FIRAT UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
TÜRKİYE

THE HYDROGEOCHEMICAL INVESTIGATION OF GROUNDWATERS IN ERBIL BASIN (NORTH OF IRAQ)

Salman Kareem Hamad BNDYAN

Master's Thesis

DEPARTMENT OF GEOLOGICAL ENGINEERING

Division of Hydrogeology

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THESIS APPROVAL

This thesis, which was prepared according to the thesis writing rules of the Graduate School of Natural and Applied Sciences, Fırat University, was evaluated by the committee members who have signed the following signatures and was unanimously approved after the defense exam made open to the academic audience.

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DECLARATION

I hereby declare that I wrote this Master's Thesis titled “The Hydrogeochemical Investigation of Groundwaters in Erbil Basin (North of Iraq)” in consistent with the thesis writing guide of the Graduate School of Natural and Applied Sciences, Firat University. I also declare that all information in it is correct, that I acted according to scientific ethics in producing and presenting the findings, cited all the references I used, express all institutions or organizations or persons who supported the thesis financially. I have never used the data and information I provide here in order to get a degree in any way.

27 June 2022

Salman Kareem Hamad BNDYAN

PREFACE

This study, titled" The Hydrogeochemical Investigation of Groundwaters in Erbil Basin (Iraq)" is very important to know the properties and the quality of groundwater in the study area and its suitability for drinking or irrigation purposes, and its important to estimate the age and the source of groundwater in the area.

The strong point of this study is the isotope hydrology study, which is part of this study and it is a very important and new topic in the area. It is one of the methods not used in the Erbil Basin so far, and it is considered the second of its kind in isotope in Erbil province.

First and foremost, I owe my gratitude to the creator, "Allah," for providing me with the strength and patience to make this dream a reality. Allah is praised for the accomplishment of this thesis. My special thanks to my family, my lovely mother, My children Mustafa and Safa, my wife, and Mr.Adel for his continuous support in all respects during my stay in Turkey.

The author wishes to thank the Turkish Government/University of Fırat/Institute of Science and Technology/Department of Geological Engineering/Applied Geology(Hydrogeology) for providing me with the opportunity to achieve a master's degree in the Geological Engineering Department and for making available facilities and administrative and financial support by Fırat university scientific research projects(FÜBAP) with the project number.

I cannot fully express my sincere thanks and appreciation to Asst. Prof. Dr. Özlem Öztekin Okan, for her kind supervision of this project, insightful discussions, and unwavering support throughout this study.

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Finally, I'd like to thank everyone who helped me and who I've forgotten to thank.

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Salman Kareem Hamad BNDYAN

ELAZIG, 2022

TABLE OF CONTENTS

ABSTRACT

The Hydrogeochemical Investigation of Groundwaters in Erbil Basin (North of Iraq)

Salman Kareem Hamad BNDYAN

Master's Thesis

FIRAT UNIVERSITY
Graduate School of Natural and Applied Sciences

Department of Geological Engineering

June 2022, Page: xiii + 99

This study aims to investigate the chemical and trace element hydrogeochemistry of groundwaters in the Erbil Basin. The analyses of groundwaters were carried out in the rainy and dry seasons. Samples were collected for isotopic analyzes during the dry season. The pH, temperature, and EC measurements of the groundwaters were made in the field.

The temperature, pH, and EC of the groundwaters in the rainy season were between 21.9 ºC and 27.2 ºC; 7.8 and 9.1, 60 µS/cm and 3310 µS/cm, respectively. In the dry season, ranged from 20 °C to 25 °C; 7.4 to 7.8, and, from 380 µS/cm to 5178 µS/cm, respectively. The chemical analysis results were evaluated with the help of Piper, Scholler, and Gibbs diagrams. The dominant cations in the groundwaters were Mg^{2+}, and Ca^{2+}, whereas the dominant anions were HCO_3^- and Cl^-. Related to the Gibbs diagrams groundwater-rock interaction is the major source of chemical compositions of groundwaters. The $\delta^{18}O$ and $\delta^{2}H$ contents of groundwaters were ranged from -4.65‰ to -7.02‰, and from -25.98‰ to -42.68‰, respectively. The ^{3}H contents of the groundwaters were analysed between 0.27TU and 2.77 TU. According to the results of isotope analysis, the investigated groundwaters are of meteoric origin.

The concentrations of Mg^{2+}, HCO_3^-, NO_3^-, B, and Pb are high and exceed the permissible limits of WHO and Iraqi drinking water standards. The reasons are urbanization, septics, sewage, waste disposal leaking, fertilizers, and pesticides. For sustainability of groundwater quality, it should be avoided to use excessive fertilizers in agriculture, implementations such as septic tanks and domestic waste must be discharged into an appropriate sewage system.

Keywords: Erbil Basin, Hydrogeology, Hydrogeochemistry, Alluvium aquifer, Sulfate, Isotope

ÖZET

Erbil Havzası (Irak'ın Kuzeyi) Yeraltı Sularının Hidrojeokimyasal İncelemesi

Salman Kareem Hamad BNDYAN

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Çalışmanın amacı, Erbil Havzası'ndaki yeraltı sularının ana ve iz element hidrojeokimyasının incelenmesidir. Bu çalışmada kapsamında, yeraltı sularının kimyasal ve iz element analizleri yağışlı ve kurak dönemleri temsil edecek şekilde Mayıs (2021) ve Ekim (2021) aylarında yapılmıştır. Suların izotop analizler için su örnekleri sadece kurak dönemde örneklenmiştir. Su örnekleri alınırken suların pH, sıcaklık (T) ve elektriksel iletkenlik (EC) değerleri arazide yerinde ölçülmüştür. Suların kimyasal ve izotop analiz sonuçları çeşitli grafikler yardımıyla değerlendirilmiştir.

İncelenen yeraltı sularının yağışlı dönemde, sıcaklık, pH ve elektriksel iletkenlik (EC) değerleri sırasıyla 21.9 ºC ile 27.2 ºC; 7,8 ile 9,1 ve 60 µS/cm ile 3310 µS/cm arasındadır. Kurak dönemde ise suların sıcaklıkları 20 °C ile 25 °C arasında, pH'ları 7,4 ile 7,8 arasında ve EC'leri ise 380 µS/cm ila 5178 µS/cm arasında değişmektedir. İncelenen suların kimyasal analiz sonuçları Piper, Scholler ve Gibbs diyagramları yardımıyla değerlendirilmiştir. Yeraltı sularında baskın katyonlar Mg^{2+}, Ca^{2+}, baskın anyonlar ise HCO_3^- ve Cl^-'dür. Gibbs diyagramları yardımıyla, incelenen yeraltı sularının kimyasal bileşiminin temelde yeraltı suyu-kayaç etkileşimine bağlı olduğu belirlenmiştir. İncelenen suların $\delta^{18}O$ içerikleri -4,65 ‰ ile -7,02 ‰ arasında değişirken $\delta\ ^2H$ içerikleri ise -25.98 ‰ ile -42,68 ‰ arasındadır. Suların trityum içerikleri 0,27 TU ile 2,77 TU arasında analiz edilmiştir. Suların izotop bileşimleri, incelenen yeraltı sularının meteorik kökenli olduğunu işaret etmektedir.

Yeraltı sularının Mg^{2+}, HCO_3^-, NO_3^-, B ve Pb konsantrasyonları Dünya Sağlık Örgütü (WHO) ve Irak içme suyu standartlarında izin verilen maksimum sınır değerlerini aşmaktadır. Şehirleşme, septik tanklar, kanalizasyon ve atık bertarafından sızıntılar, ayrıca tarımsal alanlarda kullanılan fazla miktardaki gübreler ve böcek ilaçları bu iyonların başlıca kaynaklarıdır. Havzada yeraltı suyu kalitesinin sürdürülebilirliğini sağlamak için tarımda aşırı gübre kullanımından kaçınılmalı, ayrıca fosseptikler yerine düzenli kanalizasyon sistemleri kullanılmalıdır**.**

Anahtar Kelimeler: Erbil Havzası, Hidrojeoloji, Hidrojeokimya, Alüvyon Akifer, Sülfat, İzotop

LIST OF FIGURES

Page

LIST OF TABLES

Page

ABBREVIATIONS

Abbreviations

EC : Electrical Conductivity

FHZ : Food Hill Zone

GPS : Global Positioning System

HFZ : High Folded Zone

IAEA : International Atomic Energy Agency

ICP-MS : Inductively Coupled Plasma Mass Spectrometer

IQS : Iraqi Standards

IZ : Imbricated Zone

LFZ : Low Folded Zone

meq : Milliequivalent

mg/L : Milligrams per Liter

pH : Hydrogen Potential

ppm : Parts Per Million

TAKK : Teknik Araştırma ve Kalite Kontrol

TDS : Total dissolved solids

USGS : United States Geological Survey

UTM : Universal Transverse Mercator

VSMOW : Vienna Standard Mean Ocean Water

WHO : World health organization

ZSZ : Zagros Suture Zone

DSI : Devlet Su İşleri

1. INTRODUCTION

The present study subjects to determine the major anion, cation, trace element, and isotopic contents of groundwaters in the Erbil Basin and to evaluate them by using some diagrams. Groundwater geochemistry is the study of the processes that govern the chemical composition of groundwater, as well as the quality of groundwater. Groundwater may contain toxic substances that are harmful to human health when consumed or that harm the environment when water is carelessly spilled at the surface. Much of the drinking water comes from surface waters, but groundwater is frequently preferred, particularly in the areas far from the city, because it requires less treatment and has a higher bacteriological quality (Appelo and Postma, 2005).

The movement of groundwater along its flow paths beneath the ground surface generally leads to the accumulation of the substances. As a result, groundwater chemistry may give valuable information about the geological history of aquifers as well as the suitability of groundwater for drinking, industrial, and agricultural purposes (Aghazadeh and Mogaddam, 2010). The hydrogeochemical assessment of groundwater resources is typically based on the availability of a considerable volume of groundwater chemistry information. Because of the suitability of water for different purposes, groundwater quality is equally important to its quantity (Schiavo et al., 2006). The chemistry of groundwater is influenced by a variety of factors, including geology, the intensity or level of chemical weathering of different rock types, the quality of recharge water, and received from sources that have not interacted (Aghazadeh and Mogaddam, 2010). These factors, as well as their interactions, contribute to complex groundwater quality.

The history of drilling wells in Iraq goes back to the twenties of the last century, nearly a hundred years ago. The Erbil governorate is very important in agriculture; most of the area consists of farmlands irrigated by the water of drilled wells. Due to the government's lack of surface water projects and strategic planning, residents in Erbil and nearby regions rely on water from drilled wells. They use these wells for all purposes including, industrial, construction, livestock, poultry, agriculture, and irrigation (Dizayee, 2014). The government provides people with water using groundwater by drilling wells and surface water bringing water by big pipes from the Greater Zap treatment called Ifraz project, but this project provides the surface water to a narrow zone in central and does not cover the whole city and surrounded areas.

Human activities had a considerable influence on surface and groundwater in Erbil, such as rapid expansion, population increase, industry, urbanization, and agricultural operations. All of this raises demand and exploitation, reduces availability, and increases the susceptibility to groundwater pollution in the Erbil Basin (Al-Manmi, 2002). As per the groundwater directorate in Erbil, a total of around 7,416 legal wells have been drilled within the Erbil basin (3,729 wells for agricultural

purposes, a total of 3,424 wells for drinking, a total of 75 wells for big and small parks, and 188 wells for industrial purposes). More than 6,000 illegal wells have been drilled everywhere.

Groundwater exploitation has become increasingly vital for the Erbil plain as the population has grown and agricultural and industrial enterprises have been established. Furthermore, the arid climatic condition has impacted the quantity and quality of recharged water to the aquifers; this indicates risk in the extraction of non-contaminated groundwater in its current amounts (Raju et al., 2011). Since 2003, Erbil City has been rapidly growing and expanding, and immigration to the city is increasing as a result of growing economic activities. Population growth increased economic activity, the provision of recreational facilities, and changes in inhabitants' lifestyles all place enormous strain on the city's water resources' availability and sustainability. Furthermore, partly treated municipal and industrial sewage pollutes both groundwater and surface water.

As per quality control department technicians in their laboratories, the results of the previous chemical analyses of the groundwaters in Erbil Basin figured out that some of the wells located in the area contain high nitrate (NO^{3-}) concentrations, high electrical conductivity (EC), high sulfate (SO_4^{2-}), and other physic-chemical parameters higher than the permissible limits of drinking water standards used in Iraq and people suffering from problems related to the contaminated water and various chronic disease. Moreover, the high concentration values of trace elements are one of the main causes of groundwater pollution as a result of anthropogenic activities that affect the health of humans, animals, and plant's life via the food chain (Shashikanth et al., 2008).

For a highly populated city like Erbil, the quality of the water must be studied alongside the age and origin of the water. Research and studies were conducted related to water quality in the Erbil sub-basins separately, but the current study includes the entire Erbil basin including the three sub-basins. In addition to that, the author tried to study the area in terms of isotopes which is the first attempt to focus on the Erbil Basin only.

The study area is known as the Erbil basin which consists of Erbil city and its surrounding areas. The Erbil basin was chosen as the study area, because i) it has a high population, particularly in Erbil city, which is why it is vital to study, ii) in recent years, the water table has dropped dramatically, and some wells have dried up and contaminated, the land is becoming more desertified while precipitation is decreasing, and iii) because groundwater in the basin has been extensively used for human consumption and agriculture, the investigation of this basin is critical to determine the quality alongside with the amount of groundwater.

The aims of the thesis are; i) to determine sources of major anions and cations and trace elements in groundwaters, ii) to evaluate the groundwater quality and its suitability for drinking and irrigation purposes, iii) to determine the residence time, origin, and ages of groundwaters in Erbil Basin.

1.1. Description of the study area

The governorate of Erbil, after Bagdad, Basra, and Mosul, is Iraq's fourth biggest province, located in the northern part of Iraq. Its boundary lines between longitude 43°15 E to 45°14 E and latitude 35°27 N to 37°24 N with a land area of 15,074 km^2 (3.5 % of Iraq's total land area) (Rezoska, 1980). The altitude of the city is 412 meters above mean sea level. According to the census or population statistics in 2015, the population of the Erbil Governorate was about 1,530,722 (Erbil Governorate, 2012), and increased by 2.9 percent yearly over the last two decades (Dizayee, 2014). Erbil city within Erbil Governorate is located between the latitudes 36°09′04″ and 36°13′13″ N and the longitudes 43°57′59″- 44°03′04″ E, with a total land area of around 92 km^2 (Mohammed et al., 2013). The province is flanked on the south by Kirkuk, on the southwest by Salah al-Din, on the west by Mosul, on the northwest by Dahuk, and on the east by Sulaymaniyah (Figure 1.1).

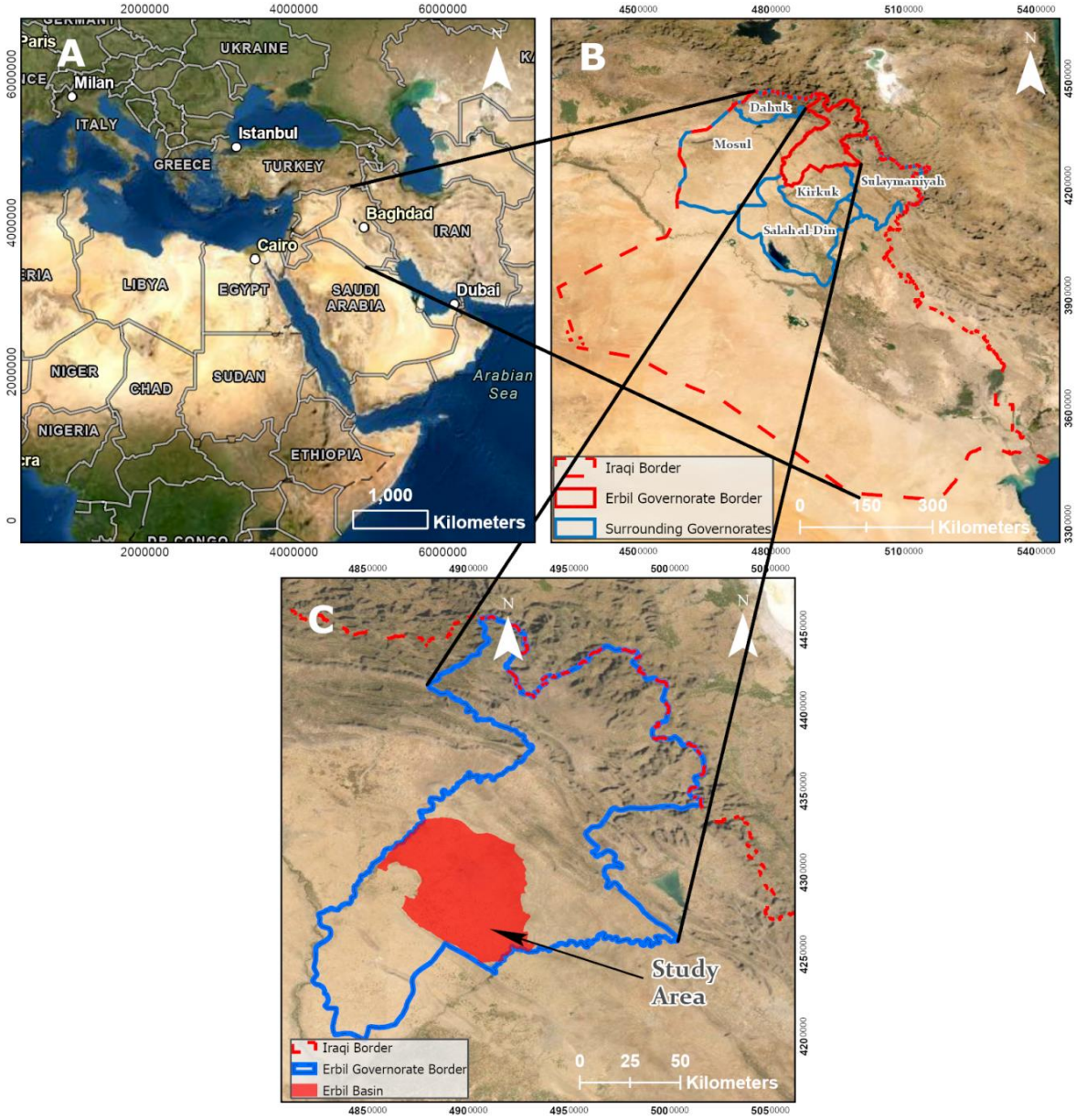

Figure 1.1. Maps of the studied area's location (A) the location of Iraq, which is located in the Middle East. (B) represents Erbil Governorate within Iraq, (C) Erbil Basin within Erbil Governorate

To the direction of north and northeast of the northern region of Iraq, the Zagros Mountains exist with a complex topography and the highest point is 3,600 meters above sea level, while to the direction south of the region, the area is consist of alluvial plains (Hameed, 2013). Mountainous uplands and fertile plains surround the province of Erbil. More than thirty-four percent of the Erbil province is farmland used for agricultural purposes, with the remainder consisting of grassland, urban, and forests. The Erbil province consists of 41% arable land and 59% non-arable land.

The Erbil plain has one of the most significant basins in the whole region called the Erbil basin which contains enough amount of groundwater with convenient quality, plus fertility of its

soil. It has a unique geological structure, stratigraphy, and geomorphological condition (Hameed, 2013). The topography of the basin mainly ranges from gentle to moderate and steep slopes.

1.2. Previous studies

Because this research focuses on hydrogeochemical assessment and groundwater quality, thus, besides the information about the hydrologic condition of the suited area, the spotlight will be cast primarily on three major subjects; the chemical ion analyses (major cations and major anions), the trace element analyses, and the isotope analyses. Some international studies have been done related to hydrogeochemistry and others are regional studies have been done on the same basin or near the area. These studies are summarized below:

Habib Al-Saigh and Hassan (1990) performed a study that was primarily concerned with assessing the quality of Erbil's groundwater. They collected some water samples from wells in the Erbil basin and studied the hydrogeochemistry of water samples to decide their suitability for human consumption.

Shekha (1994) analyzed the main sewage channel wastewater of Erbil city at several points along its course and discovered that nitrate concentration increases near the city center and then decreases in the surrounding areas.

Chnaray (2003) researched the hydrogeology and hydrochemistry of the Kapran sub-basin. Water balance, chemical and physical properties of water samples, water quality in the sub-basin, and the suitability of groundwaters for various uses were studied.

Shwani (2008) studied the hydrology and hydrochemistry of the Bashtapa sub-basin, which determined the type of aquifers and the source of groundwater recharge. Depending on the hydrogeochemistry of groundwaters, he determined the source and type of groundwater in this sub-basin and its uses in different purposes like industrial, drinking, agriculture, and irrigation.

Hussien (2010) used environmental isotope techniques mechanism of recharge interpretation of Mullusa aquifer in east Rutba region in Iraq, and he obtained that the recharge is from meteoric water infiltration from outcrops of Hauran catchments area in a depression called Indian depression. The isotope contents represented that the groundwater contains both old and younger water near the Rutba area. During his study, he detected that the Mullusa aquifer in the Dhabaa area stored water with a low recharge rate and the time of recharging is around 29,000 years determined by traditional hydrological techniques.

Aghazadeh and Mogaddam (2010) have taken water samples to determine the groundwater parameters in the Oshnavieh area, Northwest Iran. Electrical conductivity (EC), pH, total dissolved solids (TDS), Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, CO_3, SO_4^{2-}, NO_3^-, NH_3, PO_4^{3-}, Fe, and F, were measured. Permeability index and chemical indices such as percentage of sodium, sodium adsorption ratio, and residual sodium carbonated were calculated. Based on the results, the quality

of water, and hydrochemical faces were determined. From the hydrochemical data plotted in the Gibbs diagram, it is observed that the water was rock dominant and the chemical of the water is a result of interaction with the lithology of the aquifer. This study declared the suitability of water for drink and agriculture purposes.

Dara (2011) studied the hydrology and hydrochemistry of the Kalar basin, northeast Iraq. The concentrations of major cations and anions in the rainy season are lower than the concentrations in the dry season because of precipitation influence. The sources of ions mentioned like aquifer lithology and soil plus anthropogenic activities. As per the study, the water type is Ca-HCO_3 type and the chemical weathering of rocks controls the process. After the trace element analyses, all water samples were below the maximum permissible limit of WHO, and IQS standards and are considered suitable for drinking, agriculture, and other purposes.

