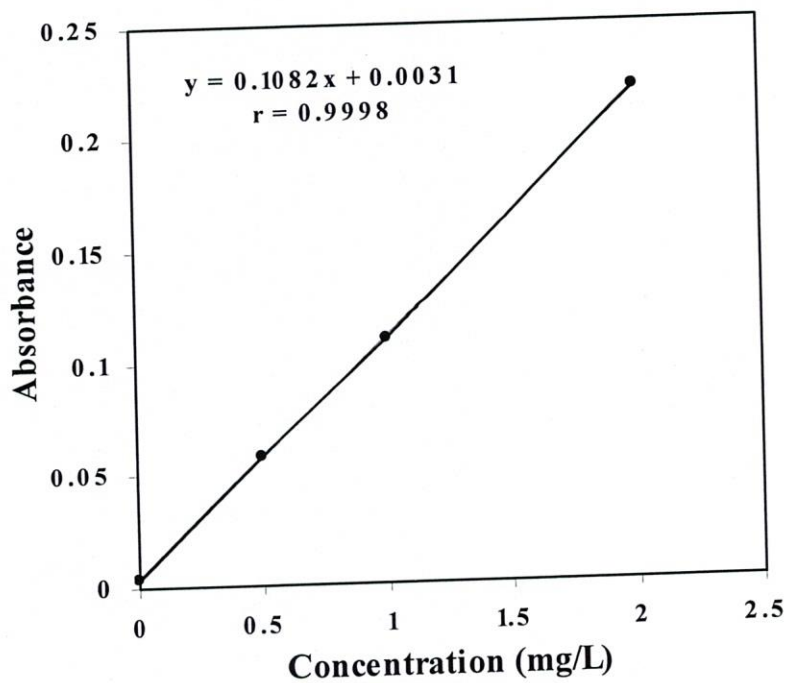
Figure 2.4. Standard curve of calcium (Ca).

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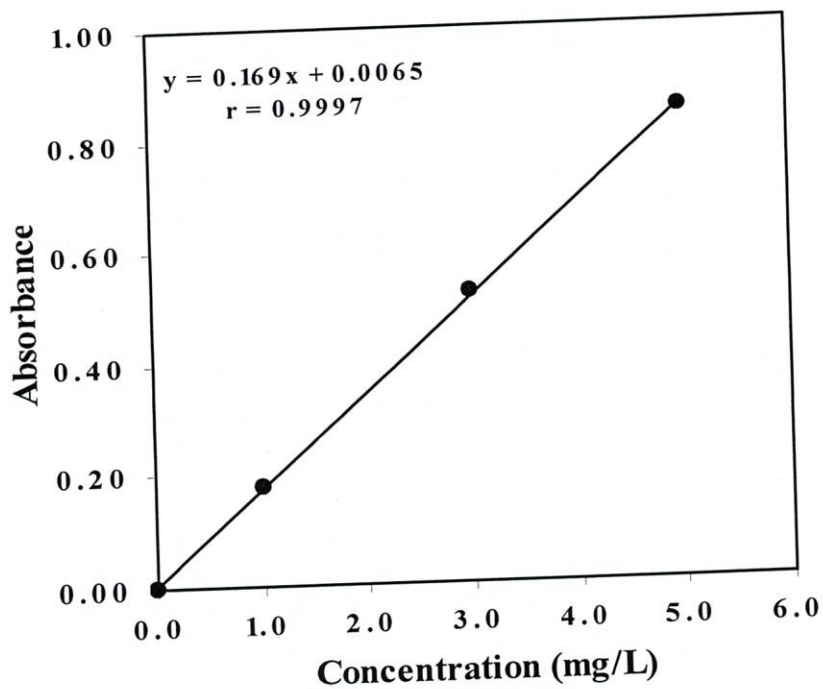
Figure 2.5. Standard curve of manganese (Mn).

$y = 0.169x + 0.0065$

$r = 0.9997$
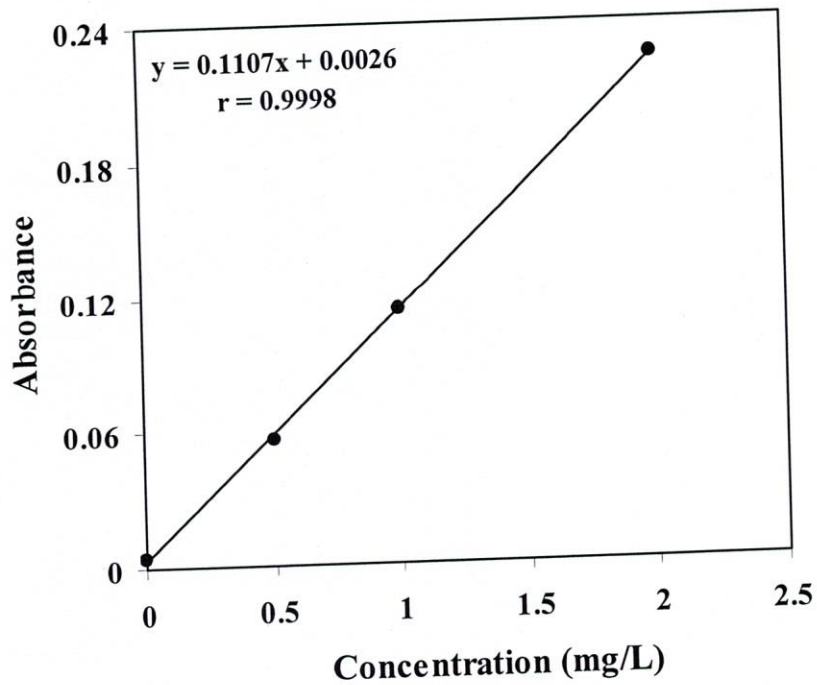
Figure 2.6. Standard curve of iron (Fe).

$y = 0.1107x + 0.0026$

$r = 0.9998$
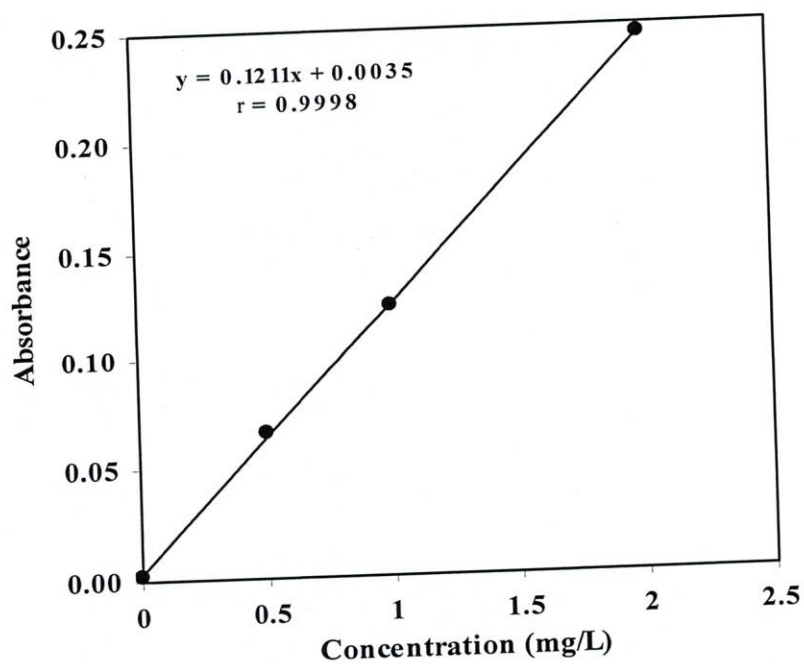
Figure 2.7. Standard curve of copper (Cu).

$$y = 0.1211x + 0.0035$$
$$r = 0.9998$$
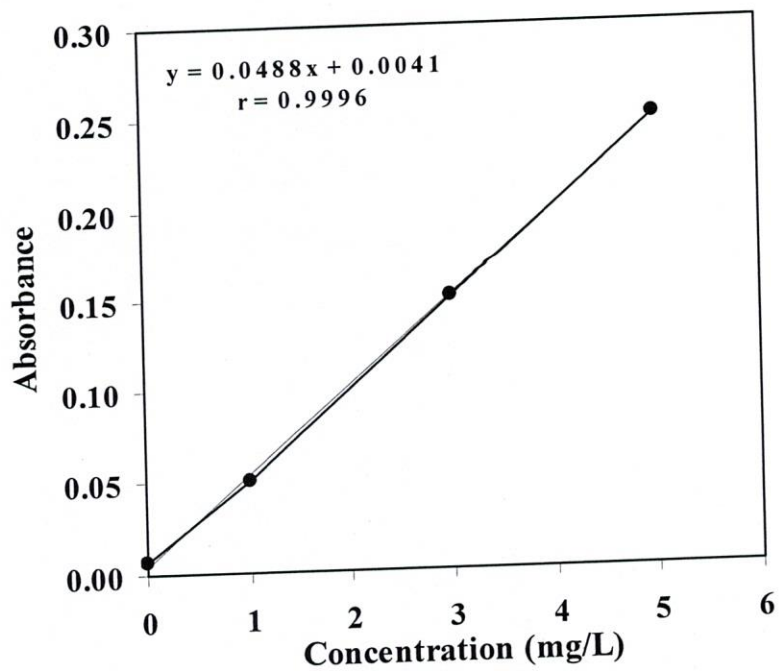
Figure 2.8. Calibration curve of zinc (Zn).