Dizayee (2014) studied the properties of the two major aquifers in the Erbil Basin, the Bakhtiary Formation, and the alluvium deposits inside the entire Erbil Basin. The study also attempts to evaluate the sustainability of these aquifers within the sub-basins using raw data of wells over five years. Groundwater levels are measured both statically and dynamically, ground surface elevations, water depth, well-depth, and types of soil. Climate data such as water availability data and water loss have been used to evaluate water budget and understand the availability of groundwater throughout the basin.

The geochemical properties of groundwater and the quality of drinking water were investigated by Logeshkumaran et al. (2015). The findings were assessed and compared to WHO and Indian water quality standards. The Piper and Gibbs diagrams were used while interpreting the quality of water in the studied area.

Mohammed et al. (2015) examined groundwater in a semi-aired area for the Wadi - Ouazzi basin in Morocco. The findings of isotope content in groundwaters show that there is little evaporation of precipitation throughout the process of infiltration. The tritium value in the basin of Ouazzi groundwater is less than 1.5 tritium units.

Seeyan and Merkel (2015) determined recharge by using isotopes and water chemistry in Shaqlawa-Harrir Basin in Iraq. Stable isotopes and chemical analyses of waters were used to obtain the origin of surface and groundwater in the Shaqlawa-Harrir basin (northern part of Iraq). The study indicated that the reason for $\delta^{18}O$ depletion in some water samples were related to the altitude effect.

Ander et al. (2016) collected water samples in a metalliferous and arsenic area of mineralization called Cornwall in the United Kingdom. The Iron and Manganese concentrations in some waters exceeded the drinking water standards related to the mineralizations in the studied area.

Aydınoğlu (2019) studied the hydrogeochemical properties of mineral waters in Elazığ city. The relationship between the chemical composition of the waters and lithology was determined and explained. The chemical composition of these waters is compared with various standards for mineral water (drinking purposes). Isotope analyzes were performed on water samples taken during the dry season to determine the origin and age of the waters. According to the results of the isotope analysis carried out during the dry season, the studied waters are of meteoric origin since they are located on and near the meteoric water lines of the Mediterranean and Dalbahçe (Erzurum).

Mawlood and Mamand (2021) used the environmental isotopes (^{18}O and ^{2}H) to determine the age of groundwater in the Erbil governorate. The high values of ^{2}H represent recharging from the high altitudes, and some water samples are older and some are younger related to the tritium contents.

1.3. Climate

The climate of Erbil province changes with area change within the province. There are two areas of climate, the first one in the north and northeast area which is characterized by a Mediterranean climatic zone. The average annual rainfall is 600 to 800 mm. The second climate area in the south and southwest area of the Erbil province has a hot climatic zone. The average annual rainfall is 500 mm. In winter, the weather is very cold and snowy, while in the summer, it is very dry and hot (Hameed, 2013).

The minimum degrees of temperature is in January, and the average temperature in winter is 7.9 °C (Hameed, 2013). The topography of the province consists of lands in the form of mountains, semi-mountains, hills, and plains; each of them has its influence on precipitation. The plains have a semi-arid climate. From October till May, there is Precipitation and reduces in the area from NE to SW, in another way, the quantity of precipitation in the NE areas is more than the quantity of precipitation in the SW areas. The rainfall ranges from 200 millimeters per year in the south to 1,200 millimeters per year in the north, and the annual average reaches 700 millimeters per year (**Figure 1.2**) (UNDP-Iraq, 2011).

There are two groups of parameters in meteorological data: 1) water availability factors include precipitation and relative humidity, and 2) water loss factors include temperature, wind speed, sunshine, and evaporation (Hassan, 1998). The meteorological data were obtained in 2022 from the general directorate of meteorology and seismology.

1.3.1. Precipitation

Precipitation is one of the most essential factors in the water cycle and the recharging of aquifers. In northern Iraq, Precipitation (rainfall and snow) provides internal surface water and groundwater resources. It together with inflows from Turkey and Iran makes up the region's overall water supply (Ismaiel, 2018). The majority of the precipitation falls as rain or drizzle. Snow may also fall on hills and mountains, and hail is common during thunderstorms. The topographical characteristics of northern Iraq have a considerable influence on the rainfall regime. The amount of rainfall increases from southwest to northeast (Figure 1.2) (Abbas, 2008). The area's rainy season is characterized by a lack of precipitation throughout the summer (Stevanovic and Markovic, 2004). Erbil is in a region influenced by the Mediterranean climatological system, precipitation falls primarily in the winter and spring seasons.

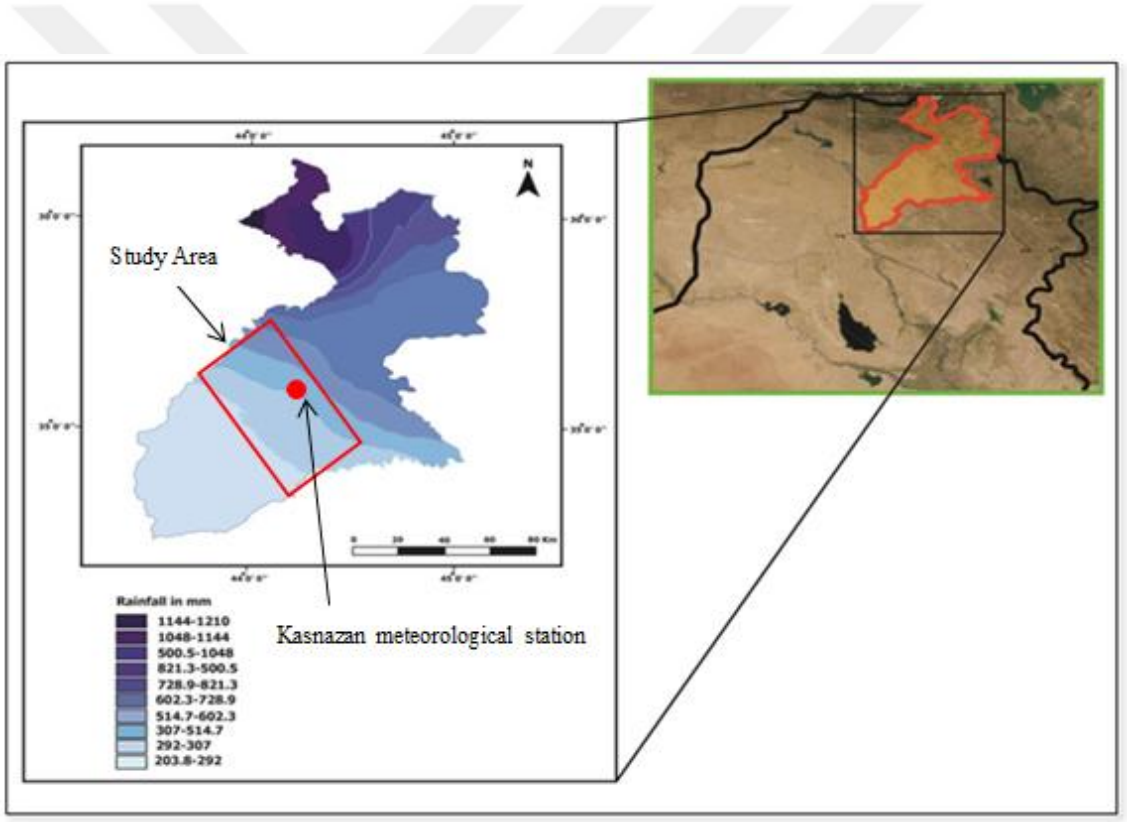

Figure 1.2. Average annual rainfall in Erbil province (Hameed, 2013)

The maximum average monthly rainfall is 70.39 mm in March and the minimum average is 0.05 mm in August. Annual rainfall was 397.50 mm for the period between 2001 and 2021 (Table1.1; Figure 1.3).

Table 1.1. Average monthly rainfall at the Kasnazan meteorological station in the Erbil basin for the period between 2001and 2021(related to the data from the General Directorate of Meteorology and Seismology)

Months	Rainfall (mm)	Months	Rainfall (mm)
Oct.	24.11	Apr.	45.58
Nov.	38.59	May.	15.30
Dec.	69.52	Jun.	1.65
Jan.	67.20	Jul.	0.08
Feb.	62.02	Aug.	0.05
Mar.	70.39	Sep.	3.05
Average		397.50	
Max.		70.39	
Min.		0.05	

1.3.2. Relative Humidity

Relative humidity is defined as the ratio of actual water vapor pressure in air to maximum water vapor pressure. It is a measure of the amount of moisture in an air mass, and it is connected to temperature and evaporation in reverse order. The relative humidity of an air mass is often measured as a percentage. Relative humidity values exceeding 80% indicate humid environments with limited evaporation rates, and relative humidity values less than 60%, on the other hand, indicate dry environments with high evaporation rates (Serrano, 1997). The major source of humidity in the region is Mediterranean cyclones that move eastward throughout the winter. Southerly cyclones in the Arabian Sea, on the other hand, will carry a lot of rain because of their high moisture content.

The maximum average monthly humidity value is 71.68% in January and the minimum average is 27.14% in July. During the period between 2001 and 2021, the annual value of humidity was 48.78 % (Table 1.2; Figure 1.3).

Table 1.2. Average monthly humidity at the Kasnazan meteorological station in the Erbil basin for the period between 2001and 2021(related to the data from the General Directorate of Meteorology and Seismology)

Months	Humidity (%)	Months	Humidity (%)
Oct.	45.14	Apr.	53.62
Nov.	59.74	May.	40.05
Dec.	67.98	Jun.	29.85
Jan.	71.68	Jul.	27.14
Feb.	67.48	Aug.	29.10
Mar.	60.06	Sep.	33.50
Average		48.78	
Max.		71.68	
Min.		27.14	

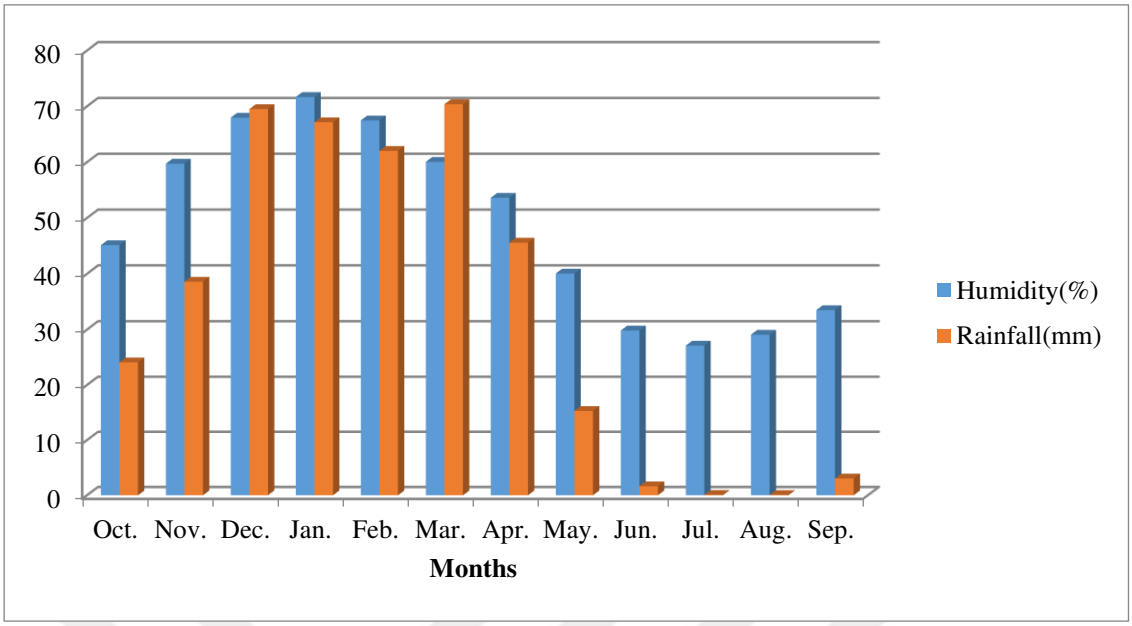

Figure 1.3. Average monthly rainfall and relative humidity in Erbil Basin for the period between 2001 and 2021(related to the data from the General Directorate of Meteorology and Seismology).

1.3.3. Temperature

The temperature has a significant effect on both evaporation and evapotranspiration, and it has an essential role in raising evaporation and evapotranspiration values.

The maximum average monthly temperature value is 35.04°C in July and the minimum average is 8.99 in January. During the period between 2001 and 2021, the annual average temperature was 21.99 °C. Table 1.3 and Figure 1.4 represent the average monthly temperature during the period between 2001 and 2021 (related to the data from the General Directorate of Meteorology and Seismology).

Table 1.3. The average monthly temperature at the Kasnazan meteorological station in the Erbil basin for the period between 2001 and 2021(related to the data from the General Directorate of Meteorology and Seismology)

Months	Temperature (°C)	Months	Temperature (°C)
Oct.	24.36	Apr.	19.90
Nov.	15.89	May.	26.56
Dec.	10.54	Jun.	32.09
Jan.	8.99	Jul.	35.04
Feb.	10.74	Aug.	34.70
Mar.	14.98	Sep.	30.05
Total		263.84	
Average		21.99	
Max.		35.04	
Min.		8.99	

In winter, the Mediterranean cyclones move across the Erbil Governorate and the surrounding area from east to northeast. Cyclones in the Arabian Sea move northward, passing over the gulf and bringing big amounts of moisture and precipitation. The region is also affected by extremely cold polar air masses. These air masses descend to the gulf and then move to the north, taking moisture with them, resulting in a massive increase in precipitation.

1.3.4. Wind speed

Wind and air turbulence are important factors in the vapor removal process. This moves a lot of air across the evaporating surface.

The maximum average monthly wind speed value is 2.19 m/s in April and the minimum average is 1.49 m/s in September. During the period between 2001 and 2021, the annual average wind speed is 1.87 m/s (Table 1.4; Figure 1.4).

Table 1.4. Average monthly wind speed at the Kasnazan station in the Erbil basin for the period between 2001and 2021 (related to the data from the General Directorate of Meteorology and Seismology).

Months	Wind speed (m/S)	Months	Wind speed (m/S)
Oct.	1.76	Apr.	2.19
Nov.	1.59	May.	2.12
Dec.	1.72	Jun.	2.01
Jan.	1.85	Jul.	1.75
Feb.	2.05	Aug.	1.74
Mar.	2.15	Sep.	1.49
Average		1.87	
Max.		2.19	
Min.		1.49	

1.3.5. Sunshine duration

Sunshine represents the day. The average monthly sunlight duration is at its peak in June, whereas January had the shortest average monthly sunlight duration.

The maximum average monthly sunshine value is 12.09 hr. /day in August and the minimum average is 4.88m/s in January. During the period between 2001and 2021, the annual average of sunshine was 8.30 hr. /day (Table 1.5; Figure 1.4).

Table 1.5. Average monthly sunshine at the Kasnazan station in the Erbil basin for the period between 2001and 2021 (related to the data from the General Directorate of Meteorology and Seismology)

Months	Sunshine (hr./day)	Months	Sunshine (hr./day)
Oct.	7.78	Apr.	7.57
Nov.	6.44	May.	9.42
Dec.	5.32	Jun.	11.68
Jan.	4.88	Jul.	11.88
Feb.	5.72	Aug.	12.09
Mar.	6.59	Sep.	10.20
Average		8.30	
Max.		12.09	
Min.		4.88	

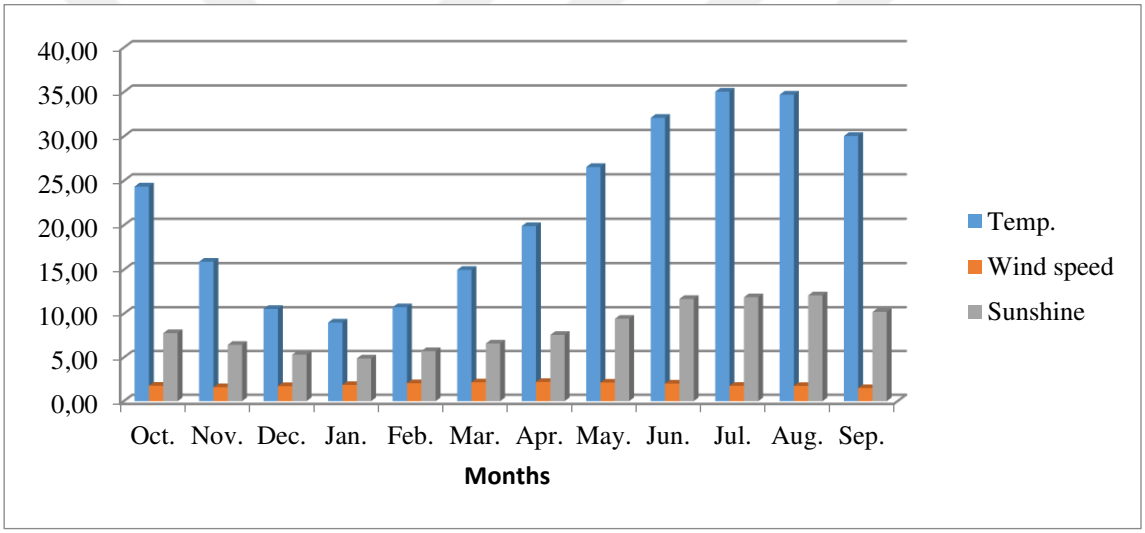

Figure 1.4. Relationship between Temperature, wind speed, and sunshine at the Kasnazan climatic station in Erbil basin for the period between 2001and 2021 (related to the data from the General Directorate of Meteorology and Seismology)

1.3.6. Evaporation

When a liquid changes into a gas, this is referred to as evaporation; water from a moist surface evaporates into the air above. Evaporation is a cyclic variable that is influenced by several other variables and physical conditions (Shwani, 2008). It is a changeable factor that is affected by many factors, like temperature and humidity. Many factors impact evaporation, including high air temperature, intense solar radiation (sunshine), wind speed, low humidity values (saturation deficiency), the nature of surface evaporation, and atmospheric pressure, particularly during the dry period increase evaporation and evapotranspiration processes (Stevanovic and Markovic, 2004).

The maximum average monthly evaporation value is 14.68 mm in August and the minimum average is 1.71 mm in January. During the period between 2001and 2021, the annual average of evaporation was 7.14 mm (Table 1.6; Figure 1.5).

Table 1.6. Average monthly evaporation at the Kasnazan station in the Erbil basin for the period between 2001and 2021 related to the data from the General Directorate of Meteorology and Seismology

Months	Evaporation (mm)	Months	Evaporation (mm)
Oct.	6.40	Apr.	5.79
Nov.	3.17	May.	9.40
Dec.	1.88	Jun.	12.76
Jan.	1.71	Jul.	13.63
Feb.	2.49	Aug.	14.68
Mar.	4.02	Sep.	9.75
Max.		14.68	
Min.		1.71	
Average		7.14	

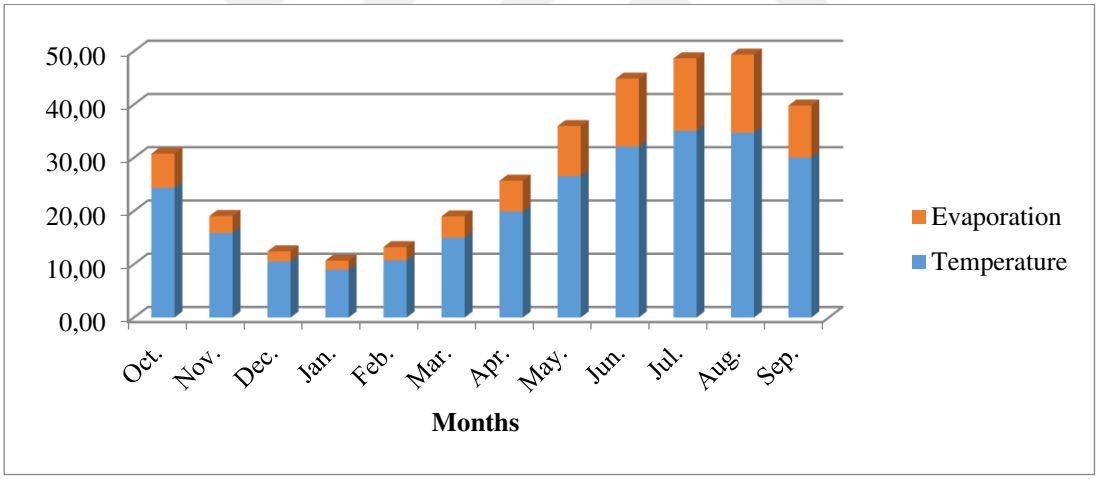

Figure 1.5. Relationship between temperature and evaporation at Kasnazan meteorology station in Erbil basin for the period between 2001and 2021 (related to the data from the General Directorate of Meteorology and Seismology)

2. MATERIAL AND METHOD

This study relies on raw wells data for the year 2021. Data include static groundwater level, ground elevations, water depth, total depths of the drilled wells, and a climate data set includes precipitation, humidity, temperature, and evaporation data. These data are used besides chemical, isotope, and trace elements analysis data to evaluate and explain the hydrogeochemistry of groundwater in the basin. Realizing the hydrogeochemical properties of water is critical for groundwater planning and management in the study area.

This study was carried out in four stages, namely pre-field work, fieldwork, laboratory work, and office work. Before starting these studies, literature studies were initiated and continued at every stage of the study. Within the scope of literature studies, articles, books, thesis, and projects on the geology, hydrogeology, and hydrogeochemistry of the study area and its immediate surroundings have been compiled.

2.1. Pre-field Work

For fieldwork preparation, all accessible data from various sources and respective offices, many sorts of maps of appropriate scale for the area, and satellite images for mapping purposes were collected. Systematization and analysis of all existing documentation on the basin's hydrology, geology, and hydrogeology were performed. Also, any data from the site on land use drilled wells, well documentation (well-logs), and geophysical data were collected. The well-logs are obtained from the Directorate of Erbil Groundwater. The coordination of the wells was provided by the Directorate of Erbil water.

All equipment has been ensured that is working with no errors and properly calibrated before moving into the field.

2.2. Fieldwork

Within the scope of the study, the locations of the wells were determined by the GPS instrument (UTM) model Garmin -72S (Table 2.1). For hydrogeochemical studies, water samples were taken from the well locations in May (2021) representing the rainy period, and in October (2021) representing the dry period, and chemical analyzes were made. In May (2021) and October (2018), a total of 20 water samples were collected for major anion, and cation analyses. Some of the samples were taken twice (Two samples in the same well water) to ensure the data accuracy of the water samples. Monitoring of the wells is carried out once per month starting from April 2021 to April 2022 for each well. The static water levels of the wells were measured using a water level meter in collaboration with the groundwater directorate team (Figure 2.2).

A total of 16 water samples (eight samples for each season) were collected for metal and trace element analyzes. All sample containers are washed and rinsed thoroughly at least three times with the same water that discharges from the well inside the well chamber before sampling, and were acidified using the following procedure: four drops of concentrated hydrochloric acid solution (HCl) were added to every 100 milliliters of the water sample polyethylene bottle to prevent reactions that may occur after sampling (Figure 2.1). The samples were kept in a refrigerator at +4 °C until they were sent for analysis and sent analysis as soon as possible.

For isotope analysis, only in October (2021), ten water samples for $\delta^{2}H$ and $\delta^{18}O$ contents were taken, eight water samples for tritium contents were taken and 1.5-liter polyethylene bottles were used while sampling, and the bottles were filled with no air left, and exposed to sunlight exposure is prevented. While the water samples were being taken, the pH, temperature (T), total dissolved solids (TDS), and electrical conductivity (EC) parameters of the water were measured in the field by (HANNA-H19811-5) model multi-parameter measuring device. For major anion and cation analysis, water samples were taken in one-liter polyethylene bottles.

Table 2.1. The coordinates of the sampled groundwaters

No.	Well Name	Location	X	Y	Altitude (m)
1	E1	Erbil City	423124	4006805	616
2	E2	Erbil city	413903	4005368	444
3	E3	Erbil city	408556	4003289	405
4	E4	Erbil city	408867	4004642	407
5	E5	Kani Qirzhalla village	397767	4007731	440
6	E6	Kawrgoesk Camp	393349	4022907	313
7	E7	Lajan Village	427147	3990382	330
8	E8	Sirawa Village	395199	3992894	315
9	E9	Qurshaghlu village	402862	3975869	359
10	E10	Qushtapa sub-district	413250	3982921	394

Figure 2.1. Sampling and sample measurements in the field

Figure 2.2. Static water level measuring for the wells in the study area using a water level meter

Sample Preserving and Storing

For each sample, the bottle preparation, preservation, and storage requirements are shown in (Table 2.2). Some analysis has more than one method, and methods different than the common or preferred technique are given in italics.

Table 2.2. Sampling, analysis methods and preservation requirements for each analysis

Determined parameters or elements	Container	Sample size	Preservation	Maximum storage	Analysis Method
Alkalinity (HCO_3^-) (mg/l)	P	One liter	Refrigerate	One day	Titration
Chloride (Cl^-) (mg/l)	P	One liter	Refrigerate	One day	Titration
Nitrate (NO_3^-) (mg/l)	P	One liter	Refrigerate	One day	EMC-11-UV Spectrophotometer
T °C, pH, EC,and TDS	Nil	Nil	Analyzed immediately	Nil	Portable multi-meter
Sulfate (SO_4^{-2}) (mg/l)	P	One liter	Refrigerate	One day	2100N Turbidimeter
Turbidity (NTU)	P	One liter	Analyzed same day or store in dark for up to 24h, refrigerate	One day	2100N Turbidimeter
Calcium (Ca^{+2}) (mg/l)	P	One liter	Refrigerate	One day	Titration
Magnesium (Mg^{+2}) (mg/l)	P	One liter	Refrigerate	One day	Titration
Sodium (Na^+) (mg/l)	P	One liter	Refrigerate	One day	Flame photometer
Potassium (K^+) (mg/l)	P	One liter	Refrigerate	One day	Flame photometer
Total Hardness (TH) (mg/l)	P	One liter	Refrigerate	One day	Titration
Trace and Metal analyses	P	100 milliliters	Refrigerate	5 months	ICP-MS
Isotope analyses	P	1.5 Liters	Stored in a dark place	2 months	IAEA Optical Method-VSMOW

For determinations, not listed refrigerate and analyze as soon as possible.

P = Plastic (polyethylene or equivalent)

Refrigerate = Store at less than 4°C.

Nil = no storage allowed.

2.3. Laboratory Work

Major anion (Cl^-, SO_4^{-2}, HCO_3^-) and cation (Ca^{+2}, Mg^{+2}, Na^+, K^+) analyses of water samples taken in May (2021) and October (2021) were performed in the quality control department's laboratory in Erbil water directorate.

The metal and trace element analysis was performed by ICP-MS (Inductively Coupled Plasma-Mass Spectrometer) at ACME Laboratories in Canada.

Isotope analyzes of the water samples taken in October (2021) were performed at the Isotope Laboratory of the Technical Research and Quality Control (TAKK) Department of DSI in Ankara,

using Micro-mass 602C Mass Spectrometer by IAEA (International Atomic Energy Agency) optical method- VSMOW standards.

2.4. Office Work

The office duties involved representing the fieldwork, reviewing, and analyzing laboratory findings. Microsoft Office Word 2010 was used for typing. Microsoft Office Excel was used to type, tabulate data, solve equations, and create charts and diagrams such as climatic parameter graphs, and Gibbs diagrams. While drawing the location and geological maps of the region in the digitization process, ArcGIS version10.6.0.8321 and Map-info programs were used in the metric projection system (WGS84-38N), and Google Earth software. All water sample locations were shown in (Table 2.1).

AquaChem program version 3.7 was used to transfer the chemical analysis results of the waters to Schoeller's (1972) diagram. Phreeqc Interactive 3.7.0 program by USGS was used to calculate the saturation indices of the waters. The results of the chemical analysis of the waters were interpreted in terms of hydrochemical facies and origin on Piper's (1944) diagram by GW-Chart version 1.30.0.0 scientific program by the United States Geological Survey. In addition, in terms of drinking water, the waters were interpreted by comparing them with various standards.

3. GEOLOGY

The study area consists of Late Miocene- Pleistocene Bakhtiary Formation and Quaternary deposits (Figure 3.1).

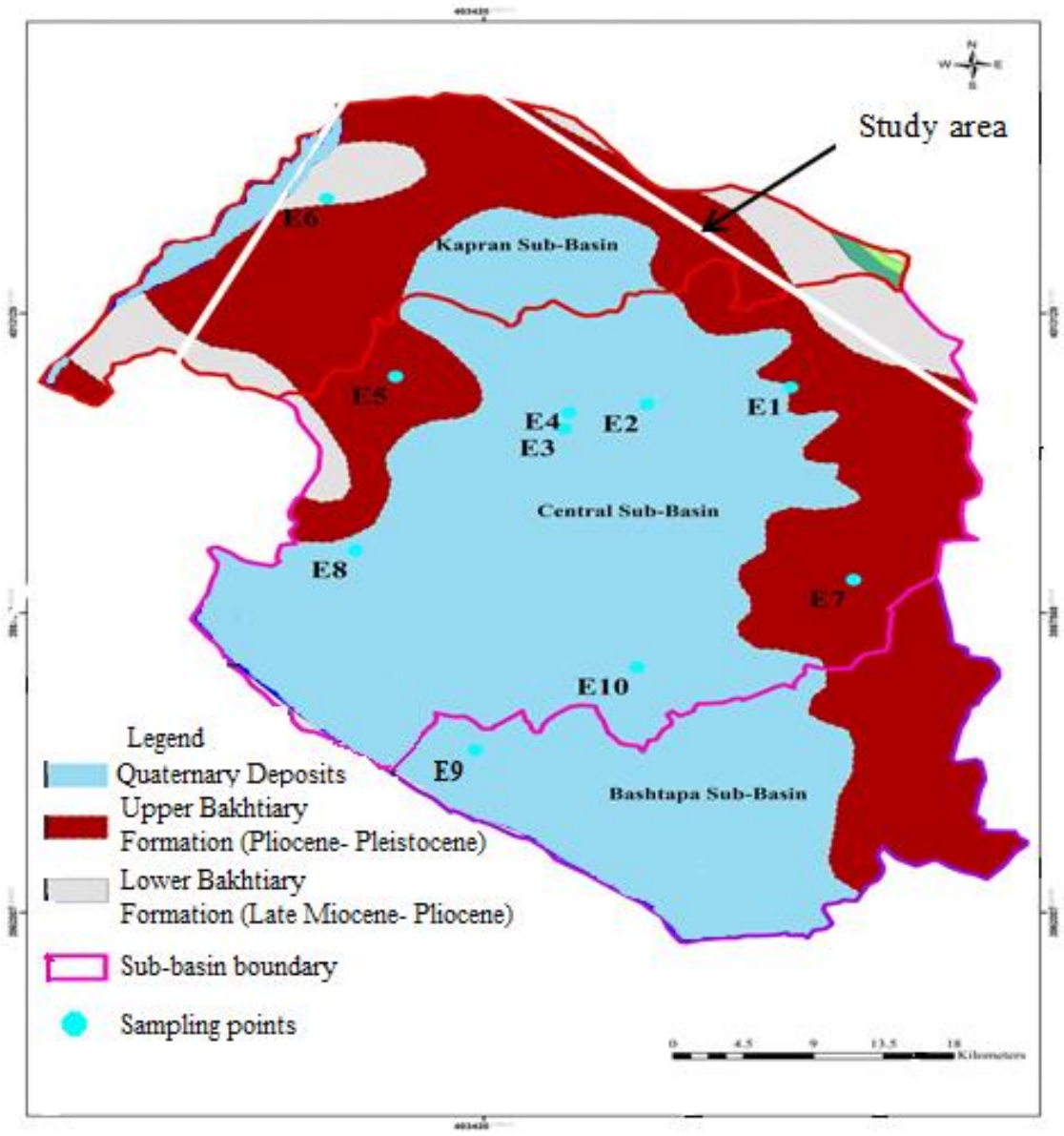

Figure 3.1. Geological map of Erbil Basin (Simplified from Hameed (2013))

3.1. Bakhtiary Formation (Late Miocene- Pleistocene)

The Bakhtiary Formation was first revealed in Iran as a result of a geological survey by Busk and Mayo in 1918 and then studied in Iraq. This Formation is located in the food hill zone and high folded zone. Late Miocene- Pliocene Lower Bakhtiary (also called Mukdadiya) Formation consists of an alternation of bedded sandstone, partly pebbly, siltstone and claystone. Pliocene-

Pleistocene Upper Bakhtiary (also called Bai Hassan) Formation consists of thick conglomerate and reddish-brown claystone, with thin grey sandstone (Sissakian, 2013).

From the center of the Erbil city towards the east, at a distance of about 20 km, the outcrops of layers of the Bakhtiary Formation are visible and clear on the earth's surface (Figure 3.2). These outcrops comprise thick layers of conglomerates, sandstone, and shale in the northeast of Erbil city, and the basin's eastern and western sides near the study area's recharging zone.

Figure 3.2. The outcrop of terrestrial deposits of Bakhtiary Formation close to the study area

The Quaternary gravels and alluvium deposits overlying the Upper Bakhtiary Formation in the study area. More than 80% of the research area is covered by the Bakhtiary Formation. The Upper and the Lower Bakhtiary Formations have different thicknesses in different places (Al-Tamir, 2008). According to many types of research, the thickness of this formation is more than 1,800 m in the plain of Erbil (Jawad and Hussien, 1988).

3.2. Quaternary deposits

The Quaternary deposits cover more than a third of the earth's surface area in Iraq, and most of them are in central Iraq. These deposits are situated in the unstable shelf in northern Iraq, where the wide synclines are filled with deposits in the low folded zone of river terraces with little depressions in the high fold zone (Jassim and Goff, 2006). The Quaternary deposits that are above the top of the Bakhtiary Formation and are spread over a wide range over the Erbil Basin are from the age of the Pleistocene epoch in the period of Quaternary, are mostly composed of soils, gravels, and conglomerates, with minor amounts of sand, silt, and clay. It comprises alluvial fans, flood plain deposits, slope deposits, and river terraces deposits (Jassim and Goff, 2006). The thickness of these deposits varies, although it might reach over 100 meters in some areas of the basin. The fine-

textured clay layers are interbedded with the sand and silt layers that have mixed with the gravel and pebble layers in the coarse alluvial deposits.

The researched area has a variety of Quaternary deposits, including Pleistocene and Holocene ages. The Pleistocene terraces are developed along the Greater Zab River. The deposit type and thickness are the same as in alluvial fans. Pleistocene – Holocene alluvial fan sediments are represented in different parts of the studied area. The main component of alluvial fan deposits is grains of various sizes from various rocks cemented by calcareous material and sand. The thickness of this unit is only a few meters. Holocene flood plain deposits are also represented in the study area. These deposits dominantly consist of sand, silt, and clay with some small-sized pebbles. The thickness ranges from less than 0.5 m to 1.5 m, occasionally may be more (Sissakian, 2013).

3.3. Tectonic

In the late Tertiary, a tectonic event happened in the north and north-east part of Iraq as a part of the Arabian plate. Due to the Arabian and Eurasian plates' collision, the Arabian plate was subducting beneath the Eurasian plate. The margins of the plates compressed. As a result of this collision the Zagros fold-thrust belt was formed (Jassim and Goff, 2006). The tectonic activity in this belt has launched since the Late Cretaceous and continued to its compressional state; even so, the latest structure has been formed during the Miocene- Pliocene (Numan, 1997).

The region in the northern part of Iraq can be divided into two different sections in terms of tectonics, where each of these two sections is called the shelf: the first section is the stable shelf where the anticlines, synclines, and other geologic structures are buried under the surface of the earth and they are hidden, because of the deposits above these structures. This shelf covers most of the central, southern, and western areas of Iraq . The second section is the unstable shelf where the folds are exposed on the surface of the earth and not hidden. The number, size, and complexity of geological structures increase as we move in the northeast direction of the region (Al-Juboury, 2012) (Figure 3.3). The unstable shelf can be divided into four different tectonic zones with the strike direction NW-SE:

- Foot Hill Zone (FHZ) or low folded zone (LFZ): It consists of long anticlines and broad synclines (Wide scales structures).

- High Folded Zone: It contains a large number of folds.

- Imbricated (Balambo-Tanjero) Zone: It is characterized by imbricated structures with domination anticlinal structures.

- Zagros Suture Zone:Zagros suture zone is an uplifted zone where it formed and developed along the collided plate margin and it is characterized by thrusted anticlinal structures (Numan, 1997; Jassim and Goff, 2006) (Figure 3.3).

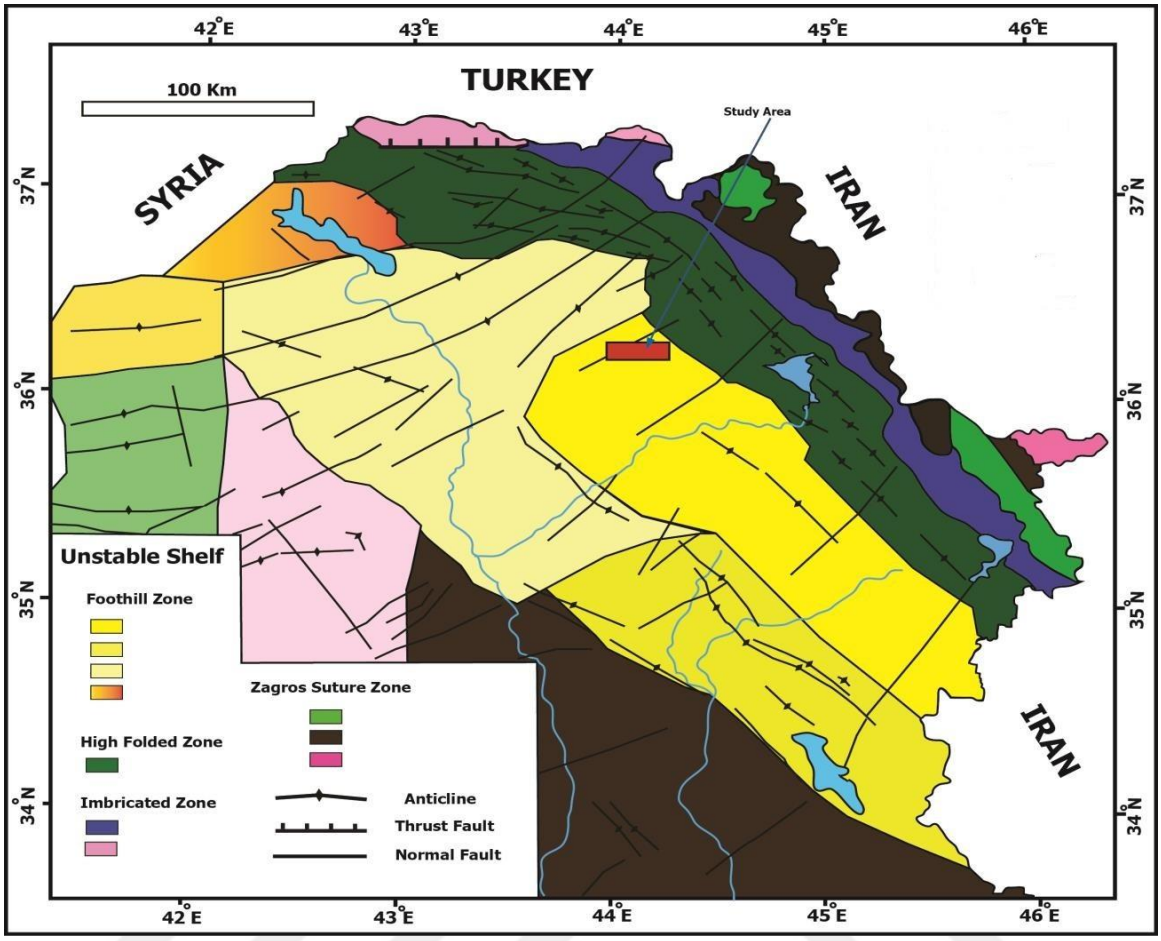

Figure 3.3. Tectonic map- Northern Iraq (modified from Jassim and Goff, 2006)

As shown in the Figure 3.3, the Erbil Basin is situated in Foot hill zone. As per Dizayee (2014), the Foot hill zone is a tectonic unit that has low tectonic events. Open folds with wavelengths ranging from 5 to 10 km are common in anticlines and small synclines.

As per Buday and Jassim (1987), the middle part of the Erbil plain lies in the synclinal area between these anticlines, which is divided into three sub-basins (Figure 3.1) (Dizayee, 2014):

1- Kapran (Northern) sub-basin.

2- Central sub-basin.

3- Bashtapa (Southern) sub-basin.

Towards the south and south-east, the depth of the Erbil basin increases, and the folds are subsurface and the formations are thicker, while towards the north and north-east, the depth of the basin decreases, and the folds are where we can see the outcrop of the layers.

4. RESULT AND DISCUSSION

The results of the present study are given and discussed in terms of hydrogeology and hydrogeochemistry.

4.1. Hydrogeology

The Erbil Basin (Dashty Hawler) is the largest and most important groundwater reservoir in Erbil Governorate and the Middle East, because it is easily accessible, as it is close to the surface of the earth, despite the quantity and quality of the water inside the reservoir. The Erbil Basin is 3,200 km^2 in area and 800 meters deep (Ahmed, 2010).

The Erbil Basin has a wide range of geomorphological and geological features, consisting of river valleys, flat alluvial plains, and hills. There are regional fault structures, anticlines, and synclines with axes direction to the NW-SE parallel to the main Zagros orogeny that has an impact on the drainage pattern's orientations (Jassim and Goff, 2006).

The boundary of the basin in the north and northwest is the Greater Zab River, whereas in the south and southeast is the Lesser Zab River. On the other hand, the eastern part of the basin is the watershed that separates the Erbil Plain from the valley of the Shalga River. The basin's southern border is the anticline between the Erbil Plain and the Makhmur Plain, and the Bastora valley is the northeastern border of the basin (Jassim and Goff, 2006; Ur et al., 2013). The direction of groundwater flow for a portion in the basin is from NE towards the Greater Zab River, and another portion of the groundwater flows from NE to the S and SW towards the Lesser Zab River (Erbil Groundwater Directorate, 2012) (Figure 4.1).

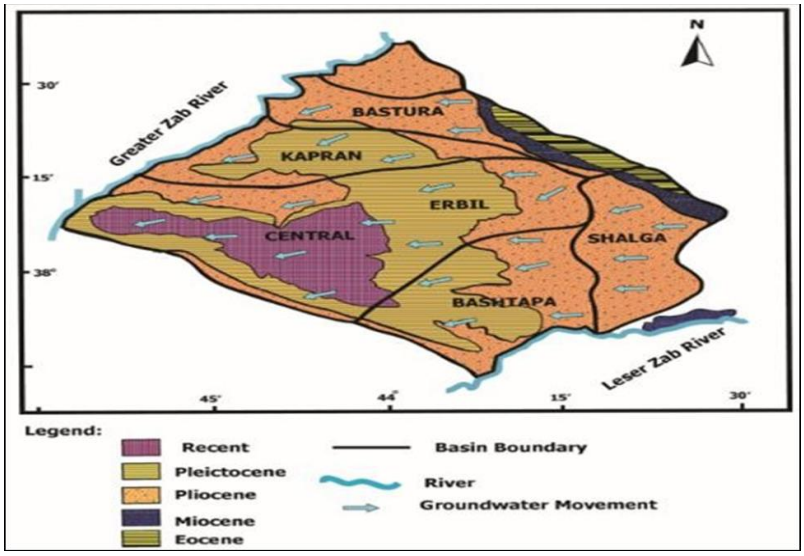

Figure 4.1. The geological map of the Erbil Basin contains sub-basins and groundwater flow directions (modified from Hameed (2013))

There are three sub-basins inside the Erbil basin (Figure 4.1):

i- Kapran (Northern) sub-basin

ii- Central sub-basin.

iii- Bashtapa (Southern) sub-basin.

The division of the basin was created by researchers based on hydrogeological parameters gathered from well data. Minor surface and subsurface features divide the sub-basins. Other parts in the basin such as Shalga and Bastura, however, whether or not they are part of the Erbil Basin is debatable (Majeed and Ahmad, 2002).

4.1.1. Kapran sub-basin

This basin covers an area of 915 km^2 in the northern part of the low folded zone in the unstable shelf. The Upper Bakhtiary Formation is under a few meters of Quaternary deposits in the lower part of this sub-basin, and sometimes, these deposits, from one place to another place, reach 50-60 m in thickness. The materials of the Bakhtiary Formation and Quaternary deposits are inter-granular, where the Bakhtiary Formation includes layers of gravel, sandstone, siltstone, conglomerate, and claystone, while the Quaternary deposits include interbedded layers of sandstone, siltstone, claystone, and gravel, This would be a good feature for forming aquifers to store water under the surface of the earth (Majeed and Ahmad, 2002). Aquifers of the Kapran sub-basin are unconfined, but in some locations, due to the presence of thick layers of clay on top, the aquifers are confined or semi-confined. All the above is as per drilled well records in the area (Dizayee, 2014). The depth of the groundwater reaches approximately 40 m. The depth of drilled wells reaches more than 200 m in this sub-basin.