$$y = 0.0488x + 0.0041$$
$$r = 0.9996$$
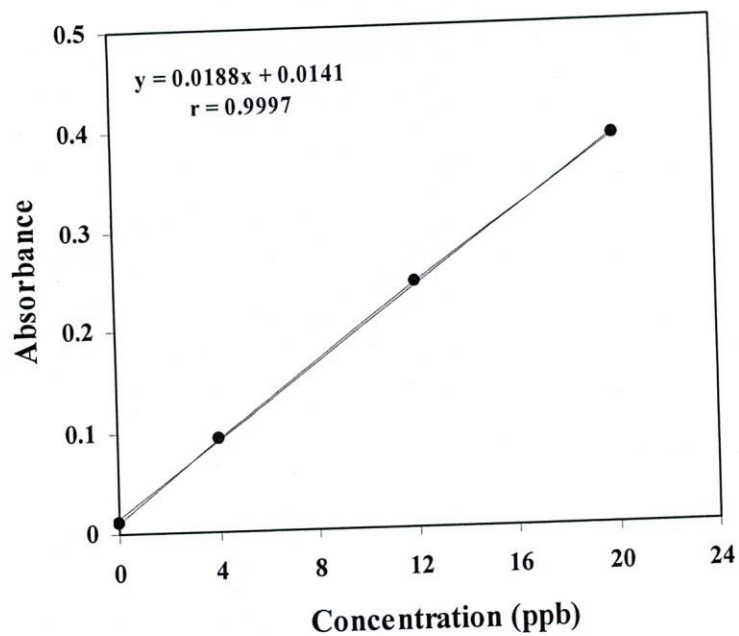
Figure 2.9. Standard curve of arsenic (As).
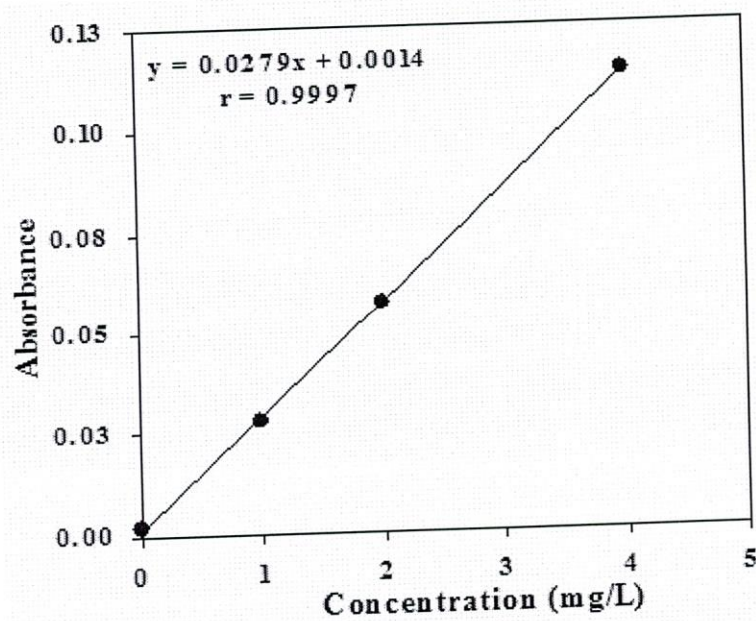
Figure 2.10. Standard curve of cadmium (Cd).

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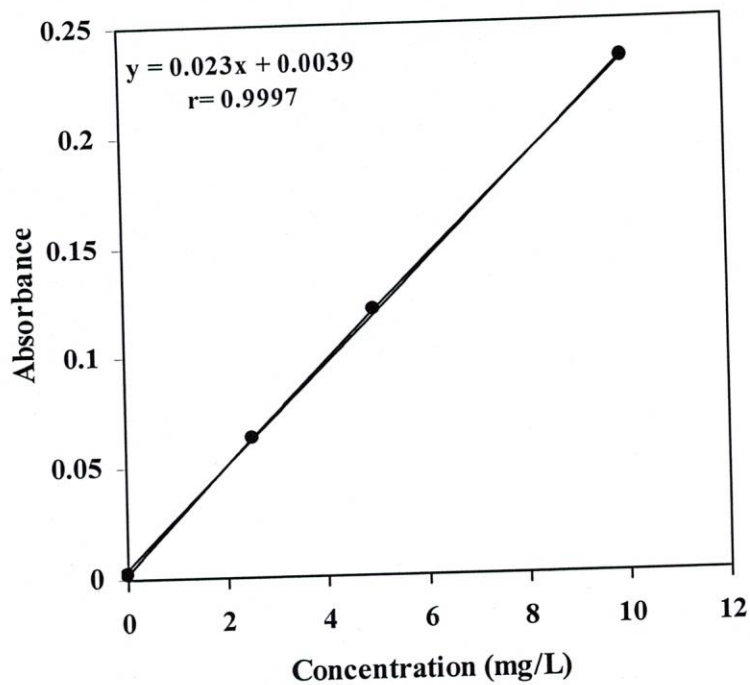
Figure 2.11. Standard curve of lead (Pb).

Plot annotations: $y = 0.023x + 0.0039$, $r = 0.9997$. Y-axis: Absorbance. X-axis: Concentration (mg/L).
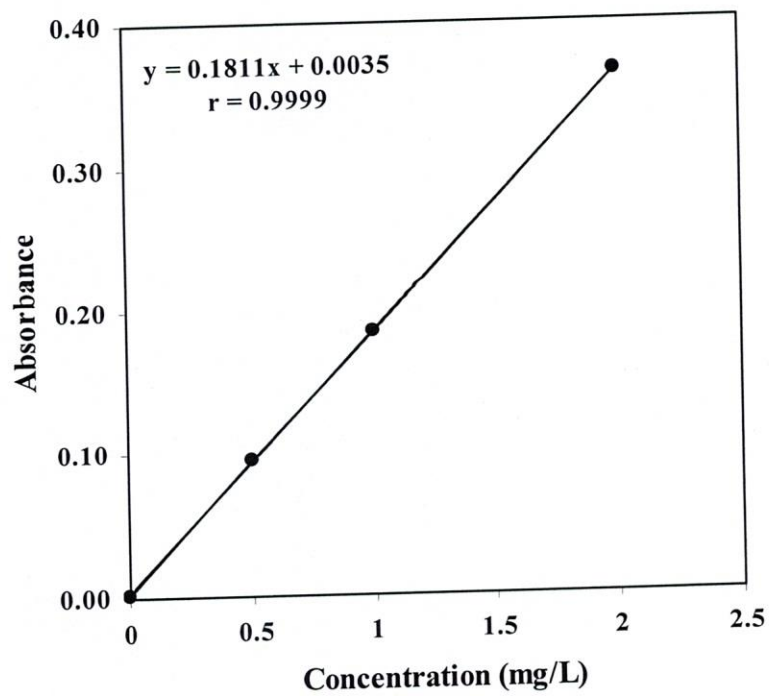
Figure 2.12. Standard curve of nitrate (NO_3^-).

Plot annotations: $y = 0.1811x + 0.0035$, $r = 0.9999$. Y-axis: Absorbance. X-axis: Concentration (mg/L).
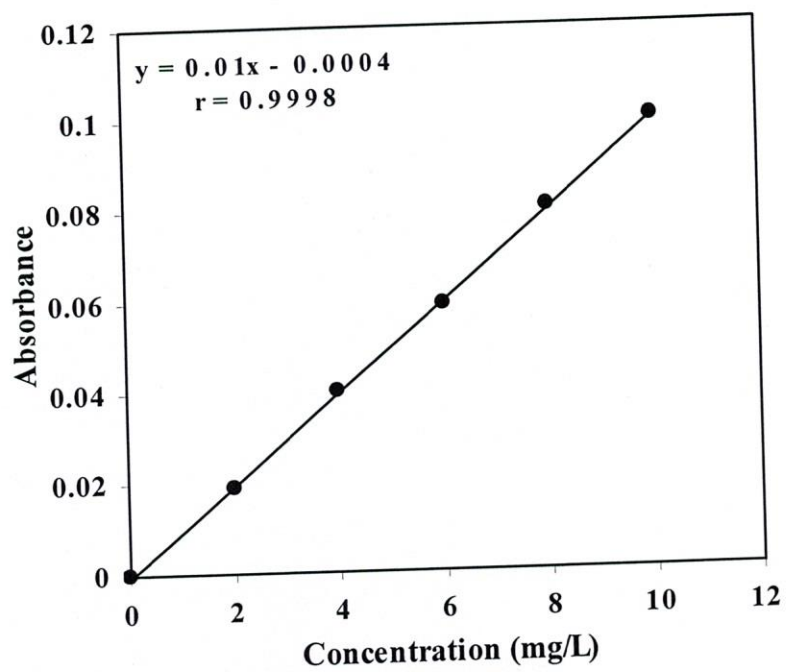
Figure 2.13. Standard curve of sulphate (SO_4^{2-}).

The chart shows a linear plot of Absorbance versus Concentration (mg/L) with the equation $y = 0.01x - 0.0004$ and $r = 0.9998$.

Appendix-3: Physico-chemical parameters of shallow aquifer soil samples during monsoon season in 2010 in

Rajshahi City

Location	EC	HCO$_3^-$	Cl$^-$	NO$_3^-$	SO$_4^{2-}$	Na	Mg	K	Ca	Mn	Fe	Cu	Zn	As	Cd	Pb
ASS-1	1809	360.00	78.00	13.65	56.00	54.62	166.80	19.50	170.00	8.50	8.70	0.700	0.170	0.500	0.199	0.580
ASS-2	1800	580.00	95.76	9.54	89.60	48.26	140.40	11.70	220.00	11.00	11.40	0.230	0.190	0.750	0.029	0.552
ASS-3	1671	220.00	59.76	6.28	74.20	38.76	109.20	11.70	150.00	9.70	8.80	1.003	0.140	0.098	0.024	0.594
ASS-4	1782	380.00	75.78	10.90	63.00	50.16	84.00	11.70	156.00	8.50	9.20	1.150	0.150	0.850	0.298	0.538
ASS-5	1632	418.00	67.78	7.13	42.00	53.10	79.20	7.80	114.00	3.60	8.50	0.902	0.240	0.695	0.027	0.722
ASS-6	1824	395.00	121.78	9.43	63.00	61.02	94.80	11.70	186.00	4.70	10.90	1.310	0.880	0.760	0.016	0.778
ASS-7	1735	392.17	83.14	10.23	54.33	52.08	130.29	14.43	177.09	5.46	6.23	1.080	0.080	0.372	0.023	0.235
ASS-8	1220	204.00	75.00	6.23	43.89	40.64	91.91	20.20	135.90	5.39	8.72	0.601	0.650	0.412	0.383	0.090
ASS-9	1040	267.00	79.00	7.56	67.28	64.41	105.60	18.58	163.09	4.86	11.86	0.363	0.750	0.126	0.028	0.544
ASS-10	1615	345.00	92.00	12.23	48.49	44.97	83.69	13.09	146.14	3.80	9.40	0.826	0.770	0.373	0.028	0.170
ASS-11	1310	366.00	80.00	7.56	63.93	54.39	90.76	11.11	136.36	5.27	8.31	0.401	0.880	0.173	0.023	0.269
ASS-12	1120	409.00	97.30	9.23	48.44	45.73	60.30	15.06	184.81	6.48	5.93	0.305	0.720	0.384	0.080	0.255
ASS-13	1220	267.00	108.20	11.67	53.88	57.97	87.45	11.07	109.36	2.20	10.10	0.749	1.096	0.311	0.025	0.136
ASS-14	2025	323.00	90.00	6.98	61.45	64.41	74.77	15.95	195.78	11.43	8.85	0.442	0.733	0.260	0.021	0.243
ASS-15	1570	451.00	115.29	12.89	42.51	41.13	24.52	8.34	205.02	6.19	9.24	1.490	0.618	0.471	0.065	0.093
ASS-16	1955	246.00	82.56	8.98	57.75	44.97	20.13	9.12	217.12	5.37	6.82	0.980	0.878	0.287	0.300	0.189
ASS-17	2631	234.25	70.56	5.72	49.69	69.19	69.86	19.48	171.91	4.29	11.41	0.433	1.519	0.068	0.177	0.434
ASS-18	2291	315.35	61.66	8.35	64.35	54.17	82.40	7.25	193.17	9.76	8.03	0.760	0.734	0.760	0.299	0.231
ASS-19	2710	275.50	86.06	6.83	53.82	81.01	116.05	11.90	156.95	7.02	7.66	1.033	1.379	0.075	0.240	0.186
ASS-20	2192	306.50	58.04	6.45	57.55	50.11	98.94	13.34	213.11	10.35	6.82	0.151	0.736	0.583	0.189	0.260
ASS-21	1813	233.49	64.51	10.36	70.23	62.98	63.90	18.23	170.59	3.86	7.31	0.370	0.941	0.552	0.285	2.198
ASS-22	1539	231.66	71.15	12.87	45.49	43.65	131.71	20.44	180.64	6.56	6.80	0.280	1.316	0.607	0.081	3.331
ASS-23	1300	267.60	36.04	4.78	53.22	53.41	6.39	12.25	127.39	4.87	8.15	1.082	0.927	0.269	0.274	4.014
ASS-24	1782	205.34	59.96	7.53	45.67	59.66	102.49	16.36	153.16	7.15	10.41	0.710	0.545	0.095	0.025	0.354
ASS-25	2364	487.34	55.70	8.45	47.81	65.30	96.31	19.29	154.52	8.11	9.79	1.340	1.000	0.074	0.021	0.277
ASS-26	2928	213.60	79.80	10.45	59.07	65.94	54.94	13.72	170.40	7.25	6.36	0.121	1.599	0.058	0.170	0.331
ASS-27	2049	187.31	49.99	3.87	43.87	53.66	119.44	7.45	118.12	6.35	8.41	0.845	0.774	0.175	0.320	3.510
ASS-28	1852	430.00	88.75	8.73	50.34	47.06	83.89	9.27	192.09	2.93	9.28	0.580	0.580	0.067	0.140	0.394
ASS-29	1479	351.30	49.47	10.34	47.13	53.68	52.70	16.55	133.60	6.29	11.37	1.600	0.757	0.064	0.029	0.236
ASS-30	1747	405.33	70.49	6.84	38.73	70.89	79.68	7.23	180.11	3.17	8.90	0.670	0.565	0.230	0.180	0.237

*ASS- Aquifer Soil Sample   Units: All the results in mg/kg except EC in µS/cm

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Appendix–4: *Physico-chemical and microbial parameters of shallow tubewells water samples of Rajshahi City*

Table 4.1: *Temperature, pH and EC of shallow tubewells water samples of Rajshahi City in 2009 and 2010*

Sample No.	Temperature °C Pre-monsoon 2009	2010	Monsoon 2009	2010	Post-monsoon 2009	2010	pH Pre-monsoon 2009	2010	Monsoon 2009	2010	Post-monsoon 2009	2010	EC, µS/cm Pre-monsoon 2009	2010	Monsoon 2009	2010	Post-monsoon 2009	2010
STW-1	28.00	29.00	27.00	25.00	26.00	26.50	8.34	7.18	6.59	6.40	7.30	7.10	391	363	352	389	740	293
STW-2	27.00	28.00	27.75	28.00	25.50	25.00	7.48	7.51	6.32.	6.17	6.80	6.90	405	178	505	475	810	328
STW-3	29.00	28.50	26.00	25.50	26.50	26.50	7.50	7.23	4.94	4.79	7.20	6.80	237	157	253	223	820	307
STW-4	25.00	27.50	26.50	25.50	26.00	25.50	7.51	7.80	6.09	5.94	7.30	7.13	181	258	366	336	594	391
STW-5	27.50	29.00	27.50	26.00	25.00	26.00	7.43	7.29	5.54	5.39	6.80	6.80	209	726	345	365	720	433
STW-6	27.25	28.50	27.00	26.00	26.00	27.00	7.57	7.34	5.68	5.53	6.90	6.70	237	230	320	290	780	810
STW-7	27.00	28.00	28.00	26.25	26.25	26.25	7.59	7.52	6.55	6.44	6.70	6.80	712	314	376	406	447	559
STW-8	28.00	28.50	27.00	26.75	27.00	25.00	8.42	7.54	6.13	5.85	6.90	7.10	419	225	255	225	870	258
STW-9	28.50	29.00	26.50	26.00	26.00	25.50	7.71	7.39	6.20	6.05	7.20	6.90	391	391	295	285	481	314
STW-10	28.25	28.75	26.00	26.00	25.50	26.25	7.74	7.21	6.18	6.03	7.30	7.20	949	405	309	322	477	349
STW-11	28.00	27.75	27.25	27.00	25.50	26.00	7.50	7.82	6.71	6.43	7.12	7.10	398	300	388	348	750	405
STW-12	27.50	28.50	29.00	28.50	26.50	27.00	7.25	7.62	6.38	6.23	7.20	6.70	189	262	393	298	730	531
STW-13	28.50	29.00	27.00	27.75	25.75	27.00	7.45	7.71	6.32	6.19	7.30	6.80	198	276	434	467	715	572
STW-14	27.75	27.75	28.00	27.00	26.25	25.50	7.34	7.54	6.04	5.89	7.40	6.70	239	323	417	293	754	650
STW-15	29.00	28.00	29.00	29.50	25.50	25.00	7.11	7.23	5.93	5.78	6.90	7.12	196	437	285	372	684	593
STW-16	28.50	28.50	31.00	30.00	25.00	26.50	7.54	7.69	5.83	6.67	7.10	7.14	740	209	265	377	672	775
STW-17	27.00	28.50	28.50	29.00	25.50	27.00	7.13	7.41	6.65	6.56	7.20	7.20	670	253	146.5	418	580	838
STW-18	28.00	29.00	27.00	27.50	26.50	26.00	7.61	7.29	6.65	6.50	7.10	7.10	545	490	265	401	740	743
STW-19	28.50	28.00	28.50	28.00	27.00	25.50	7.51	7.21	7.00	6.85	6.90	7.30	852	209	297	267	812	496
STW-20	28.25	29.00	31.00	30.00	27.00	27.00	7.32	7.39	6.00	5.98	7.30	7.90	223	179	419	389	853	518
STW-21	29.00	28.50	28.00	26.00	25.50	25.50	7.41	7.18	6.82	5.68	6.80	7.40	742	269	302	272	745	672
STW-22	28.50	27.00	27.00	25.00	26.00	25.00	7.55	7.51	5.55	5.40	7.23	7.23	607	196	285	255	578	455
STW-23	27.00	28.50	29.50	26.00	27.00	25.50	7.28	7.43	6.12	5.97	6.45	6.58	269	465	489	459	625	378
STW-24	29.00	30.00	30.00	28.00	26.25	26.50	7.48	7.50	6.07	5.92	7.45	7.49	196	323	558	528	802	722
STW-25	27.25	28.75	31.50	34.50	25.00	25.50	7.67	7.32	5.99	5.84	7.24	7.30	465	675	268	238	489	379
STW-26	27.50	29.00	29.50	33.00	25.50	28.00	7.35	7.39	6.22	6.07	6.90	7.10	702	458	344	314	529	488
STW-27	30.00	28.00	27.75	26.00	27.00	27.50	7.58	7.48	6.34	6.17	7.30	7.30	565	179	287	257	673	688
STW-28	29.00	29.00	28.25	27.71	26.50	27.00	7.11	7.54	6.75	6.50	7.20	7.40	387	526	377	347	538	788
STW-29	27.75	27.75	28.00	27.50	25.75	26.00	7.29	7.70	6.53	6.38	7.40	7.20	567	465	394	364	624	598
STW-30	29.25	28.00	28.50	29.00	26.00	25.50	7.32	7.56	6.58	6.60	6.90	7.10	466	378	267	297	409	808

Table 4.2: TDS, TSS and Total Hardness of shallow tubewells water samples of Rajshahi City in 2009 and 2010