4.1.2. Central sub-basin

The area of the central sub-basin in the Erbil Basin is about 1,400 km^2. It contains both Bakhtiary Formation and Quaternary deposits. The Upper Bakhtiary Formation includes gravel, sandstone, claystone, and conglomerate, while the Lower Bakhtiary includes thin layers of gravel, sandstone, and conglomerate. The Quaternary deposits are characterized by the presence of layers of siltstone between the other layers instead of the claystone layer (Majeed and Ahmad, 2002).

4.1.3. Bashtapa sub-basin

This sub-basin is located in the south area of the Erbil Basin. It has an area of 663 km^2. The main Formations within this basin are the Bakhtiary Formation (Upper and Lower Bakhtiary) and the Quaternary deposits. The aquifers are confined or unconfined. Since the materials of the

different layers are granular, the porosity and permeability are high with good recharge (Shwani, 2008) (Table 4.1).

Table 4.1. Aquifer system lithostratigraphy in the Taurus-Zagros series' Low Folded Zone (Stevanovic and Markovic, 2004).

Age		**Formation**	**Lithology**	**Water bearing characteristics**
Quaternary	Pleistocene to recent	Alluvium	Gravel, Clay, and Sand	Hydraulically connected; from one aquifer system in the low folded zone
Neogene	Pliocene	Upper Bakhtiary, Lower Bakhtiary	Conglomerates and Claystone, Partly sandstone and siltstone	

The static groundwater levels were measured for one year in the selected wells in the study area (Table 4.2 and Figure 4.2). The groundwater depths in the monitoring wells mostly increase in March and April months indicating the precipitation effect, whereas the groundwater depths begin to decrease between July and November months indicating the evaporation effect and excessive pumping from the wells (Figure 4.2). However, there was no significant groundwater fluctuation observed in some wells, especially E6, E7, and E9 numbered ones, which indicates that the static groundwater levels were not affected by the recent precipitations. Generally, the groundwater level fluctuations in the study area might be related to the i) precipitation, ii) type (confined, unconfined, semi-confined), and also iii) some anthropogenic factors such as excessive pumping from the wells and irrigation purposes.

Table 4.2. Static groundwater level for the wells in the study area

2021										2022			
Sample No.	**Apr.**	**May**	**Jun.**	**Jul.**	**Aug.**	**Sep.**	**Oct.**	**Nov.**	**Dec.**	**Jan.**	**Feb.**	**Mar.**	**Apr.**
E1	146.10	147.40	147.80	148.45	149.40	149.50	160.40	160.50	160.20	158.30	158.10	157.20	155.90
E2	118.20	114.10	114.50	113.80	116.20	118.00	118.20	120.40	118.20	104.80	104.65	104.55	107.50
E3	72.70	73.65	74.00	---	75.30	---	80.00	750.00	---	74.50	---	73.85	73.70
E4	84.90	85.10	88.40	88.60	94.35	94.40	95.35	95.36	78.10	75.85	75.80	75.55	74.60
E5	106.50	106.60	126.20	141.70	142.00	147.40	147.00	137.50	135.20	125.20	125.10	122.45	123.30
E6	42.80	45.50	46.70	47.40	48.00	49.10	49.20	47.80	49.28	48.30	48.50	47.05	45.40
E7	18.68	20.28	22.28	24.64	22.00	22.83	22.48	21.25	21.50	21.50	21.30	21.10	21.80
E8	52.00	52.80	59.30	61.20	76.50	77.60	64.80	65.00	65.10	65.63	63.60	64.70	68.20
E9	69.60	70.30	74.20	77.30	76.40	77.10	78.10	77.80	77.00	75.80	76.60	78.00	80.10
E10	---	131.80	130.98	133.63	138.28	142.20	142.50	136.20	137.50	---	137.00	136.00	142.00

(---: not measured)

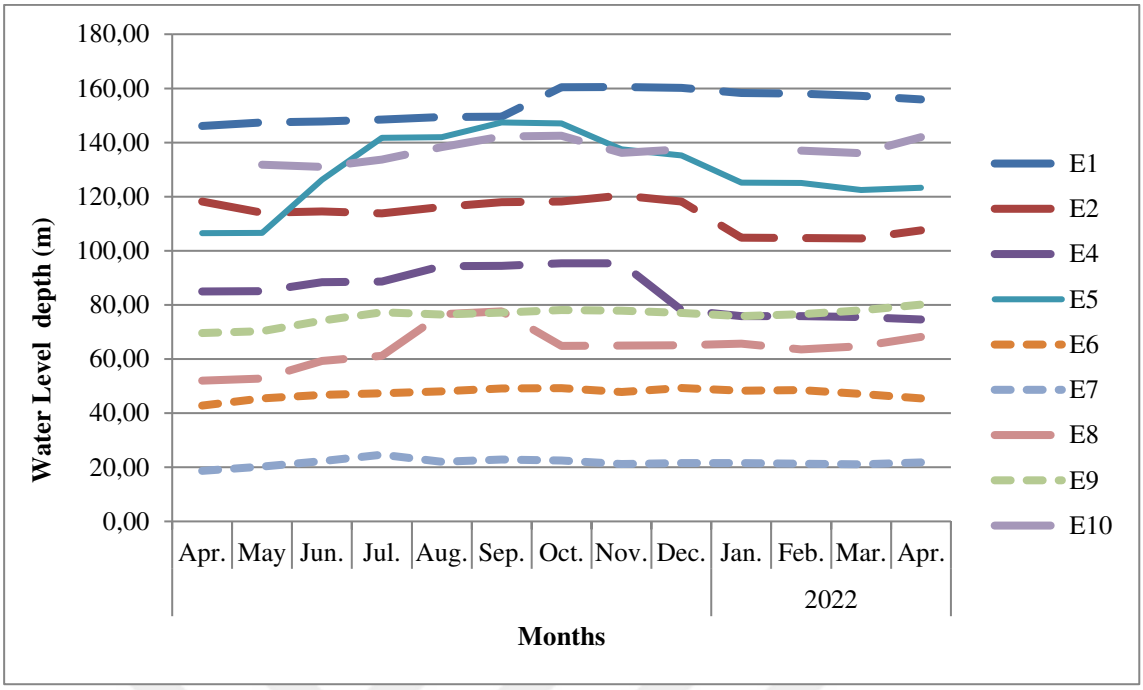

Figure 4.2. Static groundwater level fluctuations for the investigated wells

4.2. Hydrogeochemistry

Groundwater geochemistry is an interrelated science that deals with the chemistry of water for the subsurface environment, as the chemical composition of groundwater is the dual result of water entering the groundwater reservoir and interactions with rocks containing various minerals. Groundwater has a wide range of chemical compositions resulting from the difference in origin, the amount of recharge, interaction with the atmosphere and rocks, industrial pollution, pressure, and temperature (Appelo et al. ,1999).

The hydrochemistry of water is of great importance in the process of evaluating groundwater sources because the quality of water is no less important than its quantity. In other words, the chemical, physical and biological specifications are of great importance to determine the suitability of water for different uses. Environmental factors such as rock, climate, terrain, and time play an important role in determining the relationship between water chemistry and determining the dissolved elements in it. The main objective of hydrochemical studies is to know and determine the existence of the distribution of hydrochemical elements within the region and to know the relationship between water quality and its suitability for different purposes (Al-Basrawi, 2007)**.**

A total of (20) samples were collected for chemical analyses from various wells as part of the study's scope. Ten water samples during the rainy period (May 2021) and ten samples in the dry period (October 2021). The locations of the wells from which samples were taken are shown in (Figure 4.3).

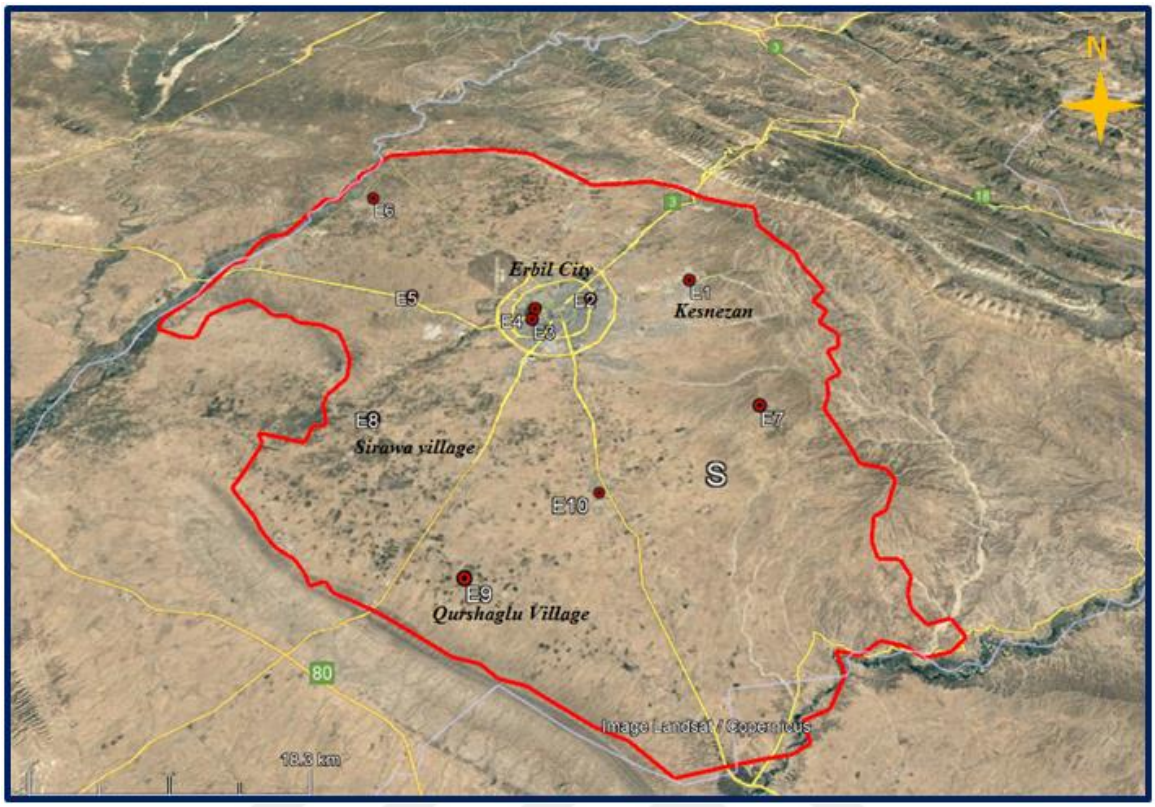

Figure 4.3. Location map of the wells in the study area

The chemical analyses performed for the groundwater samples comprised values of four major cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and three major anions (HCO_3^{-}, SO_4^{-2}, Cl^{-}), in addition to temperature, potential hydrogen (pH), total dissolved solids (TDS), electrical conductivity (EC), total hardness (TH), and turbidity. The results of the chemical analysis of groundwater samples are given in Table 4.3 and Table 4.4.

Table 4.3. Chemical analysis results of experimented samples of the wells in May (2021)

Sample No.	Temp.	pH	EC	TH	TDS	T.Alk.		Ca^{+2}		Cl^{-}		$SO4^{-2}$		Na^{+}		K^{+}		NO_3^{-}		Mg^{+2}	
	°C		µs/cm	mg/L	mg/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
E1	21,90	8,00	610	220	305	180	2,95	16,00	0,80	30,00	0,85	30,00	0,63	11,00	0,48	9,70	0,25	41,00	0,66	43,20	3,60
E2	25,10	8,10	650	200	320	204	3,34	16,00	0,80	28,00	0,79	27,00	0,56	17,00	0,74	2,70	0,07	19,00	0,31	38,40	3,20
E3	22,70	8,00	1050	372	530	256	4,20	16,00	0,80	65,00	1,83	11,00	0,23	15,00	0,65	2,80	0,07	61,00	0,98	79,68	6,64
E4	22,90	7,90	1060	360	530	280	4,59	22,00	1,10	58,00	1,63	14,00	0,29	20,00	0,87	5,50	0,14	61,00	0,98	73,20	6,10
E5	27,20	8,40	60	268	30	94	1,54	16,00	0,80	90,00	2,54	130,00	2,71	21,00	0,91	2,50	0,06	23,00	0,37	54,72	4,56
E6	26,90	8,30	1090	220	540	260	4,26	11,00	0,55	83,00	2,34	63,00	1,31	25,00	1,09	2,10	0,05	30,00	0,48	46,20	3,85
E7	22,50	7,80	630	208	310	212	3,48	18,00	0,90	38,00	1,07	5,00	0,10	9,00	0,39	1,20	0,03	26,00	0,42	39,12	3,26
E8	23,20	9,10	3310	1000	1660	400	6,56	26,00	1,30	120,00	3,38	10,00	0,21	59,00	2,57	3,10	0,08	13,00	0,21	224,40	18,70
E9	24,00	8,30	1910	548	960	320	5,25	26,00	1,30	43,00	1,21	54,00	1,13	49,00	2,13	3,70	0,09	56,00	0,90	115,92	9,66
E10	25,20	9,00	780	216	390	260	4,26	18,00	0,90	30,00	0,85	45,00	0,94	32,00	1,39	3,80	0,10	27,00	0,44	41,04	3,42
IQS(2010)		8,5	2000	500	1500	200	-	200	-	250	-	400	-	200	-	250	-	50	-	150	-
WHO(2011)		8,5	1500	500	1000	500	-	200	-	250	-	250	-	200	-	20	-	50	-	150	-

(-: not determined)

Table 4.4. Chemical analysis results of experimented samples of the wells in October (2021)

Sample No.	Temp.	pH	EC	TH	TDS	HCO_3		Ca^{+2}		Cl^-		SO_4^{-2}		Na^+		K^+		NO_3^-		Mg^{+2}	
	°C	…	µs/cm	mg/L	mg/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
E1	21,80	7,60	422	220	211	152,00	2,49	48,00	2,40	35,00	0,986	5,00	0,10	13,00	0,57	1,00	0,03	37,00	0,60	24,00	2,00
E2	23,50	7,70	380	220	191	160,00	2,62	40,00	2,00	38,00	1,070	2,00	0,04	24,00	1,04	2,00	0,05	15,00	0,24	28,80	2,40
E3	20,00	7,40	786	420	393	220,00	3,61	144,00	7,20	65,00	1,831	12,00	0,25	13,00	0,57	1,20	0,03	66,00	1,06	14,40	1,20
E4	21,80	7,50	736	440	367	220,00	3,61	144,00	7,20	48,00	1,352	35,00	0,73	20,00	0,87	1,20	0,03	68,00	1,10	19,20	1,60
E5	25,00	7,80	880	240	441	80,00	1,31	56,00	2,80	105,00	2,958	87,00	1,81	69,00	3,00	3,40	0,09	21,00	0,34	24,00	2,00
E6	23,40	7,60	878	232	439	200,00	3,28	45,00	2,25	110,00	3,099	87,00	1,81	67,00	2,91	3,50	0,09	48,00	0,77	28,68	2,39
E7	20,00	7,70	444	240	222	180,00	2,95	40,00	2,00	27,00	0,761	4,00	0,08	5,00	0,22	0,80	0,02	28,00	0,45	33,60	2,80
E8	20,00	7,40	5178	1160	2590	320,00	5,25	80,00	4,00	89,00	2,507	105,00	2,19	146,00	6,35	2,70	0,07	12,00	0,19	230,40	19,20
E9	21,80	7,40	1422	660	711	280,00	4,59	88,00	4,40	71,00	2,000	43,00	0,90	79,00	3,43	2,40	0,06	75,00	1,21	105,60	8,80
E10	25,00	7,70	614	240	307	140,00	2,30	42,00	2,10	55,00	1,549	19,00	0,40	33,00	1,43	2,70	0,07	14,00	0,23	32,40	2,70
IQS(2010)		8,5	2000	500	1500	200	-	200	-	250	-	400	-	200	-	250	-	50	-	150	-
WHO(2011)		8,5	1500	500	1000	500	-	200	-	250	-	250	-	200	-	20	-	50	-	150	-

(-: not determined)

4.2.1. Mineral saturation indices

Mineral saturation of water is related to the Gibbs free energies and ion activities of ions and minerals in the water. It is a logarithmic concept that includes values that change with temperature and partial pressure for each mineral. The mineral saturation state is useful for interpreting the mineral controls on ion concentrations in water, and for predicting probable reactions (Appelo and Postma, 2005). Mineral saturation index calculated by thermodynamic methods are interpreted as follows:

If SI = 0 Water is in equilibrium (saturated) with the corresponding mineral

If SI > 0 Water is supersaturated with the relevant mineral (mineral precipitating)

If SI < 0 Water is not saturated with related mineral (mineral has solubilizing property)

The saturation indices of the minerals in the groundwaters calculated in May (2021) and October (2021) are given in Table 4.5 and Table 4.6.

The groundwaters in the study area were mostly oversaturated with respect to aragonite, calcite, and dolomite minerals, whereas they were undersaturated with respect to anhydrite, gypsum, halite and sylvite minerals (Table 4.5; Table 4.6). The saturation indices of aragonite, calcite, and dolomite minerals were higher than zero (SI > 0) reflecting that these minerals are precipitated. The saturation indices of anhydrite, gypsum, halite and sylvite minerals for all groundwaters were calculated less than zero suggesting that these minerals will continuously dissolve in groundwaters.

Table 4.5. Saturation indices for the sampled wells in rainy season (May 2021)

Mineral	Chemical formula	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10
Anhydrite	$CaSO_4$	-3.07	-3.09	-3.60	-3.35	-2.46	-2.93	-3.78	-3.71	-2.79	-2.90
Aragonite	$CaCO_3$	-0.12	0.08	0.01	0.09	0.01	0.19	-0.17	1.16	0.55	0.97
Calcite	$CaCO_3$	0.03	0.22	0.15	0.23	0.16	0.34	-0.03	1.30	0.70	1.12
CO_2	CO_2	-2.70	-2.73	-2.55	-2.41	-3.37	-2.82	-2.42	-3.68	-2.78	-3.60
Dolomite	$CaMg\ (CO_3)_2$	0.82	1.18	1.33	1.32	1.19	1.66	0.62	3.91	2.39	2.96
Gypsum	$CaSO_4$: $2H_2O$	-2.74	-2.78	-3.27	-3.03	-2.18	-2.64	-3.45	-3.39	-2.48	-2.60
Halite	NaCl	-8.04	-7.88	-7.58	-7.51	-7.30	-7.25	-8.02	-6.76	-7.27	-7.58
Sylvite	KCl	-7.64	-8.24	-7.86	-7.62	-7.79	-7.90	-8.45	-7.59	-7.95	-8.07

Table 4.6. Saturation indices for the sampled wells in dry season (October 2021)

Mineral	Chemical formula	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10
Anhydrite	$CaSO_4$	-3.35	-3.82	-2.63	-2.16	-2.08	-2.21	-3.56	-2.22	-2.4	-2.83
Aragonite	$CaCO_3$	-0.09	-0.03	0.26	0.38	-0.11	-0.04	-0.03	0.03	0.12	-0.05
Calcite	$CaCO_3$	0.05	0.12	0.41	0.52	0.04	0.10	0.11	0.18	0.26	0.09
CO_2	CO_2	-2.37	-2.44	-2.03	-2.12	-2.84	-2.25	-2.41	-1.91	-1.93	-2.49
Dolomite	$CaMg\ (CO_3)_2$	0.14	0.43	0.14	0.50	0.04	0.34	0.48	1.14	0.94	0.41
Gypsum	$CaSO_4$: $2H_2O$	-3.01	-3.50	-2.27	-1.82	-1.78	-1.89	-3.20	-1.86	-2.06	-2.53
Halite	NaCl	-7.90	-7.60	-7.65	-7.59	-6.71	-6.71	-8.42	-6.51	-6.85	-7.30
Sylvite	KCl	-8.56	-8.23	-8.22	-8.36	-7.58	-7.54	-8.76	-7.78	-7.91	-7.95

Table 4.7 illustrates the maximum permissible limit concentration values in drinking water for the variables in chemical analyses imposed by most authorities. The concentration limits are as per the guideline of the Iraqi standard (IQS) and the World Health Organization standard (WHO). Some of them are polluted by bicarbonate and their values exceed the IQS limit, and some of them are polluted by nitrate and their values exceed the WHO limits.

Table 4.7. The Iraqi and world health organization guidelines for chemical and physical parameters

Parameters	WHO (2011)	IQS (2010)	Unit
Turbidity	*	5	NTU
Electrical Conductivity (EC)	1500	2000	µs/cm
Potential Hydrogen (pH)	8.5	8.5	*
Alkalinity in the form of $CaCO_3$	500	200	mg/l
Calcium (Ca^{+2})	200	200	mg/l
Magnesium (Mg^{+2})	150	150	mg/l
Sodium (Na^{+})	200	200	mg/l
Potassium (K^{+})	20	250	mg/l
Chloride (Cl^{-})	250	250	mg/l
Sulfate ($SO4^{-2}$)	250	400	mg/l
Nitrate (NO_3^{-})	50	50	mg/l
Total Hardness in the form of $CaCO_3$	500	500	mg/l
Total Dissolved Solids	1000	1500	mg/l

(*: not mentioned)

4.2.2. Seasonal changes in temperature, pH, EC, TH, and Turbidity in groundwater

Seasonal temperature changes

Temperature is an essential factor in geochemical reactions. It influences the acceptability of a variety of other inorganic components and chemical contaminants that may have an impact on taste (WHO, 2006). High water temperatures boost microorganism growth and may worsen taste, odor, color, and corrosion issues (Dara, 2011). The temperature of the samples was measured during sampling in the field in May 2021. The minimum water temperature was 21.9 °C in E1 well, while the maximum value was 27.2 °C in E5 well, and the average was around 24.16 °C. The temperature value of the samples was measured during sampling in October 2021, the minimum water temperature was 20 °C in E3, E7, and E8 wells, and the maximum value was 25 °C in E5 and E10, and the average was around 22.23 °C. The temperature changes are shown in Figure 4.4.