Sample No.	TDS, mg/L						TSS, mg/L						TH, mg/L					
	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
STW-1	280	275	182	222	230	210	200	100	190	200	200	200	430	350	116.71	150.00	248	260
STW-2	290	135	349	316	250	235	100	200	200	100	100	100	312	318	182.21	176.93	260	255
STW-3	170	113	174	42	240	220	200	200	200	200	100	100	286	420	232.20	190.81	352	354
STW-4	130	185	197	165	340	280	170	150	150	300	100	200	394	409	174.49	211.49	328	332
STW-5	150	520	175	196	620	310	100	110	170	150	100	200	588	422	197.44	216.80	402	410
STW-6	170	165	147	115	560	580	100	100	190	200	300	300	402	335	195.05	203.07	420	415
STW-7	510	225	208	241	290	400	100	150	200	200	100	100	420	450	158.43	188.30	400	395
STW-8	300	161	177	144	410	185	100	100	130	250	300	100	386	332	208.32	181.18	424	318
STW-9	280	280	187	109	330	225	300	100	140	100	200	300	380	370	178.29	202.16	208	248
STW-10	680	290	135	150	550	250	200	200	200	280	200	100	310	356	194.58	208.93	244	258
STW-11	285	215	221	178	545	290	100	100	200	170	200	200	415	298	135.42	237.22	260	425
STW-12	135	188	227	123	523	380	100	100	200	150	100	300	360	322	221.37	213.74	250	386
STW-13	142	198	271	307	512	410	200	200	200	170	200	100	385	402	226.81	195.50	255	353
STW-14	171	232	253	118	540	470	250	100	150	180	100	100	315	430	271.42	183.39	227	403
STW-15	140	313	209	204	490	425	300	100	200	230	100	200	480	359	252.93	231.89	390	397
STW-16	530	150	188	209	481	553	100	150	170	170	100	200	510	378	182.41	189.24	410	388
STW-17	480	181	91	254	415	600	200	100	180	200	300	300	428	285	131.07	242.09	350	258
STW-18	390	351	188	236	530	532	100	100	190	200	200	100	330	428	91.38	170.91	402	418
STW-19	610	150	122	90	582	355	100	200	200	250	300	100	355	357	194.07	201.58	390	433
STW-20	160	128	255	222	611	365	200	130	150	150	300	200	570	328	122.37	340.07	450	363
STW-21	607	92	128	195	604	418	100	70	150	100	100	100	358	414	255.10	179.78	361	362
STW-22	459	12	109	177	681	356	100	200	100	160	300	100	370	390	127.81	196.67	336	289
STW-23	191	305	281	299	511	233	100	60	200	160	200	120	400	479	165.23	234.00	298	417
STW-24	125	151	406	374	546	505	150	100	150	180	100	180	307	432	281.26	146.62	370	370
STW-25	265	493	191	158	461	270	170	100	200	250	100	100	283	348	406.33	193.55	283	317
STW-26	563	298	174	141	648	381	200	200	180	160	100	210	261	471	190.81	207.46	329	284
STW-27	414	114	111	179	286	407	100	240	160	200	100	120	374	385	173.50	197.03	329	305
STW-28	220	372	209	177	746	480	250	120	200	150	100	150	290	499	111.49	213.50	330	380
STW-29	416	305	228	195	323	441	250	70	100	150	300	150	303	479	209.41	116.61	343	251
STW-30	306	210	190	122	318	579	100	130	100	150	100	100	383	326	227.90	188.00	351	383

* STW-Shallow Tubewells Water

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Table 4.3: HCO₃⁻, Cl⁻ and NO₃⁻ of shallow tubewells water samples of Rajshahi City in 2009 and 2010

Sample No.	HCO_3^-, mg/L						Cl^-, mg/L						NO_3^-, mg/L					
	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
STW-1	510	520	194.10	267.00	227.5	197.50	75.98	73.99	35.11	45.05	50.98	59.99	1.17	1.13	1.40	1.75	1.31	1.37
STW-2	240	310	202.28	193.00	121.5	125.00	65.98	68.98	47.26	49.56	29.99	41.99	0.93	0.96	0.86	0.67	0.25	0.34
STW-3	328	318	188.17	185.00	221.5	211.80	65.98	69.98	26.29	35.62	54.98	47.98	1.32	1.42	1.36	1.57	3.12	3.25
STW-4	372	410	194.50	262.00	171.5	161.50	85.98	88.98	35.70	39.62	87.97	81.99	1.31	1.27	1.41	1.11	3.12	3.18
STW-5	440	510	113.32	60.00	202	210.00	73.95	92.98	33.95	25.10	110.85	78.99	0.19	1.31	0.70	0.63	1.26	1.37
STW-6	360	285	131.92	240.00	143.5	143.80	63.98	68.98	31.87	30.02	19.99	71.00	0.93	0.85	2.39	1.60	7.25	3.78
STW-7	368	298	155.06	236.00	141.5	139.80	24.00	35.00	36.53	47.10	97.97	65.00	1.38	1.52	2.01	1.74	7.27	2.98
STW-8	350	310	168.28	211.00	165.5	75.20	69.58	58.98	26.46	29.51	104.97	54.00	0.10	0.30	1.30	0.57	4.68	2.56
STW-9	304	318	198.28	116.00	145.5	230.00	67.98	65.98	26.46	21.51	39.99	110.99	1.22	1.12	1.07	1.49	1.55	1.82
STW-10	304	410	131.30	134.00	76.50	215.00	55.99	60.98	30.95	34.03	44.99	38.99	1.04	1.11	1.39	3.61	1.55	1.35
STW-11	510	515	156.73	185.70	219.0	241.80	69.99	68.27	37.53	37.00	75.00	80.98	1.23	1.21	1.71	2.36	1.20	1.29
STW-12	340	345	196.01	288.60	211.0	181.30	79.99	59.99	37.94	33.00	79.00	68.99	1.29	1.35	1.28	0.16	1.41	1.13
STW-13	310	320	198.30	178.73	232.5	221.50	49.99	43.99	41.35	46.52	90.00	98.99	0.95	0.98	1.84	1.84	1.41	1.59
STW-14	410	390	107.35	197.88	235.0	171.50	82.99	80.99	39.94	32.6	80.00	49.99	0.21	0.31	1.43	1.44	1.22	1.28
STW-15	430	415	125.27	154.28	198.0	185.00	65.99	72.88	28.96	38.92	62.00	90.00	1.35	1.45	1.38	1.06	1.21	1.31
STW-16	315	325	143.27	183.98	207.5	149.80	56.99	50.00	27.29	39.32	107.30	77.29	1.39	1.49	0.74	0.98	1.23	1.52
STW-17	366	375	174.82	281.59	168.0	150.60	23.99	32.22	17.43	42.6	55.29	55.99	1.33	1.55	1.08	1.04	2.89	2.78
STW-18	380	389	194.82	82.58	161.0	155.80	92.98	82.58	27.29	41.24	92.00	83.99	1.19	1.43	1.17	0.67	4.55	1.67
STW-19	330	310	267.63	104.41	158.5	168.70	81.99	78.22	29.96	30.52	81.22	78.22	1.08	1.21	1.88	1.04	4.72	2.18
STW-20	360	345	277.46	113.28	168.0	126.00	62.98	68.22	40.11	40.28	88.99	56.98	1.55	1.10	1.27	2.03	4.68	1.12
STW-21	498	390	210.91	269.00	172.9	232.39	41.73	29.25	30.37	42.55	78.23	70.70	1.60	1.26	2.01	1.89	1.59	1.74
STW-22	336	323	189.96	225.00	155.6	201.93	43.18	21.71	28.96	42.56	61.01	48.33	1.17	2.11	1.17	1.58	1.28	0.57
STW-23	413	380	212.38	195.00	160.4	218.22	25.85	49.47	45.93	52.56	65.86	40.39	0.57	1.23	0.93	0.66	1.31	1.55
STW-24	367	413	205.25	229.00	178.9	254.80	20.08	34.82	51.67	41.66	84.11	75.86	1.49	1.20	1.48	1.99	1.22	0.54
STW-25	427	367	159.01	222.00	146.2	218.27	22.97	71.15	27.54	31.06	51.84	40.49	1.27	1.41	0.98	1.57	1.21	2.50
STW-26	410	380	173.26	230.00	150.4	238.52	25.85	48.75	33.87	35.03	55.96	51.73	1.74	1.41	1.40	1.11	2.18	2.36
STW-27	403	410	200.07	233.00	165.4	203.16	74.83	19.96	29.12	27.51	70.81	72.35	1.88	1.22	1.08	2.38	2.13	1.63
STW-28	221	190	168.11	236.00	151.3	237.98	44.62	55.70	36.61	61.56	56.89	82.66	3.61	1.17	1.68	0.62	0.90	1.39
STW-29	323	410	146.06	245.00	160.3	228.82	41.73	49.47	38.03	48.11	65.75	63.07	2.01	1.36	1.25	2.43	3.24	2.34
STW-30	271	300	118.95	209.00	137.9	256.00	89.26	40.49	27.46	45.60	43.59	89.44	3.61	1.41	1.93	0.88	1.45	1.87

Table 4.4: SO_4^{2-}, Na and Mg ions of shallow tubewells water samples of Rajshahi City in 2009 and 2010

Sample No.	SO_4^{2-}, mg/L						Na, mg/L						Mg, mg/L					
	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
STW-1	38.40	39.54	38.47	27.67	33.50	33.18	23.58	26.54	21.56	18.67	18.99	17.53	29.35	32.58	27.82	28.67	35.33	30.52
STW-2	35.20	38.23	53.54	44.20	38.90	35.97	26.39	20.12	23.41	16.55	20.12	27.31	20.96	30.22	21.55	18.98	28.25	33.45
STW-3	34.30	33.15	27.53	23.53	34.70	29.58	14.11	15.54	12.21	11.71	17.55	24.13	21.66	33.86	25.49	27.04	27.52	30.23
STW-4	55.70	53.20	39.19	32.80	36.40	40.18	21.32	24.39	23.65	26.43	22.15	28.32	27.23	25.67	23.84	24.97	20.45	29.47
STW-5	36.90	37.19	37.02	35.18	39.10	44.54	24.75	28.47	27.38	30.21	22.99	27.34	26.45	29.58	21.78	21.22	20.66	32.56
STW-6	30.40	40.18	34.44	29.03	40.30	36.23	21.11	23.33	19.06	20.44	23.33	23.17	25.66	18.33	19.70	24.59	18.33	27.78
STW-7	39.60	42.18	40.22	38.54	42.10	31.18	26.58	24.92	22.78	15.55	24.13	19.66	27.36	24.61	26.88	25.56	18.22	33.87
STW-8	66.00	68.00	27.74	23.70	41.50	36.54	24.02	20.13	20.24	11.97	22.24	26.38	20.57	23.33	28.50	24.05	23.33	23.18
STW-9	36.57	32.38	27.74	28.62	58.00	37.23	18.58	23.84	23.66	19.79	22.43	27.23	31.35	26.73	23.50	28.55	29.98	28.36
STW-10	33.51	31.22	33.31	31.65	42.34	50.00	24.61	23.64	26.92	24.60	24.44	23.18	25.73	29.84	27.67	26.86	28.58	26.32
STW-11	37.22	38.12	41.46	32.66	31.25	53.25	28.69	20.22	18.93	24.84	23.19	21.76	35.16	33.23	27.67	26.61	29.23	35.56
STW-12	28.59	27.53	41.98	29.03	34.50	48.18	23.95	23.17	16.99	24.60	23.95	31.28	27.01	25.70	27.93	26.66	30.44	34.47
STW-13	31.26	35.26	46.21	41.30	35.35	43.39	20.49	24.29	23.51	20.24	27.31	28.54	26.76	19.81	23.06	29.87	30.12	30.19
STW-14	36.15	37.61	44.45	28.67	32.90	39.22	22.17	24.68	24.30	22.93	24.33	23.84	29.61	33.30	28.00	31.57	31.22	27.56
STW-15	33.33	36.22	30.83	34.41	35.20	32.78	18.33	23.69	22.62	23.84	18.33	39.67	26.81	27.10	23.59	24.07	27.66	31.52
STW-16	33.19	31.19	28.77	34.77	37.50	31.18	29.16	18.98	20.37	27.20	19.32	27.53	31.58	20.66	22.53	29.16	21.37	29.36
STW-17	35.67	38.17	16.54	37.75	27.20	28.56	28.04	20.22	18.86	18.95	20.22	25.44	33.54	28.98	29.16	23.94	28.98	26.88
STW-18	29.76	32.19	28.77	36.51	38.25	36.00	26.04	24.65	20.37	21.68	19.39	24.21	17.04	27.52	27.53	31.62	26.57	23.22
STW-19	39.41	41.19	32.07	26.78	41.33	37.91	35.22	23.66	20.77	26.47	25.51	23.16	28.44	25.27	21.63	32.07	30.25	24.79
STW-20	40.54	39.22	44.66	35.64	36.36	31.51	20.89	25.48	22.32	19.39	25.48	22.56	26.06	20.18	28.01	24.39	20.18	31.53
STW-21	56.82	27.56	32.59	27.55	67.08	61.02	29.19	22.43	17.84	24.60	22.17	26.74	11.52	35.75	23.65	22.44	26.19	33.08
STW-22	55.62	21.50	30.83	26.16	53.21	43.01	27.03	21.40	23.62	18.03	27.41	21.75	35.30	24.17	24.59	27.30	25.92	30.14
STW-23	27.57	43.83	51.88	42.88	57.12	36.61	21.62	25.17	23.21	23.46	21.34	17.10	24.77	27.32	29.23	34.00	29.00	35.32
STW-24	21.51	32.04	59.01	48.54	71.81	65.17	18.33	23.18	24.09	21.45	26.09	19.00	26.81	29.18	25.44	26.57	26.28	21.20
STW-25	43.84	61.26	29.08	24.76	45.83	36.70	24.76	28.11	20.40	13.66	29.53	28.11	29.28	31.00	27.54	27.16	25.78	29.83
STW-26	63.51	43.25	36.92	30.99	49.15	45.74	28.55	25.07	25.37	23.57	18.47	19.02	22.64	27.20	20.78	19.79	25.85	28.22
STW-27	52.14	20.09	31.04	26.32	61.10	62.34	26.36	21.17	22.64	16.14	29.27	20.82	26.48	30.03	25.60	23.65	26.08	33.07
STW-28	37.36	48.89	40.33	33.70	49.89	70.64	23.51	26.02	21.79	27.87	20.46	23.72	32.30	27.81	22.08	24.61	25.86	35.42
STW-29	52.30	43.83	42.08	35.09	57.03	54.87	26.39	25.17	28.00	30.08	23.34	25.08	28.42	20.23	24.93	24.79	26.00	28.12
STW-30	43.92	36.61	28.97	33.41	39.19	40.99	24.78	23.95	19.55	23.55	28.67	20.16	29.25	32.58	27.08	33.56	25.65	30.52

Table 4.5: K, Ca and Mn ions of shallow tubewells water samples of Rajshahi City in 2009 and 2010

Sample No.	K, mg/L						Ca, mg/L						Mn, mg/L					
	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
STW-1	8.22	10.45	3.05	1.88	7.16	6.78	89.99	82.22	79.48	88.15	109.29	121.29	0.716	0.663	0.640	0.754	0.787	0.813
STW-2	10.16	7.34	3.47	3.83	7.80	7.22	83.94	65.23	48.63	57.70	94.98	90.22	0.892	0.739	0.715	3.721	3.910	0.787
STW-3	7.65	6.43	2.74	2.79	10.33	9.25	78.88	85.29	51.59	44.66	75.61	93.29	1.667	1.614	1.591	3.234	3.013	1.764
STW-4	9.23	7.19	3.07	3.26	4.78	6.78	72.33	80.19	63.40	69.48	90.98	105.23	0.523	0.470	0.446	2.527	2.502	0.619
STW-5	7.15	0.22	3.01	3.38	11.78	7.34	93.67	95.22	60.65	63.28	74.21	92.09	1.013	0.660	0.636	0.490	0.523	0.963
STW-6	8.34	6.79	2.94	3.07	8.23	6.38	112.70	118.29	57.37	53.45	88.59	35.23	2.675	0.622	0.598	1.375	1.440	0.771
STW-7	7.62	8.84	3.10	3.54	6.88	8.23	68.84	65.22	64.71	68.66	66.43	88.53	0.672	0.719	0.495	2.120	2.470	0.669
STW-8	6.23	7.13	2.75	2.80	9.16	4.67	100.06	105.52	58.85	64.93	96.14	60.18	3.099	4.046	4.022	3.558	3.710	4.095
STW-9	8.56	7.14	2.75	3.12	9.34	8.55	74.50	70.29	48.85	52.79	120.90	78.34	1.720	0.667	0.644	3.698	3.571	0.817
STW-10	7.88	7.88	2.90	3.12	7.16	7.16	91.57	86.32	55.93	57.64	52.66	56.31	0.695	0.642	0.618	3.968	3.710	0.792
STW-11	6.53	6.21	3.13	3.50	7.33	7.23	81.99	90.19	76.29	67.24	92.76	104.51	0.734	0.681	0.657	1.473	1.486	0.872
STW-12	7.63	3.07	3.15	3.12	8.18	3.90	110.99	108.78	66.94	62.74	82.72	78.52	2.131	2.078	2.054	2.678	2.691	2.228
STW-13	8.15	3.01	3.27	2.91	9.56	10.51	105.11	92.33	67.32	54.71	81.22	85.13	1.597	1.544	1.520	1.985	1.999	1.694
STW-14	7.14	2.94	3.22	1.38	7.14	6.64	85.22	90.55	70.09	52.09	76.46	75.38	2.748	2.695	2.671	0.699	0.871	2.845
STW-15	4.90	3.89	2.83	3.17	6.89	7.13	95.22	98.42	52.78	62.36	80.75	81.25	2.683	0.630	0.607	2.375	2.880	0.780
STW-16	7.88	6.95	2.78	1.35	8.98	9.04	100.15	105.29	50.16	63.01	85.22	83.58	0.847	2.794	0.770	1.354	1.430	0.943
STW-17	6.21	8.54	2.43	2.04	8.83	6.89	110.23	112.29	34.63	48.34	61.25	65.20	0.615	0.615	0.538	2.186	2.186	0.711
STW-18	8.84	3.76	2.78	3.09	7.40	4.21	105.51	102.49	50.16	56.13	28.31	98.04	2.267	2.214	2.190	1.556	1.569	2.363
STW-19	7.75	4.04	2.87	1.45	7.75	10.09	111.56	108.12	54.36	48.71	30.54	30.97	0.976	0.623	0.599	0.805	0.819	0.773
STW-20	8.52	7.23	3.22	4.12	8.16	8.34	120.55	115.28	70.35	54.57	35.11	68.59	0.785	0.732	0.708	0.305	0.318	0.881
STW-21	6.89	4.12	2.88	2.99	8.19	4.54	91.26	80.56	78.01	72.09	103.10	90.52	0.892	0.639	0.615	0.062	0.056	0.788
STW-22	5.99	8.27	2.83	2.92	7.72	3.50	74.50	98.32	52.78	34.96	91.20	75.07	1.011	1.958	0.934	0.060	0.060	1.107
STW-23	5.13	6.76	3.43	3.76	7.85	6.54	98.96	100.94	83.53	75.60	97.36	64.98	2.150	2.097	2.073	1.320	1.460	2.246
STW-24	8.29	3.76	3.63	4.04	8.35	4.54	100.15	91.26	58.57	64.65	120.57	110.07	0.795	0.742	0.719	0.052	0.065	0.892
STW-25	11.44	4.04	2.78	2.85	7.47	3.48	81.99	106.37	50.55	46.63	79.53	65.11	0.610	2.557	0.533	0.100	0.100	0.707
STW-26	7.77	3.17	3.00	3.17	7.58	7.50	95.66	93.70	69.52	78.59	94.78	109.40	1.550	1.497	1.474	1.310	1.099	1.647
STW-27	8.66	4.04	2.84	2.93	7.98	6.57	105.51	81.51	53.05	49.12	103.66	105.62	1.685	0.632	0.608	3.040	2.995	3.213
STW-28	8.48	4.78	3.10	3.30	7.61	3.57	70.19	63.56	44.84	36.92	95.96	104.73	3.117	3.064	3.064	0.623	4.269	3.981
STW-29	5.39	7.15	3.15	3.37	7.85	5.29	96.69	89.06	67.07	63.15	97.23	93.82	0.700	0.647	0.647	0.750	0.700	0.796
STW-30	7.83	3.30	2.78	3.89	7.25	7.41	83.52	73.70	50.42	53.37	69.04	121.35	2.596	2.543	2.543	0.519	0.499	0.692