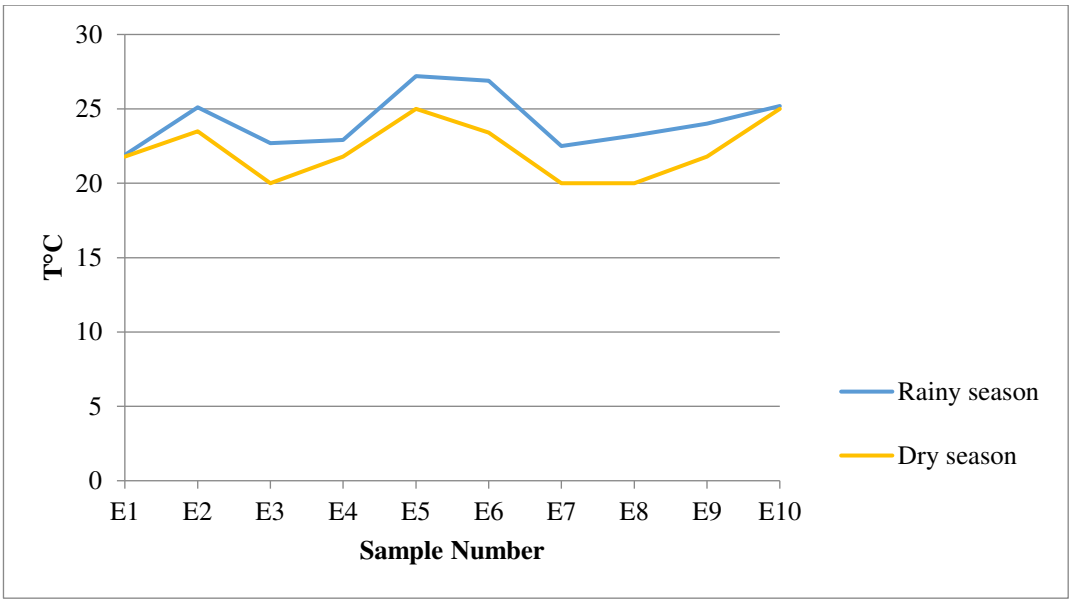

Figure 4.4. Seasonal variations of temperature in investigated groundwaters

When the temperature changes of the waters are evaluated seasonally, it has been observed that the temperatures generally increase in the rainy period (Figure 4.4). The fact that the temperatures are lower in the dry season indicates that the investigated groundwaters are not affected by precipitation in this season. The higher groundwater temperatures measured in the rainy season could be related to the increase in the water table in the rainy season in unconfined aquifers and, reflects the effect of atmospheric conditions on unconfined aquifers. The difference in the temperature of water samples may be related to the chemical processes that occur between the aquifer's rocks and its water (Hassan, 1998).

Seasonal changes in pH

The terminology pH is used universally to express the intensity of the acid or alkaline condition of a solution (Patil and Patil, 2010). It is beneficial for assessing water quality and providing crucial information for geochemical equilibrium or solubility calculations. Aside from increased anthropogenic activities, agricultural activity and fertilizer use also cause strong pH changes (Dara, 2011). The measuring processes of pH were repeated for the wells and tested two or three times to read the real value of pH.

The pH values of the water samples in May 2021 ranged from 7.8 in E7 to 9.1 in E8, with a mean pH of 8.29, while the pH values of the samples in October 2021 ranged from 7.4 in E3 to 7.8 in E5, with a mean pH of 7.58. Generally, the investigated waters are basic related to their pH values. Furthermore, the pH values of investigated waters are more basic in the rainy season (Figure 4.5). The pH values for all water samples were below the maximum permissible value of IQS and

WHO standards, except in the E8 and E10 wells in the rainy season, where the value exceeds the limits.

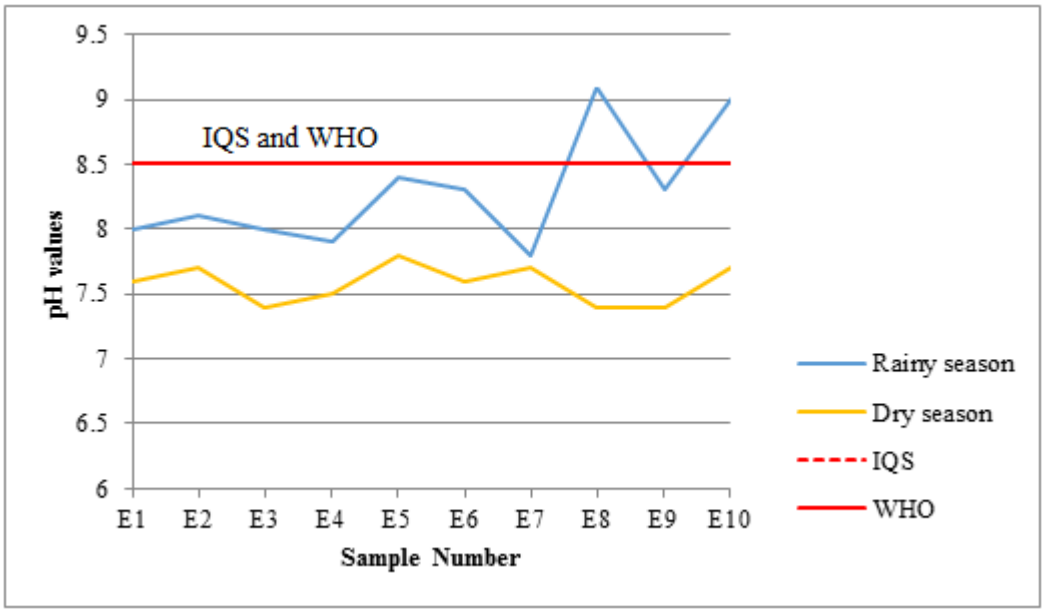

Figure 4.5. Seasonal variations of pH in investigated groundwaters

The higher pH values of groundwater, in the rainy season, are due to the dissolution of carbonate minerals in Quaternary deposits. Oversaturation of calcite and dolomite minerals in groundwater samples in the rainy season with increasing pH also supports this idea (Figure 4.6a). Conversely, saturation indices of calcite and dolomite increase with lower pH values, in the dry season (Figure 4.6b). Generally, the pH decreases due to the increase in CO_2 in groundwaters. The CO_2 content in groundwater is mostly reflecting the dissolution of carbonates. Generally, as the partial pressure of CO_2 in the water (log pCO_2) increases, the pH value of the water decreases. The fact that the pH values of the groundwaters are lower in the dry season is associated with the increase in the CO_2 concentration in the groundwater due to the increased groundwater-carbonate dissolution (Chidambaram et al., 2011). In addition, the decrease in pH values should be related to the nitrification reactions that develop in the vadose zone in relation to the nitrogenous fertilizers used in agricultural activities and also be related to the CO_2 emitting from the refineries in the study area.

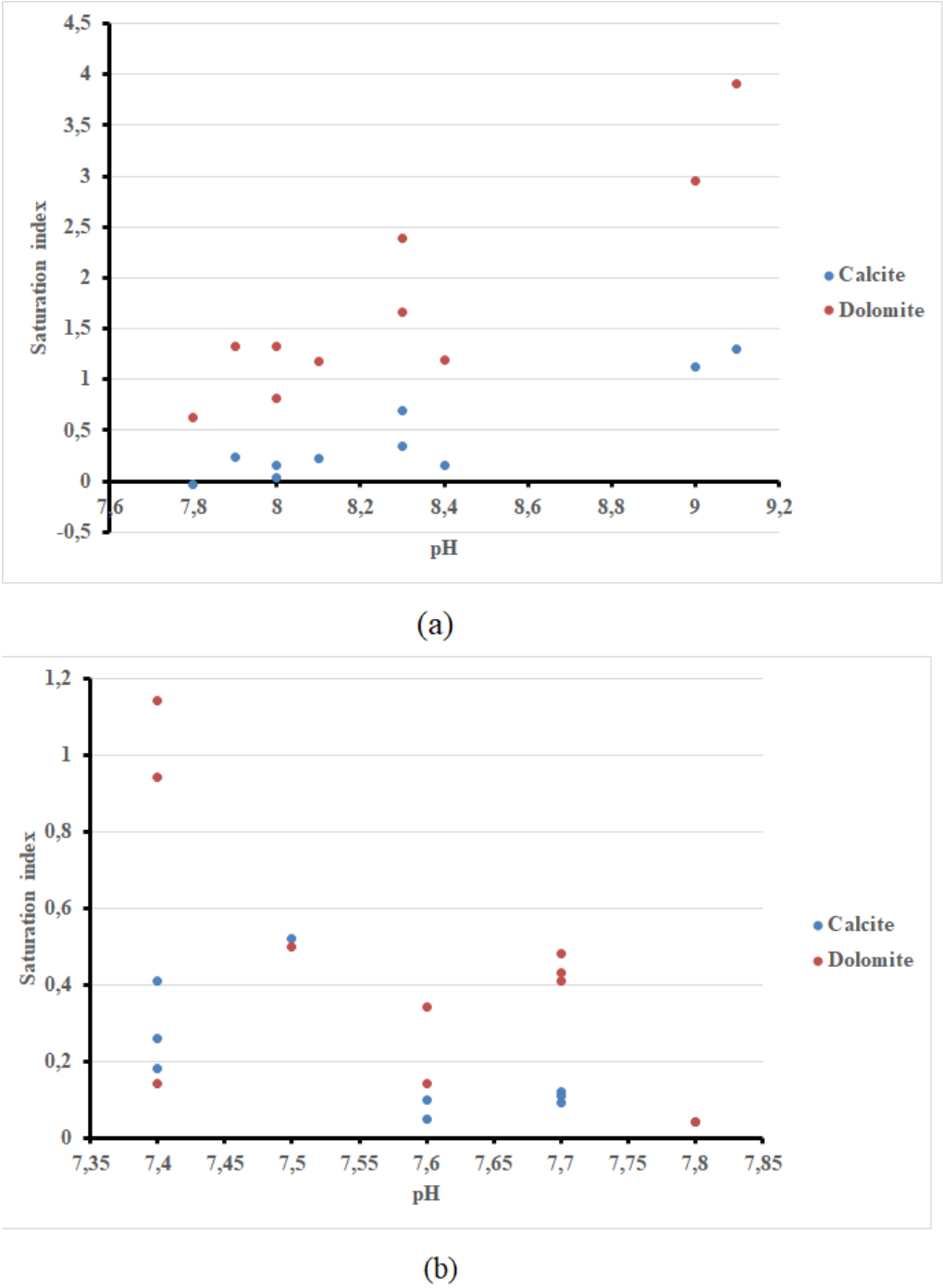

Figure 4.6. Relationship between pH and SI of calcite and dolomite in (a) rainy and (d) dry seasons

Seasonal changes in electrical conductivity (EC)

The capacity of groundwater to transmit an electrical current is referred to as electrical conductance or electrical conductivity. Conductance values represent the electrical conductivity, in micromhos, of one cm^3 of water at 25°C (Todd, 2005). The presence of ionized substances and other mineral contamination in water is linked to EC measurement. The conductance of

groundwater is a function of temperature, type of ions present, and concentration of various ions specific conductance readings and maybe of the high value of hardness. So that variations in conductance are a function only of the concentration and type of dissolved constituents present (Dara, 2011).

The groundwaters are classified into some groups related to their EC values (Table 4.8).

Table 4.8. The relationship between EC and mineralization of water according to Detay (1997)

EC Value (µs/cm)	Mineralization
< 100	Very weakly mineralized water
100 - 200	Weakly mineralized water
200 - 400	Slightly mineralized water
400 - 600	Moderately mineralized water
600 - 1000	Highly mineralized water
1000 <	Excessively mineralized water

Related to the EC values, the investigated groundwaters are classified from “very weakly mineralized water” to “excessively mineralized water” in the studied area (Table 4.9).

Table 4.9. Type of water for samples in the studied area in both rainy and dry periods (2021)

Sample Number	Rainy period	Dry Period
E1	Highly Mineralized water	Moderately Mineralized water
E2	Highly Mineralized water	Slightly Mineralized water
E3	Excessively Mineralized water	Highly Mineralized water
E4	Excessively Mineralized water	Highly Mineralized water
E5	Very weakly Mineralized water	Highly Mineralized water
E6	Excessively Mineralized water	Highly Mineralized water
E7	Highly Mineralized water	Moderately Mineralized water
E8	Excessively Mineralized water	Excessively Mineralized water
E9	Excessively Mineralized water	Excessively Mineralized water
E10	Highly Mineralized water	Highly Mineralized water

The highest EC value recorded in situ in May 2021 (Rainy period) was 3310 µs/cm for E8 well, the lowest EC was 60 µs/cm for the E5 well and the mean was 1115 µs/cm, while the highest EC value recorded in October 2021 (Dry period) and it was 5178 µs/cm for E8 well, and the lowest EC was 380 µs/cm for E2 well and the mean was 1174.5 µs/cm (Figure 4.7).

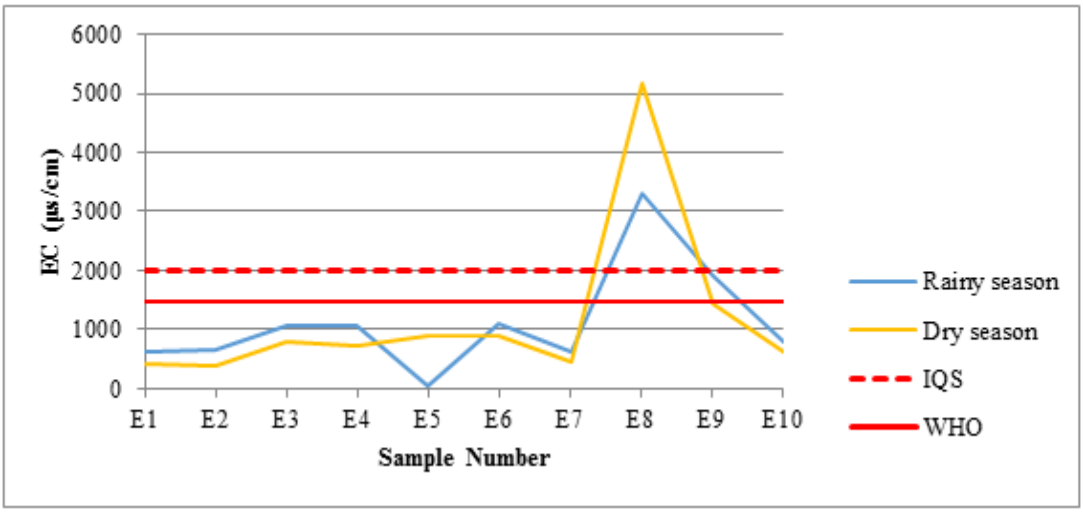

Figure 4.7. Seasonal variations of electrical conductivity in investigated groundwaters

In both seasons the EC value of E8 was too high and exceeds the maximum permissible limit values of IQS and WHO standards. Although there is no meaningful seasonal change determined of the EC values of the groundwater, the highest EC was measured in E8 groundwater (Figure 4.7). The higher EC values of the groundwater reflect the increasing dissolution of aquifer material related to the increasing groundwater level in the rainy season. Lower EC value in the rainy period in E5 is the result of the dilution of groundwater with the effect of precipitation, and higher EC values in the dry period are the result of the increased groundwater-rock interaction in this period (Figure 4.7). The highest EC value determined in E8 groundwater is the result of long residence time, long groundwater–aquifer material dissolution process, and anthropogenic sources such as the use of inorganic fertilizers in agriculture areas (Devaraj et al., 2018; Okan and Yiğit, 2022).

Seasonal changes of total hardness (TH)

Total hardness mainly reflects the water content of calcium and magnesium ions, these two major ions are found in sedimentary rocks, particularly dolomite, and other cations, including iron, magnesium, aluminum, zinc, and strontium, also increase hardness.

Depend on the total hardness values determined by the laboratory for the investigated groundwaters, the minimum TH value in May 2021 was 200 ppm in E2 well, and the maximum TH value was 1000 ppm for E8 well, while the minimum TH value in October 2021 was 220 ppm for E1and E2 wells, and the maximum TH value was 1160 ppm in E8 well. The values of E8 and E9 wells exceed the maximum permissible limit value of IQS and WHO standards (Figure 4.8).

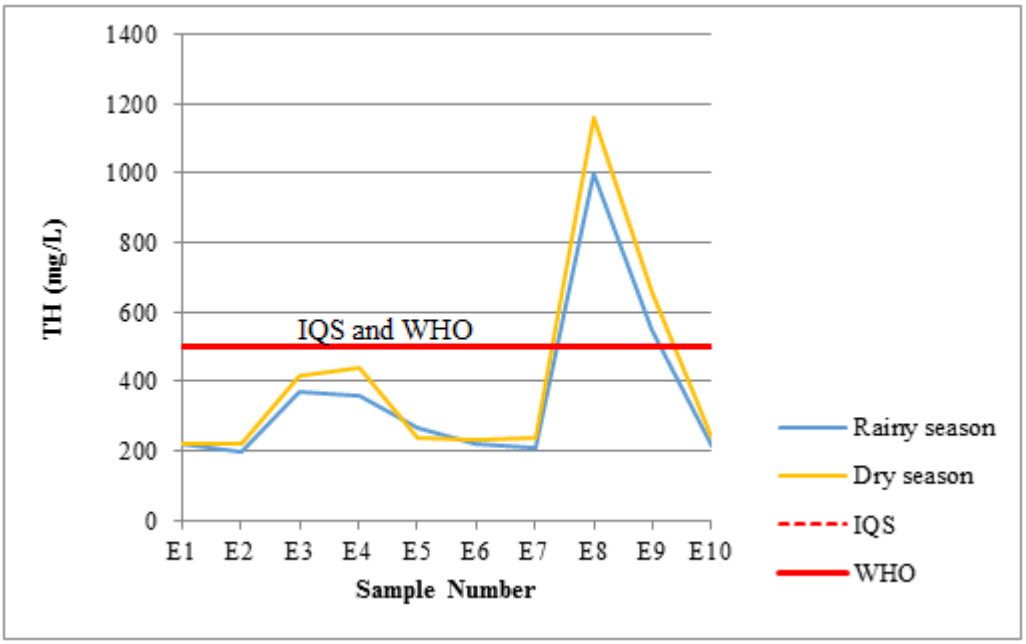

Figure 4.8. Seasonal variations of total hardness in investigated groundwaters

The lithology of the Plio-Pleistocene aquifer and the overlying alluvium influenced the TH values of the water samples because the pebbles of the Upper Bakhtiary and Lower Bakhtiary Formations are mostly limestones and dolomite, and the cementing material is calcareous (Hassan, 1981). Hammer (1986) described that hardness is more abundant in groundwater in locations with substantial geological formations of limestone, also according to Todd (1980), the hardness of water is produced from the solution of carbon dioxide released by bacterial activity in the soil in percolating water. Low pH conditions emerge, causing insoluble bicarbonates in the soil and limestone formations to dissolve and be converted into soluble bicarbonates. Impurities in limestone, such as sulfates, chlorides, and silicates, are exposed to the solvent action of water when the carbonates dissolve, and they flow into the solution as well. Thus, hard water is more likely to be found in areas where thick topsoil overlies limestone formations.

Waters with high (TH) values are undesirable, because divalent metallic cations, the most common of which are calcium and magnesium in groundwater, react with soap to generate precipitates and with certain anions in the water to form scale in water distribution pipes and tanks in buildings (Dara,2011). As a result of their undesirable reaction with soap, hard waters are unsuitable for home cleaning, necessitating the employment of water-softening techniques to remove hardness.

Classification of waters related to the total hardness is given in Table 4.10.

Table 4.10. Classification of water samples according to Sawyer and McCarthy (1967)

Hardness as $CaCO_3$	Water Class
0 - 75	Soft
75 - 150	Moderate Hard
150 - 300	Hard
> 300	Very Hard

The observed groundwaters are classified as “hard” and “very hard” waters related to their total hardness (Table 4.11).

Table 4.11. Type of water samples in the studied area according to Sawyer and McCarthy (1967)

Sample Number	Rainy Period	Dry Period
E1	Hard	Hard
E2	Hard	Hard
E3	Very Hard	Very Hard
E4	Very Hard	Very Hard
E5	Hard	Hard
E6	Hard	Hard
E7	Hard	Hard
E8	Very Hard	Very Hard
E9	Very Hard	Very Hard
E10	Hard	Hard

Seasonal changes of turbidity

Turbidity is a measurement of the amount of suspended and colloidal materials in a body of water, which includes clay, silt, organic materials, and microscopic organisms (Todd, 1980). Turbidity is reduced to a significant extent by the natural filtering created by unconsolidated aquifers, although other types of aquifers can produce turbid groundwater (Todd, 2005). NTU is the abbreviation for the measurement of turbidity (Nephelometric turbidity unit) at the name of the instrument and JTU (Jackson Turbidity Unit). Water with a turbidity of less than 5 NTU is normally suitable for consumers; however, this may vary depending on local conditions.

The minimum turbidity value in May 2021 was 0.2 NTU in E3 and E4 wells, and the maximum value was 1.1NTU in E6 and E10 wells, while the minimum turbidity value in October 2021 was 0.3NTU in E5 and E9 wells, and the maximum value was 2.7 NTU in E6 well. All the samples are below the maximum permissible limit value of IQS and WHO standards (Figure 4.9).

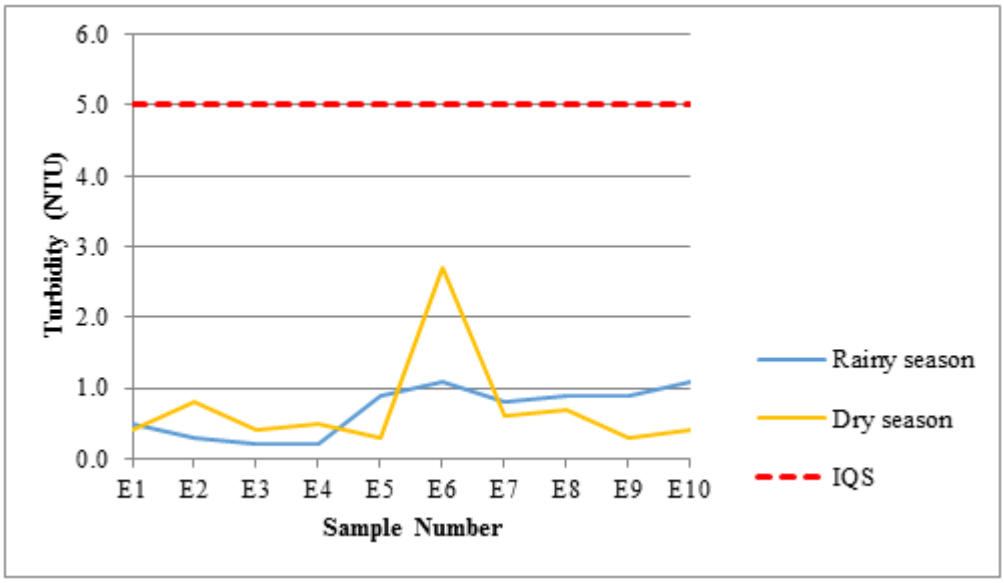

Figure 4.9. Seasonal variations of turbidity in investigated groundwaters

4.2.3. The origins and seasonal changes of major cations and anions

The groundwater quality is as important as the quantity when evaluating groundwater resources. Water with particular physical and chemical properties may be appropriate for agricultural purposes but unsuitable for other consumptions. As a result, studying water quality is critical in determining the primary method of usage.