Table 4.6: Fe, Cu and Zn ions of shallow tubewells water samples of Rajshahi City in 2009 and 2010

Sample No.	Fe, mg/L						Cu, mg/L						Zn, mg/L					
	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
STW-1	3.69	5.12	1.00	0.64	5.54	5.98	0.031	0.041	0.024	0.050	0.067	0.080	0.098	0.150	0.083	0.165	0.262	0.241
STW-2	2.89	4.56	1.29	0.32	2.69	3.22	0.012	0.015	0.010	0.040	0.067	0.065	0.077	0.130	0.036	0.002	0.240	0.292
STW-3	4.15	3.73	0.81	0.50	3.37	5.63	0.042	0.031	0.005	0.013	0.401	0.075	0.224	0.320	0.017	0.017	0.240	0.323
STW-4	3.28	3.75	0.25	3.15	5.14	2.98	0.300	0.280	0.008	0.016	0.067	0.770	0.095	0.180	0.027	0.011	0.151	0.356
STW-5	3.91	6.90	0.99	0.98	6.91	5.23	0.045	0.034	0.006	0.012	0.000	0.088	0.110	0.220	0.022	0.018	0.121	0.278
STW-6	4.06	0.33	0.84	5.03	6.70	2.89	0.056	0.060	0.008	0.015	0.268	0.072	0.319	0.420	0.029	0.043	0.185	0.291
STW-7	4.91	3.46	0.44	0.50	4.91	3.52	0.500	0.510	0.017	0.039	0.101	0.078	0.083	0.090	0.059	0.028	0.209	0.331
STW-8	2.89	1.04	0.71	0.64	2.83	5.23	0.070	0.085	0.008	0.016	0.325	0.720	0.110	0.210	0.029	0.030	0.462	0.372
STW-9	3.22	2.68	1.01	0.28	5.24	4.67	0.014	0.016	0.007	0.022	0.101	0.121	0.113	0.110	0.023	0.017	0.129	0.198
STW-10	1.72	3.52	0.92	0.32	4.93	5.78	0.042	0.085	0.016	0.008	0.000	0.001	0.108	0.080	0.055	0.074	0.156	0.212
STW-11	3.15	3.15	1.07	1.82	5.12	2.58	0.075	0.028	0.008	0.031	0.062	0.071	0.150	0.190	0.029	0.027	0.255	0.237
STW-12	3.21	3.74	0.67	0.76	5.74	2.18	0.025	0.350	0.004	0.012	0.074	0.056	0.190	0.180	0.013	0.054	0.245	0.321
STW-13	2.88	4.74	0.54	0.96	5.90	6.37	0.300	0.048	0.012	0.021	0.069	0.002	0.130	0.090	0.043	0.041	0.289	0.218
STW-14	3.69	5.73	1.12	1.75	5.38	3.88	0.042	0.025	0.010	0.012	0.063	0.003	0.170	0.130	0.034	0.054	0.261	0.271
STW-15	3.19	3.74	0.87	0.85	7.00	4.66	0.015	0.023	0.016	0.041	0.013	0.052	0.230	0.009	0.056	0.040	0.131	0.321
STW-16	1.04	0.34	0.53	2.85	6.24	3.62	0.060	0.065	0.001	0.021	0.002	0.009	0.080	0.450	0.002	0.046	0.141	0.298
STW-17	3.55	4.59	0.61	0.90	5.52	4.78	0.057	0.055	0.009	0.011	0.059	0.420	0.350	0.390	0.033	0.064	0.312	0.281
STW-18	2.87	3.64	0.83	0.88	8.04	4.29	0.060	0.015	0.013	0.021	0.425	0.490	0.320	0.510	0.045	0.045	0.276	0.292
STW-19	7.89	2.54	0.84	2.72	5.89	3.41	0.012	0.014	0.024	0.031	0.411	0.080	0.290	0.320	0.084	0.037	0.310	0.942
STW-20	2.47	3.19	1.26	1.87	4.98	4.23	0.058	0.065	0.011	0.002	0.360	0.130	0.380	0.430	0.038	0.059	0.982	0.341
STW-21	4.21	3.58	0.90	2.52	3.87	3.11	0.016	0.101	0.015	0.008	0.055	0.026	0.150	0.013	0.052	0.049	0.749	0.115
STW-22	3.46	2.62	0.87	0.50	2.81	4.80	0.008	0.325	0.004	0.007	0.006	0.062	0.224	0.043	0.012	0.090	0.099	0.413
STW-23	3.43	5.65	1.26	0.46	2.46	3.76	0.004	0.101	0.015	0.015	0.023	0.119	0.599	0.034	0.051	0.041	0.329	0.605
STW-24	1.94	4.58	1.30	0.48	5.13	2.17	0.013	0.401	0.010	0.013	0.048	0.033	0.013	0.056	0.034	0.056	0.661	0.314
STW-25	6.90	1.63	0.59	0.14	5.80	2.76	0.024	0.067	0.042	0.020	0.006	0.033	0.043	0.110	0.147	0.013	0.109	0.092
STW-26	4.13	2.68	0.36	0.39	3.00	2.89	0.015	0.023	0.067	0.027	0.001	0.150	0.059	0.330	0.235	0.055	0.035	0.709
STW-27	0.33	5.62	0.88	0.82	3.91	3.13	0.004	0.048	0.009	0.035	0.040	0.063	0.083	0.090	0.032	0.037	0.553	0.415
STW-28	6.90	3.60	1.04	0.78	5.89	3.25	0.014	0.028	0.217	0.055	0.036	0.058	0.934	0.022	0.067	0.158	0.503	0.399
STW-29	3.95	2.80	1.09	1.37	3.34	4.02	0.008	0.002	0.014	0.062	0.013	0.092	0.022	0.029	0.050	0.022	0.191	0.515
STW-30	2.89	3.59	0.54	0.32	2.56	2.27	0.017	0.059	0.066	0.054	0.060	0.026	0.110	0.059	0.230	0.034	0.815	0.116

Table 4.7: As, Cd and Pb ions of shallow tubewells water samples of Rajshahi City in 2009 and 2010

Sample No.	As, mg/L						Cd, mg/L						Pb, mg/L					
	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
STW-1	0.009	0.010	0.008	0.007	0.019	0.021	0.006	0.012	0.021	0.025	0.017	0.018	0.005	0.001	0.278	0.262	3.936	3.820
STW-2	0.009	0.020	0.009	0.004	0.020	0.019	0.007	0.016	0.013	0.022	0.001	0.001	0.006	0.018	0.130	0.113	4.014	3.290
STW-3	0.015	0.011	0.004	0.023	0.069	0.050	0.003	0.001	0.016	0.019	0.002	0.003	0.017	0.019	0.174	0.198	2.362	3.540
STW-4	0.045	0.008	0.020	0.012	0.018	0.010	0.004	0.009	0.018	0.035	0.001	0.009	0.015	0.013	0.214	0.170	3.936	3.220
STW-5	0.005	0.005	0.018	0.002	0.030	0.009	0.002	0.008	0.016	0.023	0.005	0.001	0.010	0.021	0.176	0.184	3.400	2.880
STW-6	0.003	0.060	0.007	0.008	0.007	0.005	0.011	0.002	0.021	0.038	0.001	0.005	0.020	0.022	0.278	0.262	3.621	3.750
STW-7	0.043	0.049	0.004	0.003	0.023	0.005	0.003	0.001	0.012	0.028	0.021	0.021	0.010	0.031	0.101	0.085	3.778	3.880
STW-8	0.054	0.020	0.007	0.007	0.009	0.007	0.002	0.005	0.023	0.030	0.008	0.020	0.016	0.029	0.313	0.269	3.621	3.220
STW-9	0.008	0.002	0.012	0.008	0.002	0.040	0.006	0.013	0.018	0.023	0.002	0.005	0.020	0.340	0.222	0.205	2.834	3.180
STW-10	0.007	0.015	0.034	0.004	0.002	0.004	0.002	0.001	0.018	0.028	0.003	0.010	0.025	0.021	0.214	0.198	2.519	2.180
STW-11	0.010	0.009	0.005	0.008	0.025	0.058	0.010	0.020	0.015	0.020	0.015	0.001	0.020	0.022	0.165	0.206	3.892	3.820
STW-12	0.008	0.010	0.024	0.010	0.009	0.006	0.002	0.018	0.021	0.028	0.019	0.005	0.010	0.011	0.273	0.309	3.975	3.580
STW-13	0.016	0.007	0.020	0.006	0.035	0.010	0.009	0.090	0.013	0.001	0.017	0.018	0.030	0.033	0.120	0.104	3.832	3.670
STW-14	0.018	0.005	0.008	0.010	0.007	0.018	0.007	0.008	0.019	0.027	0.017	0.013	0.005	0.005	0.233	0.301	3.946	2.210
STW-15	0.050	0.006	0.010	0.006	0.016	0.030	0.006	0.008	0.013	0.021	0.004	0.019	0.012	0.075	0.118	0.102	3.120	3.720
STW-16	0.080	0.018	0.013	0.008	0.008	0.007	0.001	0.011	0.020	0.025	0.007	0.013	0.017	0.030	0.259	0.228	3.300	3.550
STW-17	0.065	0.020	0.081	0.007	0.034	0.080	0.005	0.008	0.018	0.021	0.007	0.009	0.023	0.040	0.211	0.160	3.892	3.620
STW-18	0.009	0.018	0.044	0.007	0.020	0.068	0.002	0.010	0.017	0.023	0.007	0.012	0.020	0.011	0.189	0.166	3.552	3.370
STW-19	0.007	0.012	0.001	0.008	0.009	0.018	0.003	0.022	0.018	0.020	0.009	0.009	0.010	0.020	0.222	0.206	3.498	3.490
STW-20	0.009	0.023	0.009	0.011	0.025	0.005	0.001	0.015	0.023	0.017	0.006	0.007	0.011	0.015	0.306	0.386	3.654	3.360
STW-21	0.011	0.025	0.008	0.011	0.013	0.005	0.005	0.005	0.018	0.026	0.006	0.008	0.008	0.007	0.214	0.198	2.440	3.540
STW-22	0.015	0.009	0.007	0.007	0.008	0.007	0.024	0.018	0.017	0.020	0.001	0.007	0.011	0.003	0.203	0.255	2.780	2.950
STW-23	0.049	0.035	0.002	0.009	0.034	0.016	0.015	0.001	0.015	0.042	0.001	0.003	0.003	0.002	0.165	0.149	2.770	2.590
STW-24	0.002	0.007	0.007	0.031	0.057	0.034	0.008	0.021	0.015	0.024	0.006	0.002	0.004	0.005	0.165	0.149	3.310	2.450
STW-25	0.029	0.016	0.028	0.044	0.006	0.009	0.010	0.018	0.016	0.016	0.010	0.002	0.016	0.007	0.181	0.170	3.510	3.369
STW-26	0.066	0.012	0.009	0.003	0.002	0.017	0.013	0.090	0.021	0.033	0.006	0.003	0.008	0.002	0.271	0.255	2.450	3.426
STW-27	0.019	0.034	0.008	0.013	0.004	0.023	0.081	0.020	0.016	0.022	0.006	0.001	0.005	0.008	0.186	0.170	3.300	2.369
STW-28	0.001	0.005	0.007	0.007	0.017	0.009	0.004	0.015	0.017	0.027	0.004	0.004	0.003	0.003	0.189	0.177	2.590	3.331
STW-29	0.036	0.024	0.007	0.004	0.003	0.009	0.020	0.008	0.019	0.020	0.013	0.006	0.002	0.008	0.243	0.226	3.750	2.198
STW-30	0.041	0.012	0.004	0.007	0.019	0.014	0.011	0.013	0.014	0.029	0.003	0.008	0.004	0.003	0.136	0.184	2.620	2.980