Groundwater's chemical composition comes from the chemical composition of the rock with which it comes into direct contact and reaction between them. The composition, contact surface and duration, groundwater flow rate, temperature, environment pressure, common ion activity, and pH of the environment are all factors to consider in groundwater chemical contents. The main ions found in groundwater samples are Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{-2}, CI^{-}, and NO_3^{-}. These ions are divided into two groups which are cations and anions (Yüksel, 2007).

The study of groundwater quality requires describing the occurrence of numerous elements as well as their relationship to the aquifer material. Furthermore, groundwater quality data provide valuable insights into the geologic history of rocks as well as signs of groundwater recharge, discharge, transport, and storage. The chemical analysis of groundwater includes determining the concentrations of inorganic constituents, which are expressed as ions and include cations (positively charged ions) such as calcium, magnesium, sodium, and potassium, as well as anions (negatively charged ions) such as sulfate, chloride, fluorite, nitrate, and those contributing to alkalinity, which is usually expressed in terms of an equivalent amount of carbonate and bicarbonate (Walton, 1970).

Examining water in the field to identify its approximate chemical character is frequently beneficial, and this includes determining specific electrical conductance in the field, a portable

color scale for detecting chloride present in water, and the pH of the water using a basic portable pH meter. The concentration of the ions varies from place to place and over time since the concentration of the various ions rises along the course of the flow and the length of water contact with the rocks through which it flows. The properties of the unsaturated deposits that overlie an aquifer impact the percolated water that reaches the water table, which contains CO_2 (g), which influences the alkalinity or pH of the water along with the bicarbonates (Fetter, 1980).

The main, and trace ionic concentrations are studied in the hydrogeochemical investigation of groundwater in the Erbil Basin. In addition to these ionic concentrations, the research includes salinity in terms of total dissolved solids (TDS), electrical conductivity (EC), and reactivity in terms of (pH). Chemical testing was carried out both in the lab and in the field. All samples taken during the fieldwork were analyzed at the analytical laboratory of the water quality control unit in the Erbil Water Quality Control Department (EWCD).

i. Calcium (Ca^{2+})

Calcium is rich in the earth's crust and hydrosphere. Therefore, it is one of the most abundant ions in groundwater. It gives hardness to the water. Calcium ions are mainly sourced through the chemical weathering of rocks and minerals that contain this ion, such as sedimentary rock like limestone. Furthermore, calcium is sourced from the dissolution of Ca-bearing minerals such as calcite, aragonite, dolomite, and gypsum, or minerals of igneous rocks such as pyroxene, amphibole, and feldspar. The calcium concentration of groundwater often reflects the aquifer lithology (Shwani, 2008).

Calcium concentrations in regular drinkable groundwater typically vary between 10 and 100 ppm. Calcium in this amount has no known effect on human or animal health. Indeed, as much as 1000 ppm of calcium may be harmless. The widespread belief that calcium water leads to artery hardening, kidney stones, and liver problems is without factual support (Hassan, 1998).

The calcium contents in investigated waters are due to the dissolution of carbonates in the study area, such as limestone grains in the Upper and Lower Bakhtiary formations and those in Quaternary deposits. In addition to its cementing material which is also of calcareous type, the solubility of the carbonate rocks increases in the presence of solutions rich with dissolved carbon dioxides. Therefore, the percolated waters that are enriched with CO_2 (from the atmosphere and due to anaerobic bacterial activity in the soil) dissolve greater amounts of calcium carbonates according to the following series of the equations (Hassan, 1998):

$$\uparrow CO_2 + H_2O \leftrightharpoons H_2CO_3 \leftrightharpoons H^+ + HCO_3^- \quad (4.1)$$

$$HCO_3 \leftrightharpoons H^+ + CO_3^{-2} \quad (4.2)$$

$$CaCO_3 + H \leftrightharpoons Ca^{+2} + HCO_3^- \quad (4.3)$$

The atmosphere of cities is distinguished by a larger percentage of $CO_{2(g)}$, as well as a favorable habitat for anaerobic bacteria activities, which provide moist soils and percolated wastewater with high quantities of dissolved carbon dioxide gas, as a result, the calcium ions in urban groundwater are increasing.

The calcium ions are one of the main cations in the water samples of the wells in the study area. In May 2021, the maximum concentration of this cation is 26 ppm in E8 and E9 wells which are located on the west and southwestern side of the Erbil basin respectively, while the minimum concentration of the calcium ion is 11 ppm in the E6 well which is located in the northwestern side of the Erbil Basin. In October 2021, the value is ranging from 40 ppm in E2 and E7 wells, the E2 well is located in the center of Erbil city and the E7 is located in the eastern part of the Erbil basin to 144 ppm in both E3 and E4 wells in the central part of the Erbil Basin. In general, the calcium concentrations in the rainy period are lower than the calcium concentrations in the dry period. This reflects a long groundwater-rock interaction process in the dry season, whereas the dilution of groundwater by precipitation in the rainy season occurs. Despite the concentrations of calcium in the dry period being higher than concentrations in the rainy period, the values in both periods are below the maximum permissible limits of IQS and WHO standards as shown in (Figure 4.10).

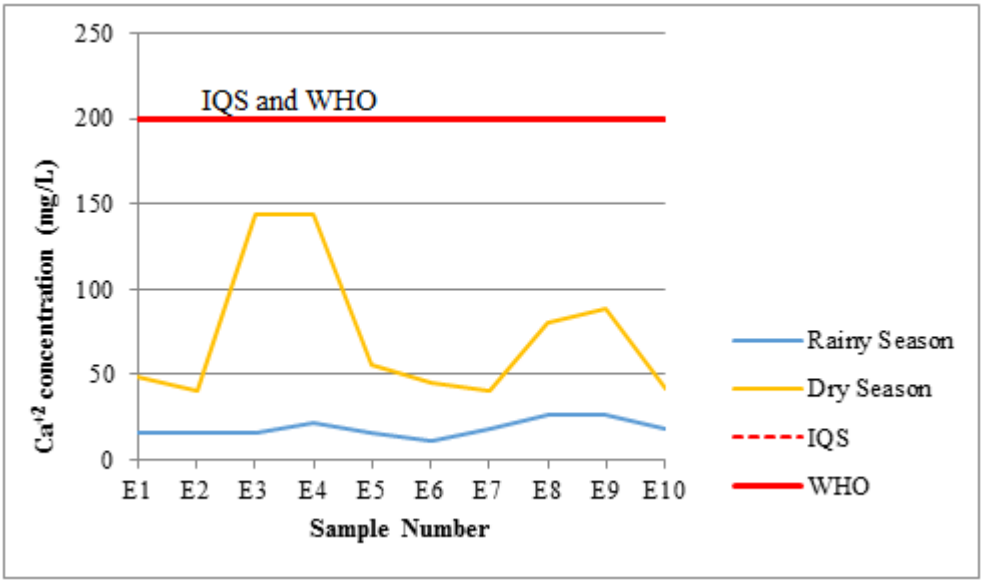

Figure 4.10. Seasonal variations of calcium contents in investigated groundwaters

ii. Magnesium (Mg^{+2})

Magnesium is one of the most common elements in the alkaline earth group, comprising around 2.1 percent of the earth's crust by weight (Collins, 1975). Dolomite in sedimentary rocks is a frequent source of magnesium in the hydrosphere, as are Olivine, biotite, hornblende, and augite in igneous rocks, and serpentine, talc, diopside, and tremolite in metamorphic rocks. It is essential for plant and animal growth and nutrition (Hem, 1985). Furthermore, because most calcite contains some magnesium, a solution of limestone often gives a high concentration of magnesium as well as calcium. Magnesium carbonate has geochemistry that is quite similar to calcium carbonate. The presence of carbon dioxide also influences the solubility of magnesium carbonate. However, the solubility of pure magnesium carbonate is much greater than that of calcium carbonate; therefore magnesium carbonate does not precipitate at normal temperatures and pressures seen in near-surface water. The magnesium content in investigated groundwaters is related to the dissolution of Mg-bearing minerals in sedimentary rocks of the Bakhtiary Formation and those in the Quaternary deposits.

In May 2021, the magnesium ions concentration values in the water samples of the studied area ranged from 38.4 ppm in the E2 well to 224.4 ppm in the E8, whereas, in October 2021, the value is ranged from14.4 ppm for the E3 well to 230.4 ppm for the E8.

Meaningful seasonal changes in magnesium contents of groundwaters are seen in E3, E4, and E5 wells which are located in the central of the Erbil Basin. However, there isn’t any seasonal change determined in magnesium contents in E7, E8, and E9 wells (Figure 4.11). Relatively high magnesium contents in E3, E4, and E5 in the rainy season might be related to the anthropogenic factors as well as groundwater-rock interaction. Hence, E3, E4, and E5 wells are located in the urban area of Erbil. The highest magnesium contents in both seasons are determined in the E8 and E9 wells which are located on the western edge of the Erbil Basin.

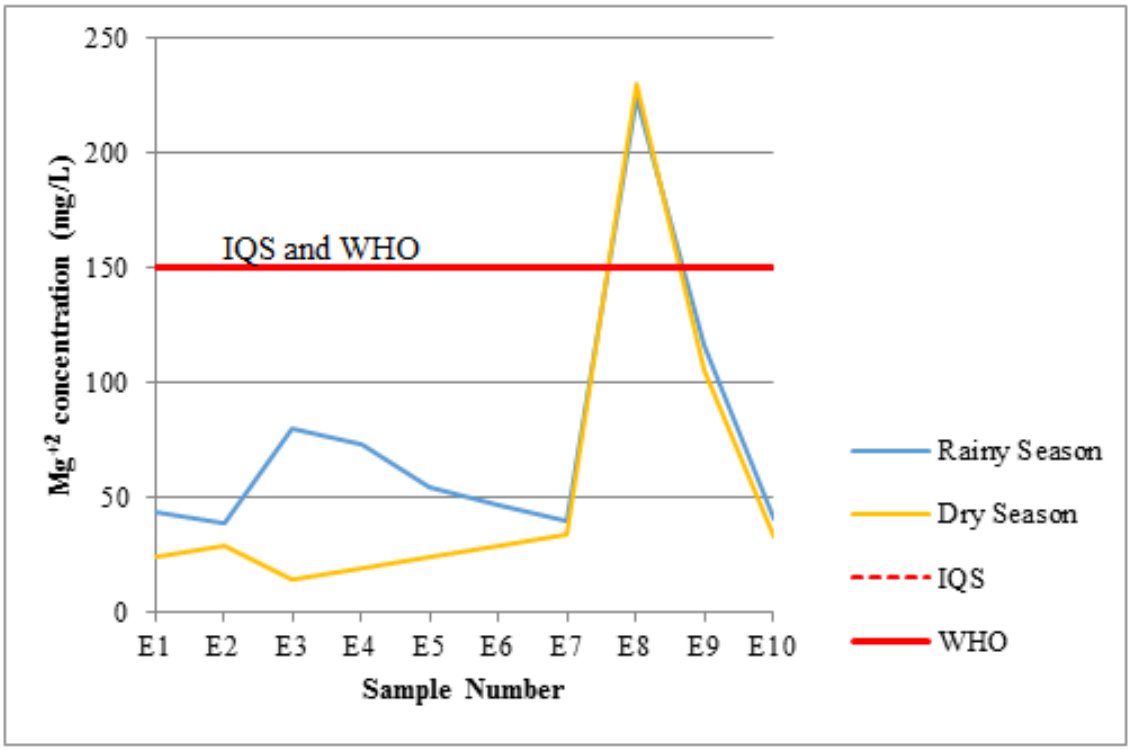

Figure 4.11. Seasonal variations of magnesium contents in investigated groundwaters

In general, the magnesium concentration values do not exceed the maximum permissible limit by IQS and WHO standards until it reaches the E8 well which is the highest and exceeds the maximum permissible limit and is higher than 150 ppm. The higher content of magnesium in the E8 well is due to anthropogenic activities (especially the usage of chemical fertilizers) and the use of insecticides on crops (Figure 4.12; Figure 4.18).

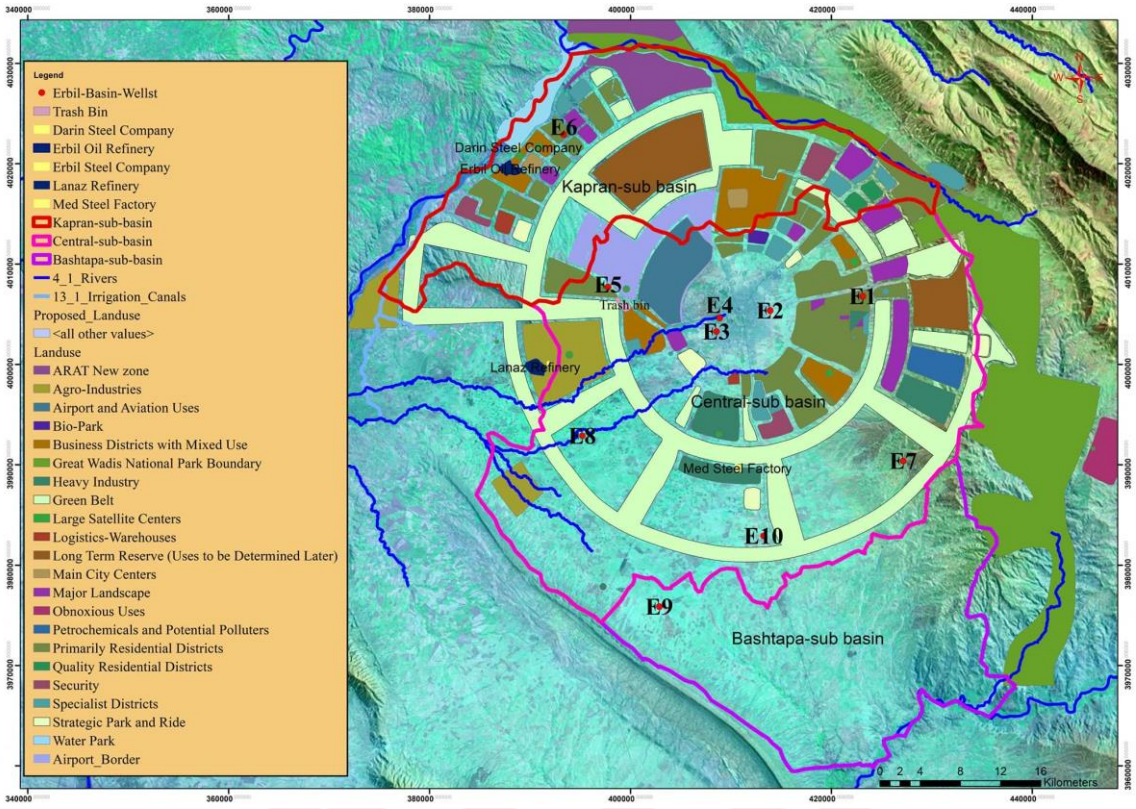

Figure 4.12. Land use map of Erbil Basin

iii. Sodium (Na^+)

The release of soluble compounds during the weathering of plagioclase feldspars is the principal source of sodium in natural water. The solution of halite is also essential in locations containing evaporate deposits, and in some cases, clay minerals may release significant amounts of sodium. Industrial waste contributes to an increase in sodium content in natural waters (Shwani, 2008). In agricultural terms, the sodium to total cation ratio is vital. High sodium levels affect permeability, cause a salty taste, domestic and industrial contamination, and change the structure of the soil (Aydınoğlu, 2019).

In May 2021, the concentration of sodium in the water samples of the studied area ranged between 9 ppm in E7 well and 59 ppm in E8 well, whereas the concentration in October 2021 ranged between 5ppm in E7 well and 146 ppm in E8 well. This means that in the rainy season, the minimum concentration was for the sample of the E7 well which lies on the eastern side of the Erbil Basin, and the maximum concentration was for the sample of the E8 well which lies on the west side of the central sub-basin of Erbil. In both seasons the sodium concentration values are located below the maximum permissible limit of IQS and WHO as shown in (Figure 4.13).

Generally, sodium contents in groundwaters are due to the groundwater-rock interaction. Furthermore, high sodium content in E6, E8, and E9 is related to the fertilizer usage in agriculture sites surrounding these wells (Figure 4.12).

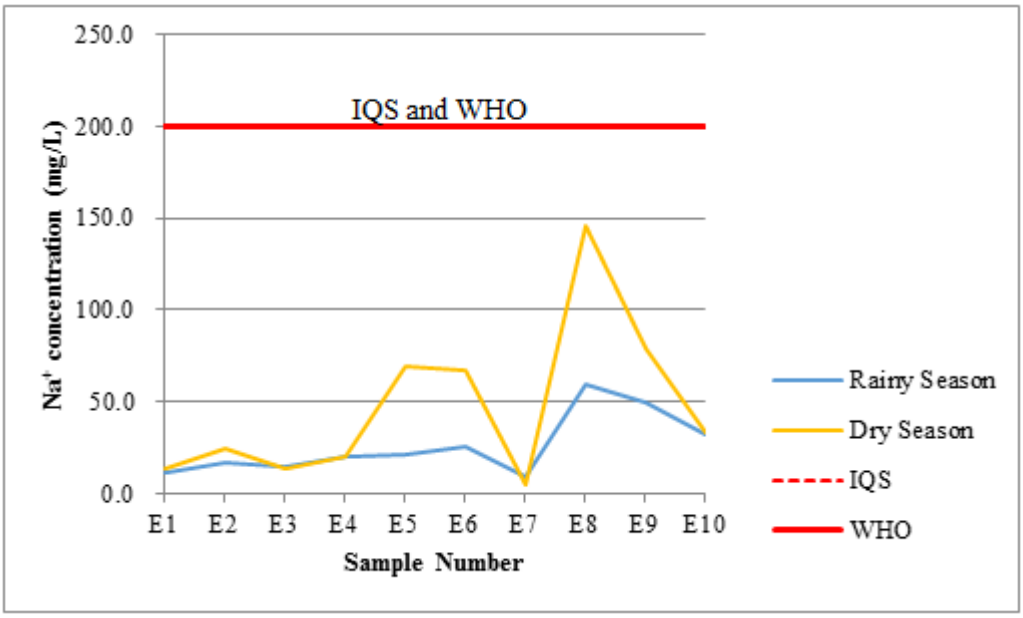

Figure 4.13. Seasonal variations of sodium contents in investigated groundwaters

iv. Potassium (K^+)

Potassium is a necessary element for humans, plants, and animals, and it is derived mostly from vegetation and soil in the food chain. It's commonly found in the weathering of biotite, nepheline, leucite, and orthoclase in igneous and metamorphic rocks, application of potash fertilizers, and irrigation with surface water. Waters percolating through evaporite deposits may contain very large quantities derived from the dissolution of sylvite. Although potassium has around the same richness as sodium in the earth's crust, potassium concentrations in natural water are often less than one-tenth that of sodium (Faure, 1998). Potassium's relative immobility is due to, first, during weathering, potassium entering the structure of some clay and clay-like minerals, and second, many potassium minerals have a stronger resistance to weathering than sodium minerals.

The potassium concentration in the study area is between 1.2 ppm in E7 and 9.7 ppm in E1 in May 2021, whereas it is between 0.8 ppm in E7 and 3.5 ppm in E6 in October 2021.

In both seasons the potassium concentration values are located below the maximum permissible limit of IQS and WHO as shown in Figure 4.14. Relatively high potassium concentrations in the rainy season reflect the effect of urbanization on groundwater hydrogeochemistry (Figure 4.12).

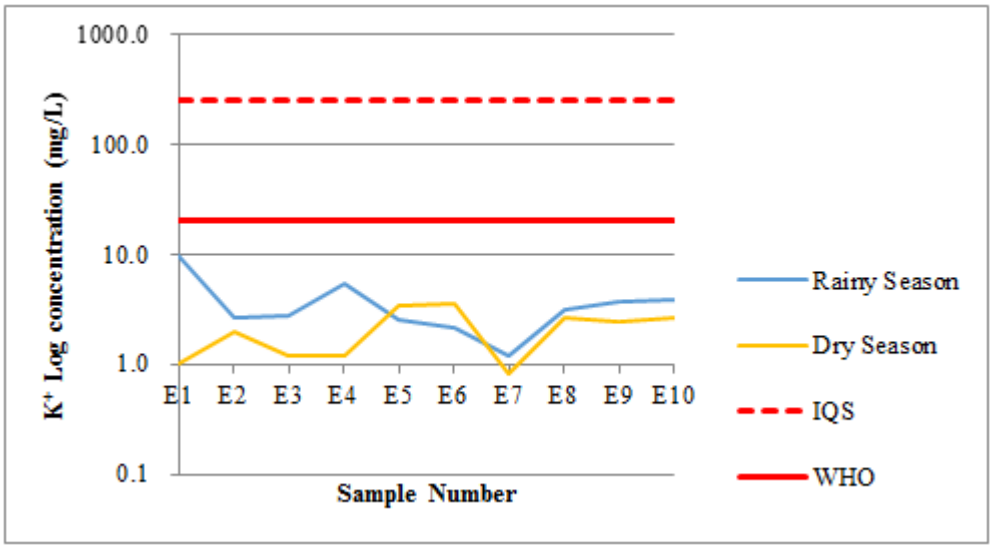

Figure 4.14. Seasonal variations of potassium contents in investigated groundwaters

v. Bicarbonate (HCO_3^-)

The majority of carbonate and bicarbonate ions in groundwater are produced from carbon dioxide in the air, carbon dioxide available in the soil, carbonate rocks' solutions, and sometimes, groundwater gets the carbon dioxide that is generated by the diagenesis of organic compounds (Ljungberg and Qvist, 2004). Bicarbonates are essential for the alkalinity of water samples from the study area. If the pH of the samples is less than 8.2 and greater than 4.5, the alkalinity is due to bicarbonates only.