Table 4.8: Total Coliform (TC) and Faecal Coliform (FC) of shallow tubewells water samples of Rajshahi City during post-monsoon in 2010

Location	TC, CFU/100mL	FC, CFU/100mL
STW-1	3	1
STW-2	10	0
STW-3	8	0
STW-4	9	0
STW-5	6	0
STW-6	5	2
STW-7	8	0
STW-8	6	1
STW-9	6	0
STW-10	4	0
STW-11	11	0
STW-12	3	0
STW-13	2	0
STW-14	16	6
STW-15	13	4
STW-16	2	0
STW-17	6	1
STW-18	11	2
STW-19	7	0
STW-20	3	0
STW-21	1	0
STW-22	0	0
STW-23	8	3
STW-24	2	0
STW-25	13	2
STW-26	1	0
STW-27	0	0
STW-28	4	0
STW-29	13	2
STW-30	5	0

Appendix-5: Physico-chemical and microbial parameters of deep tubewells water samples of Rajshahi City

Table 5.1: Temperature, pH and EC of deep tubewells water samples of Rajshahi City in 2009 and 2010

Sample No.	Temperature °C						pH						EC, µS/cm					
	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
DTW-1	26.00	26.50	31.00	33.00	25.00	25.50	7.57	7.52	6.70	6.29	7.20	7.18	335	377	517	577	802	461
DTW-2	25.50	25.00	29.00	28.50	26.00	26.50	7.83	7.78	5.94	6.61	6.70	7.22	335	398	410	345	871	398
DTW-3	26.50	26.00	28.25	28.75	27.70	27.00	7.88	7.69	6.77	6.37	6.70	7.15	419	434	356	277	885	690
DTW-4	26.00	26.50	28.00	28.00	26.50	25.00	7.88	7.61	6.45	6.25	6.90	6.90	377	307	289	346	460	628
DTW-5	25.00	25.50	27.75	28.25	27.00	27.50	7.58	7.68	6.51	6.12	7.10	6.89	405	370	367	382	842	673
DTW-6	26.00	27.75	29.00	27.25	27.00	25.50	7.81	7.82	6.56	6.39	7.00	7.12	391	412	320	270	470	384
DTW-7	25.50	28.50	31.00	32.50	26.00	26.00	7.67	7.58	6.29	6.29	7.10	7.20	293	321	267	219	730	497
DTW-8	26.50	29.00	29.25	28.00	27.00	25.00	7.82	7.78	6.43	6.04	7.25	6.70	433	405	290	237	830	727
DTW-9	25.50	28.00	27.00	26.00	26.50	27.00	7.79	7.68	5.89	5.55	7.15	6.80	349	398	388	413	630	426
DTW-10	25.00	28.50	28.75	28.00	26.00	25.50	7.55	7.58	5.75	4.96	7.11	7.10	377	433	308	219	855	674

* **DTW-Deep Tubewells Water**

Table 5.2: TDS, TSS and Total Hardness of deep tubewells water samples of Rajshahi City in 2009 and 2010

Sample No.	TDS, mg/L						TSS, mg/L						TH, mg/L					
	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
DTW-1	240	270	315.00	364.00	240	270	100	200	200	120	200	210	250	300	178.41	155.59	748	743
DTW-2	240	285	245.38	174.66	240	285	140	100	120	90	190	200	192	180	184.95	153.14	250	258
DTW-3	300	310	186.63	100.68	300	310.9	120	100	100	80	120	150	336	318	218.25	200.69	600	588
DTW-4	270	220	113.73	175.75	270	220	100	200	190	100	200	200	248	266	192.34	213.32	424	438
DTW-5	290	265	198.60	214.92	290	265	100	100	170	170	200	100	296	308	157.58	189.91	348	330
DTW-6	260	295	136.84	118.37	280	295	100	200	250	100	200	200	205	210	168.80	208.38	428	418
DTW-7	210	230	197.80	163.57	210	230	100	110	100	150	120	150	315	335	113.69	180.08	460	449
DTW-8	310	290	114.82	157.16	310	290	150	180	80	100	200	200	340	330	182.28	193.37	380	389
DTW-9	250	285	182.44	211.64	250	285	200	170	160	110	100	130	268	278	138.29	215.58	510	480
DTW-10	270	310	168.40	137.57	270	310	100	200	150	190	200	200	290	315	191.18	190.08	342	348

Table 5.3: HCO_3^-, Cl^- and NO_3^- of deep tubewells water samples of Rajshahi City in 2009 and 2010

Sample No.	HCO_3^-, mg/L						Cl^-, mg/L						NO_3^-, mg/L					
	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
DTW-1	216.80	176.98	107.71	140	262.50	237.50	55.58	60.29	32.03	30.03	42.99	45.98	1.18	1.31	1.80	1.07	1.17	1.15
DTW-2	163.99	170.58	187.00	163	200.00	185.00	43.20	40.29	21.82	15.59	48.99	47.93	1.22	1.52	0.61	1.12	1.48	1.53
DTW-3	332.00	380.00	119.00	147	145.50	160.00	83.98	88.98	31.71	41.09	39.99	37.99	1.11	1.39	2.52	1.49	1.60	1.65
DTW-4	208.00	258.00	113.00	146	145.00	135.00	53.99	48.29	31.58	36.04	29.99	31.99	0.10	0.30	3.40	1.62	3.12	3.08
DTW-5	248.00	280.00	121.00	108	122.00	171.50	81.98	83.54	39.73	31.03	87.98	80.99	0.12	0.18	0.54	1.63	1.25	1.18
DTW-6	127.50	138.00	267.00	236	68.00	150.00	54.99	59.98	31.69	25.02	25.25	29.99	1.49	1.52	2.50	1.39	2.82	2.78
DTW-7	108.55	190.11	187.00	222	109.50	421.50	49.99	52.98	51.53	24.53	35.99	34.99	1.23	1.32	2.36	1.57	4.60	3.98
DTW-8	237.00	337.00	234.00	259	123.50	131.00	41.98	38.98	49.58	40.84	32.33	34.99	3.11	2.88	2.04	1.77	1.26	1.29
DTW-9	155.00	183.00	139.00	162	191.00	168.00	45.99	52.98	31.78	39.13	33.89	31.99	1.18	1.32	1.66	2.64	2.11	2.15
DTW-10	218.00	238.00	205.00	241	118.00	131.00	82.98	78.98	31.62	29.51	38.99	34.99	1.72	1.60	1.04	0.57	1.23	1.32

Table 5.4: SO_4^{2-}, Na and Mg ions of deep tubewells water samples of Rajshahi City in 2009 and 2010