Bicarbonate concentrations of water samples of the studied area ranged between 94 ppm in E5 well and 400 ppm in E8 well during the rainy period, while the values are between 80 ppm in E5 well and 320 ppm in E8 well during the dry period (Table 4.3; Table 4.4).

The bicarbonate concentration values in the rainy period are higher than the permissible limit of IQS standard in E2, E3, E4, E6, E7, E8, E9, and E10 wells, while in the dry period, the values exceed the IQS limit in E3, E4, E8, and E9 wells, otherwise, in both periods the bicarbonate concentration values are in the same condition with slightly higher values in rainy period and are located below the maximum permissible limit WHO standard (Figure 4.15).

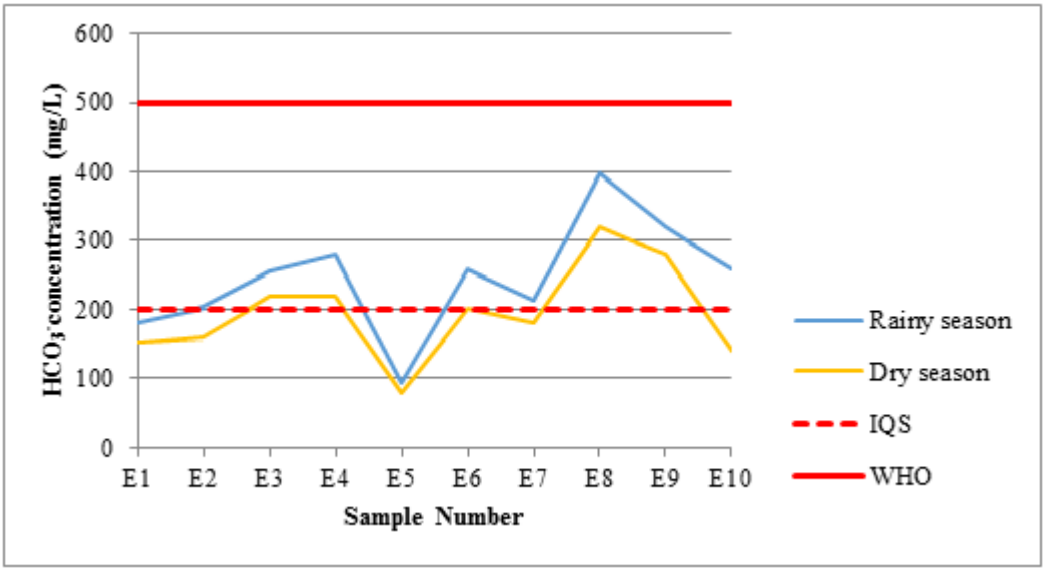

Figure 4.15. Seasonal variation of bicarbonate concentrations in investigated groundwaters

Most of the carbonate (CO_3^{-2}) and bicarbonate (HCO_3^-) ions in groundwater are formed from CO_2 in the atmosphere and soil and the dissolution of carbonate masses. Therefore, the amount of CO_3^{-2} and HCO_3^- depends on the amount of CO_2 and the pH of the water. The positive linearity between Ca^{+2} and HCO_3^- shows that HCO_3^- concentrations in the groundwaters in the study area are the result of the dissolution of the carbonates of Bakhtiary Formation and Quaternary deposits by CO_2^- rich groundwaters (Figure 4.16; Figure 4.17). The higher concentrations of HCO_3^- in the groundwaters in both seasons can be explained by the lower pH values of the waters and the corresponding increase in the solubility of the carbonate minerals.

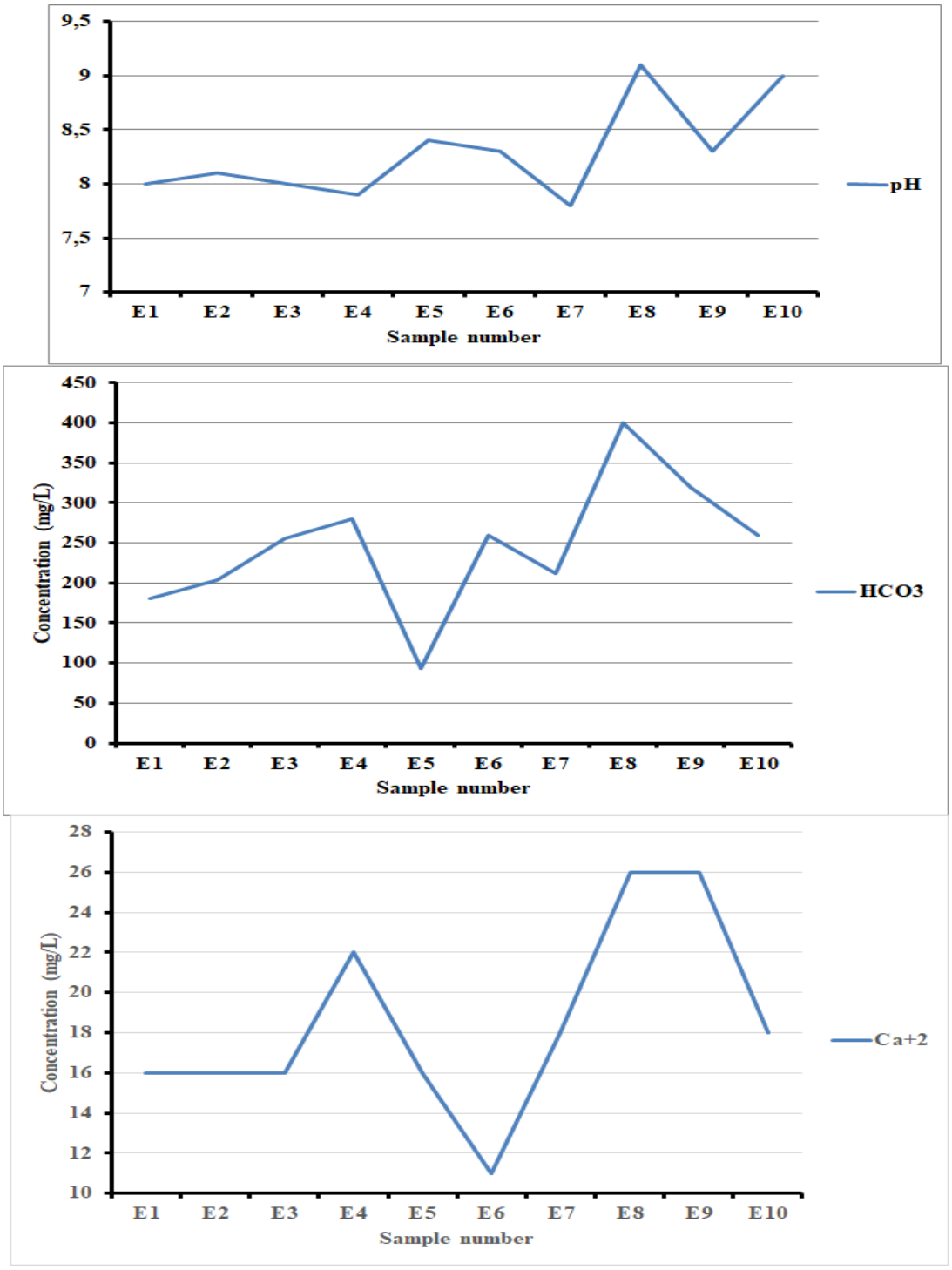

Figure 4.16. Relationship of pH with HCO_3^- and Ca^{+2} concentration in groundwaters (rainy season)

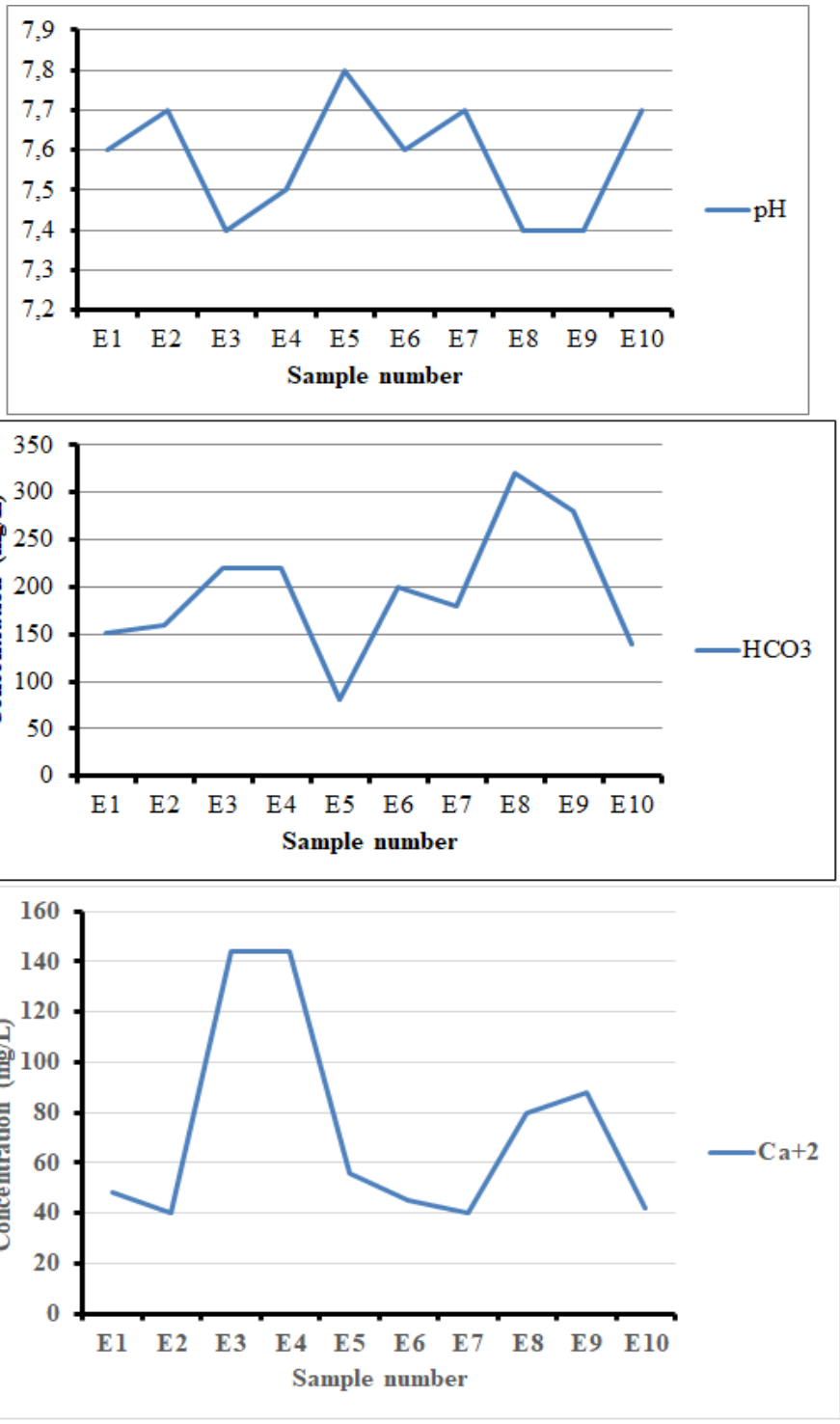

Figure 4.17. Relationship of pH with Ca^{+2} and HCO_3^- contents in groundwaters (dry season)

vi. Sulfate (SO_4^{-2})

Sulfate naturally occurs as a result of sulfate mineral dissolution in evaporates like gypsum and anhydrite, and it is present in groundwater in many minerals such as Barite ($BaSO_4$) and Epsomite ($MgSO_4.7H_2O$) (Todd, 1980). A significant amount of sulfates produces as a result of the pyrite and marcasite oxidation in clay minerals as shown in equation 4.4 (Drever, 1997):

$$FeS_2+3.75CO_3+1.5H_2O+2CaCO_3 \rightarrow Fe(OH)_3+2Ca+2SO_4+2CO_3 \quad (4.4)$$

Sulfates are largely recycled from the atmosphere and the solution of sulfate minerals in sedimentary rocks. Sedimentary rocks, particularly organic shales, may also yield a large amount of sulfates through the oxidation of marcasite and pyrite. All atmospheric precipitation contains sulfate, which although, commonly in absolute concentrations of less than 2 ppm, is one of the major dissolved constituents of rain and snow. Sulfur dioxide is released into the atmosphere through the combustion of coal and oil, as well as the smelting of ores, hence precipitation near these sources are frequently rich in sulfate (Shwani, 2008).

In addition to the natural sources of sulfate, human activity, including agricultural and industrial operations, is a significant source of sulfate. The groundwater affected by sulfate reduction has the lowest sulfate contents. Magnesium sulfate brines have the greatest amounts of sulfate. Groundwater from igneous and metamorphic rocks or sediments produced from them typically includes less than 100 ppm and may contain less than 1 ppm in sulfate-reducing bacteria that are active in the soil through which recharge water has percolated (Al-Kubaisi, 1996). More than 250 ppm in water is considered unacceptable in some uses (Todd, 1980). Except for increasing soil salinity, SO_4^{-2} has no negative effects on agriculture. It is important for plant nutrition in irrigation waters at concentrations of up to 250 mg/l, when this concentration exceeds 500 mg/l, it becomes harmful (Erguvanlı and Yüzer, 1973).

The lowest value of sulfate concentration for the samples in the rainy period is 5 ppm in the E7 well and the highest value is130 ppm in E5 well, while the lowest value in the dry period is 2 ppm in the E2 well and the highest is 105 ppm in E8. The reason for the high values of sulfate in both E5 and E8 wells are may due to anthropogenic activities (such as infiltration of landfill leachates, and chemical fertilizers) and hydrogen sulfide (H_2S) gas emitting from refineries (Natesan et al., 2022) (Figure 4.12; Figure 4.18; Figure 4.20).

Figure 4.18. Open sewage and garbage dumps in the study area

In both seasons the sulfate concentration values are located below the maximum permissible limit of IQS and WHO as shown in (Figure 4.19).

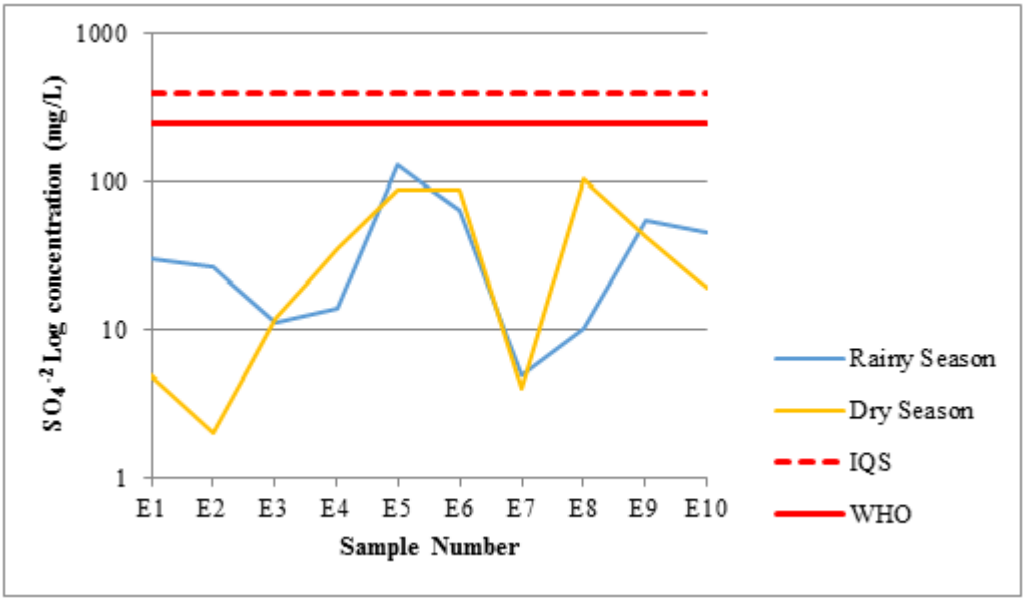

Figure 4.19. Seasonal variation of sulfate concentrations in investigated groundwaters

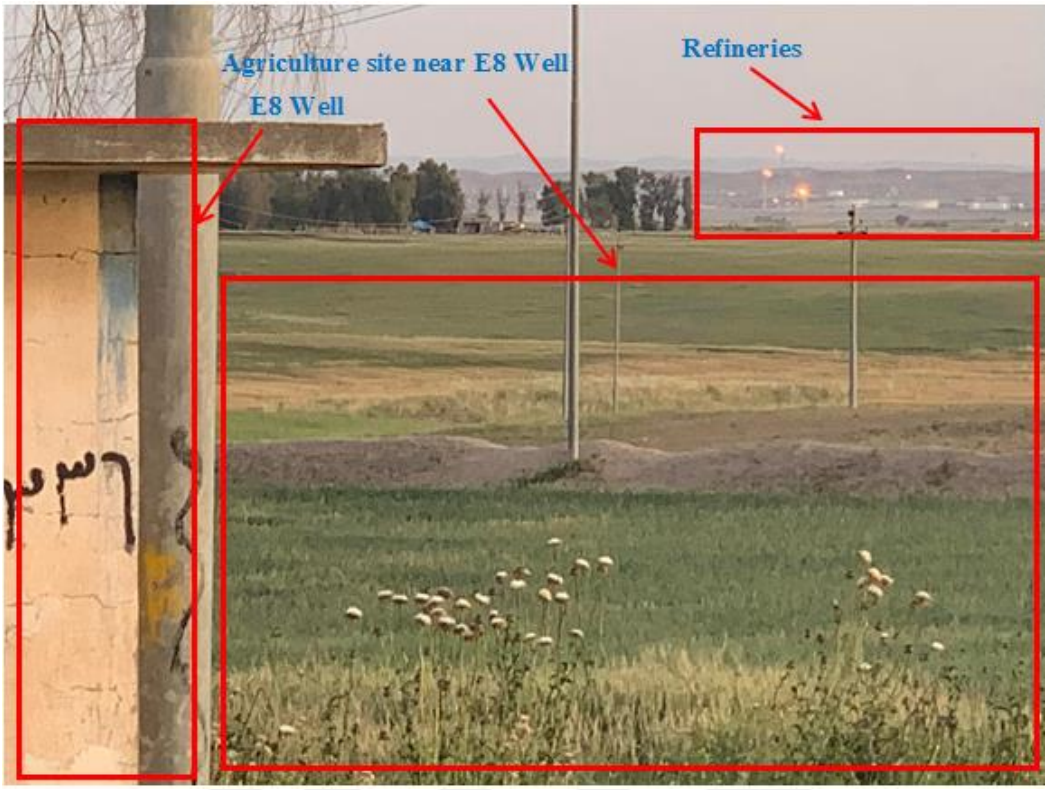

Figure 4.20. A picture of the E8 well near agricultural land and crude oil refinery stations

vii. Chloride (Cl^-)

Chloride is very common in nature. The majority of the chloride in groundwater originates from four main sources, first, chloride from ancient seawater bound in sediments, second, halite and associated mineral solution in evaporite deposits, third, evaporation of chloride provided by rain or snow, and four, dissolved dry fallout from the air, particularly in arid environments (Hassan, 1998). The main source of chloride in near-surface water appears to be chloride transferred in the atmosphere and transported to Earth by rain or snow (Meybeck, 1983). Because all chloride salts are quite soluble, chloride is seldom removed from water by precipitation unless it is frozen or evaporated. Chloride is also largely devoid of exchange, adsorption, and biological activity effects. When water dissolves chloride, it is difficult to eliminate the chloride by natural means. In humid areas, chloride concentrations in natural water are typically less than 10 ppm but can reach 100 ppm in arid areas. Concentrations of chloride higher than 100 ppm have the possibility of causing physiological danger (Shwani, 2008).

In the rainy season, chloride concentration in the studied area ranged between 28 ppm in E2 well and 120 ppm in E8 well, which means that the highest concentration was for E8 well and the lower limit was for E2 well, whereas, in the dry season, the concentration ranged between 27 ppm in E7 well and 110 ppm in E6 well (Table 4.3; Table 4.4). Meaningful seasonal change isn't determined in groundwaters. The main source of chloride in investigated groundwaters is the

dissolution of halite mineral in Quaternary deposits and sedimentary rocks of the Bakhtiary Formation.

In both seasons the chlorite concentration values are located below the maximum permissible limit of IQS and WHO as shown in (Figure 4.21).

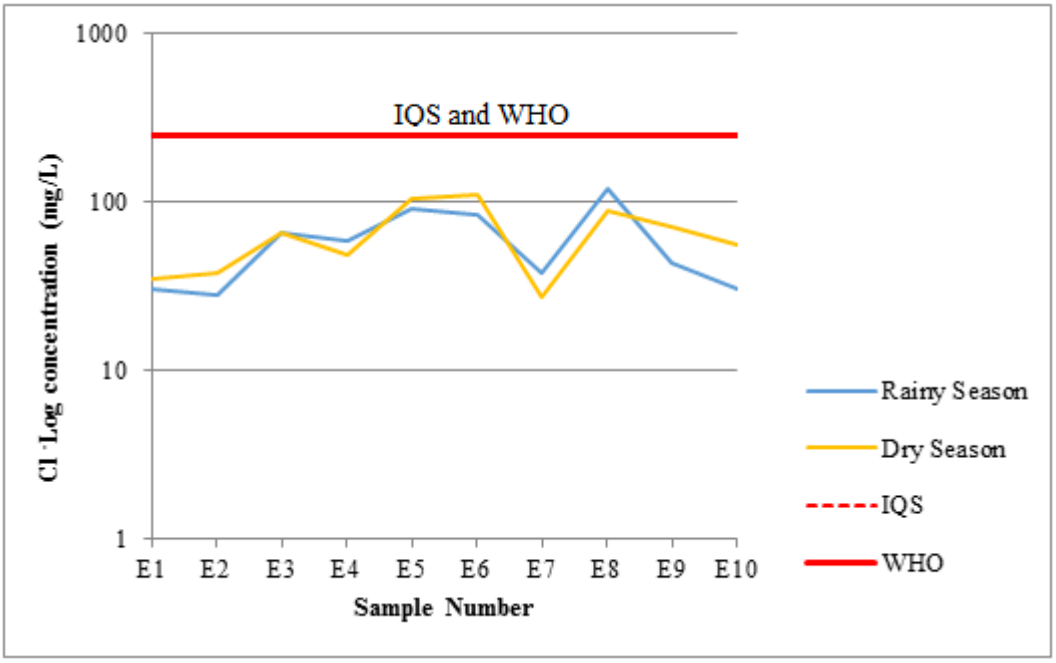

Figure 4.21. Seasonal variation in chloride concentrations in investigated groundwaters

viii. Nitrate (NO_3^-)

The majority of nitrate in natural water is either from organic sources or industrial and agricultural chemicals. Wastewater, organic oxidation, nitrogen in the soil, industrial waste, NO_2 gasses present in the air (fuel burning), and fertilizers are all sources of nitrates. Nitrates are highly soluble chemicals, yet the nitrate level of unpolluted natural waters is typically less than 5 mg/l, and water-bearing materials produce a small concentration of nitrates, the organic processes in the soil or aquifer serving as the primary source (Hassan, 1998). The oxidation of nitrogen or nitrogenous substances by bacteria in decaying organic materials or sewage is a significant source. The fertile soils and well-oxygenated natural waters have bacterial oxidation of ammonia to nitrite and ultimately to nitrate. This type of water is situated in the higher soil layers or shallow aquifers (Al-Sawaf, 1977). Public and private lawns in urban areas, as well as septic tanks, leaking sewage lines, urban runoff, and waste disposal sites, are regarded as

important sources of nitrates in urban environments (Sharma et al., 1996). High amounts of nitrates infiltrate and eventually percolate into groundwater from leaky sewers, which carry the majority of the city's domestic and industrial effluent. Denitrification refers to the effect of cities on nitrate concentrations (Grischek et al., 1996). Waters having high levels of nitrate (more than 100 ppm) taste bitter and might induce physiological distress; nitrate concentrations greater than 45 ppm have been linked to methemoglobinemia in infants (Todd, 1980).