Sample No.	SO_4^{2-}, mg/L						Na, mg/L						Mg, mg/L					
	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
DTW-1	33.10	37.92	37.06	32.56	59.47	63.23	19.42	23.72	22.23	17.84	28.40	27.23	19.22	21.55	26.31	27.07	33.12	29.55
DTW-2	44.80	42.52	33.21	33.54	67.50	32.33	20.55	19.37	20.09	17.61	21.33	26.55	21.85	23.66	24.97	24.59	28.67	26.44
DTW-3	35.90	35.95	31.27	27.96	37.00	35.92	23.22	18.12	19.01	18.75	31.33	27.88	31.45	29.95	24.29	29.49	29.75	33.17
DTW-4	31.91	50.62	28.85	33.62	38.90	33.13	28.39	17.38	17.67	27.74	29.33	29.53	29.56	25.43	23.44	19.06	23.18	30.27
DTW-5	50.60	48.55	31.66	36.57	31.23	37.23	25.94	17.96	19.23	24.84	27.54	27.34	25.75	22.54	24.42	21.36	30.24	27.83
DTW-6	37.54	39.29	30.94	31.40	35.88	33.58	21.06	21.63	18.83	24.22	25.22	22.45	27.44	23.86	23.83	19.31	29.78	22.45
DTW-7	35.29	33.58	28.06	23.20	38.24	40.29	18.55	17.18	17.23	11.19	21.52	19.45	24.87	23.95	23.16	22.00	33.20	27.31
DTW-8	31.33	33.54	28.89	24.68	47.62	48.15	21.38	24.15	17.69	13.53	31.29	28.55	18.98	33.55	23.45	28.15	28.92	29.56
DTW-9	38.54	40.48	32.42	39.11	41.55	40.13	27.22	19.36	19.65	16.51	39.67	29.14	26.20	28.34	24.69	25.61	29.54	35.52
DTW-10	40.52	39.29	29.54	23.20	48.12	47.18	19.98	23.71	18.05	11.19	39.58	31.23	25.39	24.85	23.68	19.00	30.19	28.20

Table 5.5: *K, Ca and Mn ions of deep tubewells water samples of Rajshahi City in 2009 and 2010*

Sample No.	K, mg/L						Ca, mg/L						Mn, mg/L					
	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
DTW-1	6.72	6.23	3.05	4.24	7.16	8.22	88.15	92.16	74.19	61.07	91.06	88.13	2.129	1.574	0.517	0.618	0.831	0.696
DTW-2	7.15	4.78	3.98	3.29	8.45	7.23	95.60	72.23	63.11	39.51	108.49	110.58	0.838	0.549	3.972	4.110	3.324	4.151
DTW-3	8.23	7.18	2.95	3.01	7.22	4.55	64.63	70.69	83.57	92.76	87.88	75.23	0.647	0.588	2.373	2.724	2.938	2.551
DTW-4	6.98	8.15	3.56	3.30	6.66	7.45	101.37	105.29	38.89	44.79	70.04	85.32	0.754	1.985	2.646	4.026	3.960	2.824
DTW-5	6.78	7.32	1.96	3.50	9.25	7.22	101.08	103.36	87.68	69.96	46.62	48.53	0.873	0.377	3.410	3.830	4.043	3.088
DTW-6	3.89	4.23	2.95	3.19	7.19	5.46	95.29	70.29	56.47	51.28	95.88	80.23	0.875	0.567	3.649	3.295	2.908	3.277
DTW-7	3.07	5.32	5.90	5.78	8.88	7.95	110.54	105.59	50.67	37.70	103.25	108.15	2.537	1.829	1.484	0.315	0.528	1.662
DTW-8	2.77	3.49	2.91	2.85	10.75	8.21	73.29	88.24	86.90	67.96	89.62	103.58	0.535	0.626	3.508	4.943	4.156	3.662
DTW-9	6.35	5.70	3.97	3.57	10.09	5.78	50.23	58.59	59.89	69.57	86.24	88.29	2.961	2.602	0.501	0.037	0.251	0.680
DTW-10	3.76	4.38	3.12	4.78	7.29	8.23	80.54	68.69	49.08	53.59	93.89	95.54	0.838	0.537	3.971	4.647	4.061	3.496

Table 5.6: *Fe, Cu and Zn ions of deep tubewells water samples of Rajshahi City in 2009 and 2010*

Sample No.	Fe, mg/L						Cu, mg/L						Zn, mg/L					
	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
DTW-1	1.92	1.45	0.52	0.46	5.90	4.67	0.310	0.340	0.038	0.065	0.451	0.395	0.235	0.310	0.033	0.083	0.495	0.530
DTW-2	1.56	2.13	0.93	0.39	7.01	3.42	0.240	0.530	0.025	0.040	0.368	0.380	0.132	0.250	0.059	0.036	0.111	0.130
DTW-3	2.20	0.45	0.39	0.25	4.23	5.34	0.310	0.320	0.022	0.028	0.301	0.320	0.289	0.372	0.029	0.016	0.300	0.280
DTW-4	2.39	3.80	0.64	0.43	4.66	3.29	0.420	0.130	0.040	0.015	0.036	0.100	0.161	0.170	0.034	0.013	0.109	0.150
DTW-5	2.77	1.90	0.42	0.36	2.92	3.04	0.090	0.190	0.013	0.013	4.077	3.890	0.163	0.110	0.055	0.022	0.093	0.070
DTW-6	3.03	1.85	1.54	1.03	3.50	2.24	0.540	0.510	0.005	0.038	0.151	0.020	0.290	0.320	0.022	0.056	0.032	0.036
DTW-7	0.97	0.38	0.49	0.25	4.29	2.75	0.390	0.320	0.025	0.025	0.013	0.450	0.090	0.430	0.039	0.018	0.262	0.320
DTW-8	2.27	1.56	0.51	0.60	3.80	2.28	0.280	0.420	0.003	0.013	0.376	0.370	0.220	0.270	0.021	0.014	0.725	0.750
DTW-9	2.39	1.65	0.89	0.60	4.53	4.08	0.080	0.150	0.037	0.010	0.041	0.280	0.170	0.310	0.053	0.030	0.325	0.310
DTW-10	1.03	3.23	1.83	0.55	5.38	4.16	0.890	0.790	0.001	0.019	0.021	3.820	0.130	0.192	0.070	0.018	0.089	0.130

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Table 5.7: As, Cd and Pb ions of deep tubewells water samples of Rajshahi City in 2009 and 2010

Sample No.	As, mg/L						Cd, mg/L						Pb, mg/L					
	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
DTW-1	0.010	0.006	0.017	0.010	0.010	0.018	0.010	0.018	0.040	0.031	0.003	0.001	0.009	0.011	0.093	0.113	3.936	3.890
DTW-2	0.009	0.010	0.004	0.008	0.028	0.011	0.007	0.011	0.023	0.030	0.003	0.015	0.016	0.021	0.244	0.135	3.149	3.210
DTW-3	0.008	0.056	0.005	0.009	0.017	0.015	0.005	0.023	0.039	0.037	0.007	0.013	0.025	0.032	0.098	0.198	3.385	3.310
DTW-4	0.009	0.008	0.005	0.013	0.004	0.009	0.006	0.009	0.037	0.015	0.007	0.011	0.020	0.023	0.119	0.198	3.621	3.510
DTW-5	0.009	0.019	0.017	0.009	0.014	0.009	0.002	0.013	0.024	0.014	0.001	0.002	0.020	0.028	0.240	0.184	2.440	2.620
DTW-6	0.010	0.009	0.009	0.007	0.002	0.006	0.001	0.007	0.034	0.023	0.001	0.001	0.011	0.018	0.149	0.177	2.780	3.590
DTW-7	0.015	0.009	0.003	0.008	0.008	0.013	0.009	0.008	0.026	0.017	0.027	0.001	0.018	0.025	0.218	0.198	2.770	3.180
DTW-8	0.012	0.020	0.006	0.032	0.005	0.025	0.012	0.020	0.038	0.051	0.021	0.018	0.029	0.028	0.110	0.170	3.130	2.280
DTW-9	0.008	0.016	0.002	0.029	0.002	0.019	0.019	0.022	0.034	0.015	0.017	0.029	0.025	0.032	0.146	0.269	3.530	3.090
DTW-10	0.001	0.006	0.007	0.007	0.010	0.056	0.003	0.004	0.029	0.010	0.003	0.021	0.022	0.058	0.195	0.255	2.470	3.440

Table 5.8: Total Coliform (TC) and Faecal Coliform (FC) of deep tubewells water samples of Rajshahi City during post-monsoon in 2010

Sample No.	TC, CFU/100mL	FC, CFU/100mL
DTW-1	3	0
DTW-2	1	0
DTW-3	1	1
DTW-4	0	0
DTW-5	2	1
DTW-6	0	0
DTW-7	0	0
DTW-8	2	1
DTW-9	0	0
DTW-10	3	0

List of publications from this work

Article in Journal

1. Helal Uddin, S. M., Mostafa, M. G. and Haque, A. B. M. H., 2011. Evaluation of Groundwater Quality and its Suitability for Drinking Purpose in Rajshahi City, Bangladesh. *Journal of Water Science and Technology: Water Supply.* UK, London, **11** (5), 545-558.

Articles and abstracts in the conference and symposium proceedings

1. Helal Uddin, S. M., Mostafa, M. G. and Haque, A. B. M. H., 2010. Hydrochemistry of Groundwater in Rajshahi City, Bangladesh. *Proceedings of the 1st International Seminar on Climate Change*, Institute of Environmental Science, University of Rajshahi, Rajshahi, Bangladesh, 7-9 December 2010, pp. 116-117.

2. Mostafa, M. G., Helal Uddin, S. M. and Haque, A. B. M. H., 2011. Evaluation of Groundwater Quality in Rajshahi City, Bangladesh and its Suitability for drinking Purpose. *International Conference on Integrated Water Management*, Murdock University, Perth, Australia, 2-5 February 2011, pp. 95-96.

3. Helal Uddin, S. M., Mostafa, M. G., Haque, A. B. M. H., Rahman M. R., and Sikder, M. B. H., 2012. Sustainable Management in Water Supply System in Rajshahi City, Bangladesh. *Proceedings of the 2nd International Conference on Environmental Technology and Construction Engineering for Sustainable Development (ICETCESD 2012)*, Department of Civil and Environmental Engineering, Shahjalal University of Science and Technology, Sylhet, Bangladesh, 10-12 March 2012, pp. 1473-1482.

4. Helal Uddin, S. M., Mostafa, M. G. and Haque, A. B. M. H., 2012. Geochemistry of Groundwater in Rajshahi City, Bangladesh. *Zoha Memorial Symposium*, Department of Chemistry, University of Rajshahi, Bangladesh, 15 February 2012, pp. 16.

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