In the rainy season, nitrate concentration in the studied area ranged between 61 ppm in E3 and E4 wells and 13 ppm in E8 well, which means that the lowest concentration was for E8 well, whereas, in the dry season, the concentration ranged between 75 ppm in E9 well and 12 ppm in E8 well (Table 4.3; Table 4.4).

The E3, E4, and E9 wells are above the IQS and WHO maximum permissible limits and higher than 50 ppm (Figure 4.22), the reason is because of urbanization and contamination by humans in E3 and E4 wells. The urbanization factor includes the leachate from landfills and septic tanks. The agricultural processes, the use of insecticides on crops, and nitrogen component gases from the refinery stations are the factors that cause an increase in nitrate content in E9 well (Shwani, 2008) (Figure 4.18; Figure 4.23)

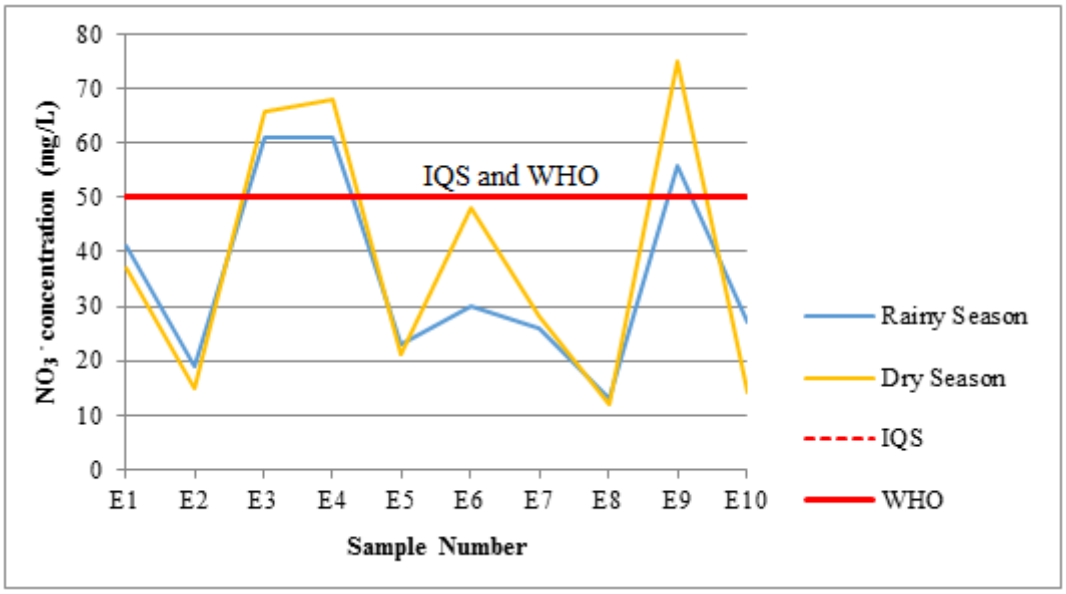

Figure 4.22. Seasonal variation in nitrate concentrations in investigated groundwaters

Figure 4.23. A picture of a well near houses located in an urban area within the city of Erbil

The wells were accompanied by an increase in the percentage of nitrate ions, especially the above-mentioned, Since the nitrate ion is very mobile in the groundwater and does not adsorb and deposit in the aquifer, its movement is controlled by the absorption processes and microbiological activity, and the adsorption process of nitrates in the soil and the aquifer is controlled by the medium's containment of organic materials, for example, sandy soils and water reservoirs composed of sandstone. Where the adsorption process of nitrate is poor, and therefore the proportion of nitrate in water reservoirs formed from sandstone is more than in others (Rodvang and Simpkins, 2001).

4.2.4. Trace Elements and seasonal changes

Contamination of groundwater by heavy metals has received great significance in recent years due to their toxicity and accumulative behavior. These elements, unlike most pollutants, are not biodegradable and are subject to a global eco-biological cycle in which natural waters play a major role. These metals can enter groundwater in a hydrogeological system in a variety of ways in nature (e.g. chemical weathering and percolation in the soil, anthropogenic processes, and depending on their concentration, they can cause contamination (Dara, 2011). The drinking water should be free of any toxic elements, living and nonliving organisms, and excessive amounts of

minerals that could be harmful to health. Some heavy metals, such as Zinc, cobalt, and copper, are extremely important to humans, but excessive amounts of them can cause physiological problems. Even in low concentrations, cadmium, chromium, and lead are extremely toxic to humans (CPCB, 2008). The data of trace elements from groundwater samples were collected in the study area during the rainy season (May 2021) and the dry season (October 2021), some elements were detected in all wells, while others were detected in some but not all wells.

Table 4.12 illustrates the maximum permissible limit concentration values in drinking water for some trace elements imposed by most authorities. The concentration limits are as per the guidelines of Iraqi and the WHO standards.

Table 4.12. The Iraqi and WHO guidelines for metals and trace elements

Parameters	IQS (2010) (mg/L)	IQS (2010) (ppb)	WHO (2011) (mg/L)	WHO (2011) (ppb)
Al	0.20	200	0.20	200
Zn	3.00	3000	5.00	5000
Mn	0.10	100	0.40	400
Cu	1.00	1000	2.00	2000
Fe	0.30	300	0.30	300
B	0.50	500	0.50	500
Pb	0.01	10	0.10	100
Ni	0.02	20	0.02	20
Cr	0.05	50	0.05	50
As	0.01	10	0.01	10
Ba	0.7(1996)	700	0.7(2006)	700
Cd	0.003(2009)	3	0.003(2008)	3
Se	0.01(2009)	10	*	*

(*: not mentioned)

i- Zinc (Zn)

Zinc is one of the essential elements. It can be found in nature as a component of minerals such as sphalerite zinc sulfide (ZnS), smithsonite ($ZnCO_3$), willemite (Zn_2SiO_4), and zincite (ZnO) (Moore and Ramamoorthy, 2012), as well as ilmenite, magnetite, muscovite, olivine, biotite, and amphibole. Zinc is associated with sphalerite and galena. It occurs in form of an ion under oxidizing and acidic conditions (Drever, 1997). It is deposited when the pH – value is greater than seven. Zinc is one of the trace elements that are important for human health. People who absorb insufficient zinc may experience a loss of appetite, a reduced sense of taste and smell, slow wound healing, and skin sores. Zinc deficiency can even harm birth. Even though humans can handle relatively high zinc concentrations, a high amount of zinc can still cause serious health issues like

stomach cramps, skin irritations, vomiting, nausea, and anemia. Extremely high zinc levels can harm the pancreas and disrupt protein metabolism or cause arteriosclerosis. Zinc has the potential to negatively affect unborn and newborn children, Children may be exposed to zinc through their mothers' blood or milk if their mothers have absorbed high concentrations of zinc (EU, 2004).

The concentration and maximum limit of zinc are shown in Table 4.13. The concentration of zinc in the samples of the study area and its maximum limit values as per Iraqi and WHO standards are tabulated and shown in (Figure 4.24).

Table 4.13. . Zinc concentration in the study area

Sample	Sample Location	Location Type	Zn (ppb) Rainy Season	Zn (ppb) Dry Season
E1	Erbil city	Well	18.90	48.30
E3	Erbil city	Well	5.90	7.80
E5	Kani Qirzhalla village	Well	19.60	19.00
E6	Kawrgoesk Camp	Well	89.90	112.40
E7	Lajan Village	Well	26.10	14.80
E8	Sirawa Village	Well	27.50	28.50
E9	Qurshaghlu village	Well	19.90	9.20
E10	Qushtapa sub-district	Well	149.30	149.30
Iraq Standards (2010)	3000 ppb			
WHO Standards (2011)	5000 ppb			

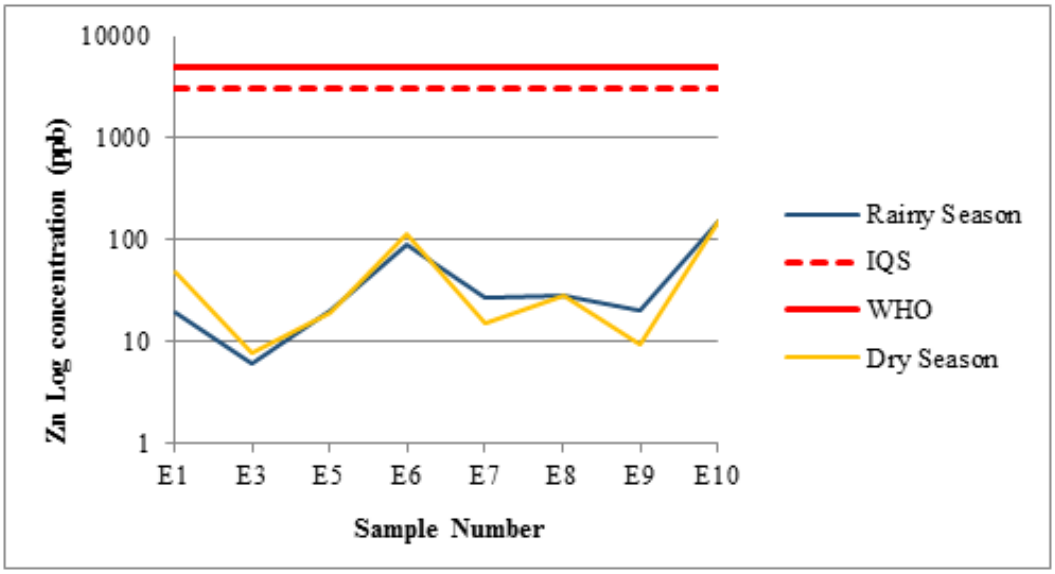

Figure 4.24. Zinc concentration in the study area

Zinc concentrations in all samples studied are below IQS (2010) and WHO (2011) limit values for drinking water.

ii- Chromium (Cr)

Soil and groundwater contamination with chromium is a major problem all over the world. The range of this issue is primarily due to its use in a variety of industrial processes (e.g. metal plating and alloying, leather tanning, wood treatment, and chemical manufacturing), but also due to its natural presence in chromium-rich rocks (Kresic, 2007). In comparison to the effects of industrial and mining practices on soil and groundwater contamination, Chromium concentrations in soil and groundwater are naturally low, frequently less than 10 µg/l (Hem, 1985). When chromium concentrations in drinking water reach more than 50 µg /l, they become toxic and cause lung and kidney cancer (Robles-Camacho and Armienta, 2000).

The concentration of chromium in the samples of the study area and its maximum limit values as per Iraqi and WHO standards are tabulated and shown in (Table 4.14).

Table 4.14. Chromium concentration in the study area

Sample	Sample Location	Location Type	Cr (ppb) Rainy Season	Cr (ppb) Dry Season
E1	Erbil city	Well	1.80	1.70
E3	Erbil city	Well	7.10	7.00
E5	Kani Qirzhalla village	Well	27.10	29.10
E6	Kawrgoesk Camp	Well	20.50	12.40
E7	Lajan Village	Well	1.80	1.80
E8	Sirawa Village	Well	9.30	9.80
E9	Qurshaghlu village	Well	27.20	27.10
E10	Qushtapa sub-district	Well	14.60	51.30
Iraq Standards (2010)	50 ppb			
WHO Standards (2011)	50 ppb			

In all of the samples tested, the chromium concentrations were below the drinking water limit values IQS (2010) and WHO (2011). The studied wells do not contain any chromium that causes a risk to human health (Figure 4.25).

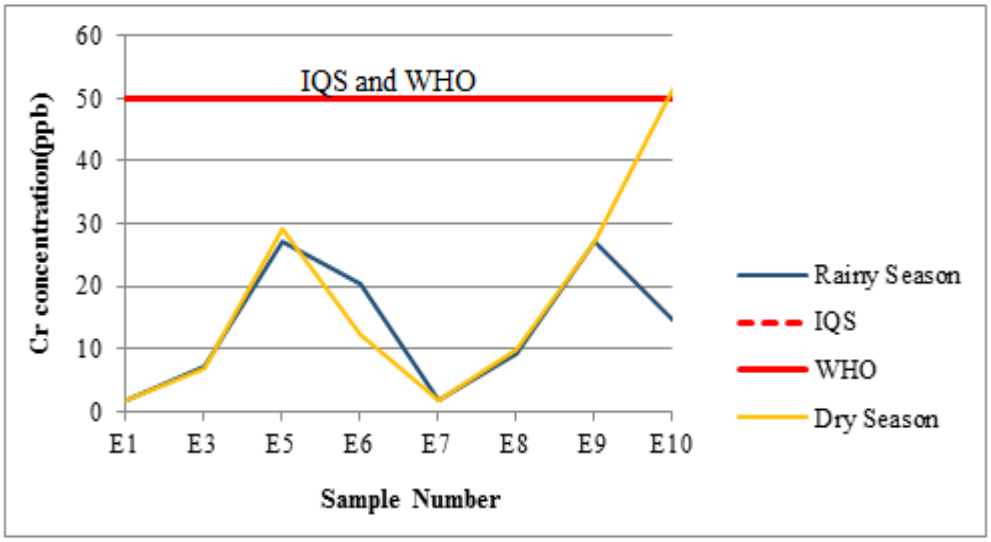

Figure 4.25. Chromium concentration in the study area

iii- Nickel (Ni)

Nickel has a geochemical behavior similar to cobalt. It occurs in an acidic environment (Drever, 1997). There is a probability that nickel levels in drinking water could be increased by leaching processes from water taps and flexures (WHO, 1996). In terms of pulmonary exposure, nickel is now classified as a human carcinogen (Shen et al., 1999). Recent research has found that a low nickel intake in the diet can help to reduce dermatitis activities (Mendoza, 2006).

The concentration of nickel in the samples of the study area and its maximum limit values as per Iraqi and WHO standards are tabulated and shown in (Table 4.15). Nickel concentrations in the study area are lower than IQS (2010) and WHO (2011) recommendations for both seasons (Figure 4.26).

Table 4.15. Nickel concentration in the study area

Sample	Sample Location	Location Type	Ni (ppb) Rainy Season	Ni (ppb) Dry Season
E1	Erbil city	Well	0.20	0.20
E3	Erbil city	Well	0.20	0.20
E5	Kani Qirzhalla village	Well	0.20	0.20
E6	Kawrgoesk Camp	Well	0.30	0.20
E7	Lajan Village	Well	0.20	0.60
E8	Sirawa Village	Well	0.20	0.20
E9	Qurshaghlu village	Well	0.20	0.20
E10	Qushtapa sub-district	Well	1.80	0.20
Iraq Standards (2010)	20 ppb			
WHO Standards (2011)	20 ppb			

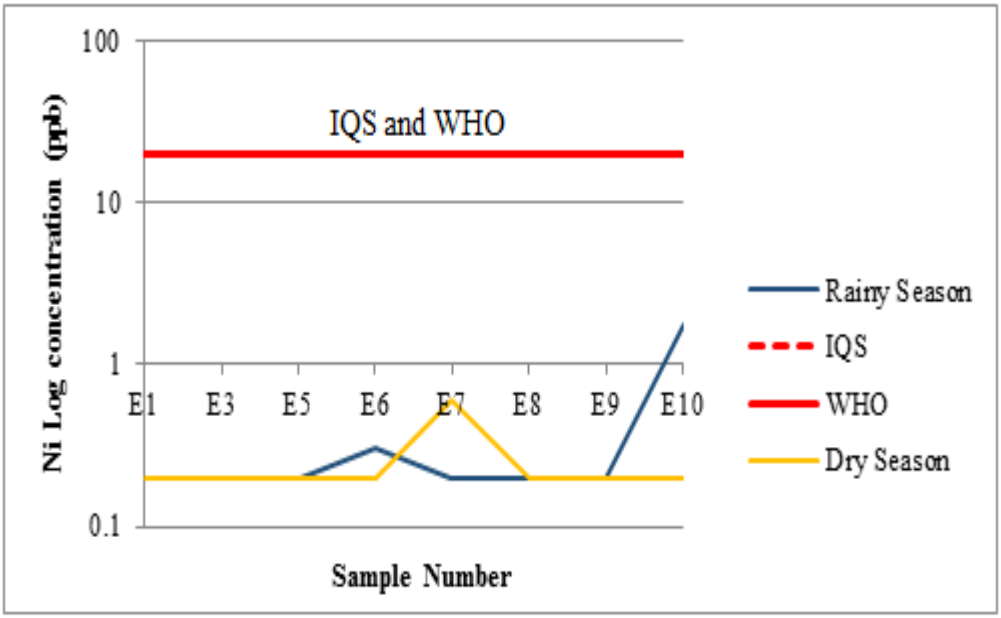

Figure 4.26. Nickel concentration in the study area

iv- Iron (Fe)

Iron is a common metal in the earth's crust. The major source of iron in groundwater is weathering of rock and the discharge of waste effluents onto land. It can be found in natural freshwater at concentrations ranging from 0.5 to 50 mg/l. The availability of iron in drinking water may be due to a reaction between the steel or cast ironic pipelines and water while water distribution. Iron was found in almost all of the well samples analyzed. JICA in 1990 notes that the iron concentrations recorded by the analysis may be underestimated because iron precipitates quickly in stored water samples. As a result, the iron concentration in the groundwater may be higher than reported. This can be a problem because its concentration above the recommended limits is objectionable in terms of taste and color (Borah et al., 2009). It has no negative physiological effects on human health, however, and it is easily removed through aeration (Alagbe, 2006). The concentration of iron in the samples of the study area and its maximum limit values as per Iraqi and WHO standards are tabulated and shown in (Table 4.16).

Table 4.16. Iron concentration in the study area

Sample	Sample Location	Location Type	Fe (ppb) Rainy Season	Fe (ppb) Dry Season
E1	Erbil city	Well	16.00	12.00
E3	Erbil city	Well	10.00	10.00
E5	Kani Qirzhalla village	Well	14.00	36.00
E6	Kawrgoesk Camp	Well	117.00	24.00
E7	Lajan Village	Well	120.00	10.00
E8	Sirawa Village	Well	10.00	10.00
E9	Qurshaghlu village	Well	40.00	10.00
E10	Qushtapa sub-district	Well	77.00	35.00
Iraq Standards (2010)	300 ppb			
WHO Standards (2011)	300 ppb			

In all of the samples examined, the concentration of iron is less than the maximum limit values for Iraqi Standards (IQS, 2010) and (WHO, 2011) in both seasons (Figure 4.27).

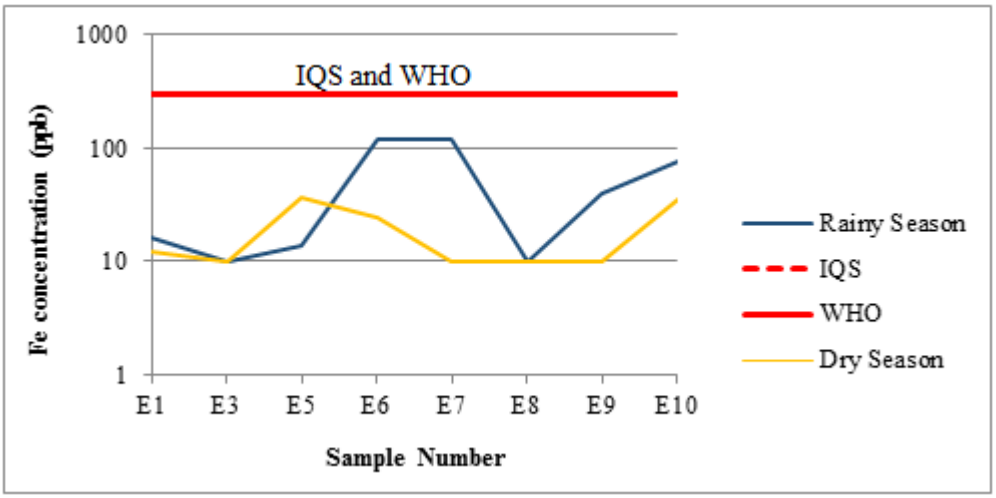

Figure 4.27. Iron concentration in the study area

v- Manganese (Mn)

Manganese is one of the essential elements, which does not occur naturally as metal but is found in various salts and minerals frequently in association with iron compounds. The occurrence of manganese in drinking water above the allowable limit frequently imparts a strange and dislike taste to the water. It also hurts domestic uses and the structure of the water supply (CPCB, 2008). The concentration of manganese in the samples of the study area and its maximum limit values as per Iraqi and WHO standards are tabulated and shown in (Table 4.17).

Table 4.17. Manganese concentration in the study area

Sample	Sample Location	Location Type	Mn (ppb) Rainy Season	Mn (ppb) Dry Season
E1	Erbil city	Well	5.62	4.74
E3	Erbil city	Well	3.25	4.65
E5	Kani Qirzhalla village	Well	4.28	6.48
E6	Kawrgoesk Camp	Well	10.62	3.73
E7	Lajan Village	Well	16.33	4.54
E8	Sirawa Village	Well	7.16	7.15
E9	Qurshaghlu village	Well	9.15	4.47
E10	Qushtapa sub-district	Well	10.72	5.53
Iraq Standards (2010)	100 ppb			
WHO Standards (2011)	400 ppb			

For both rainy and dry seasons, the manganese concentrations are found to be lower than the IQS (2010) and WHO (2011) maximum limit values (Figure 4.28).

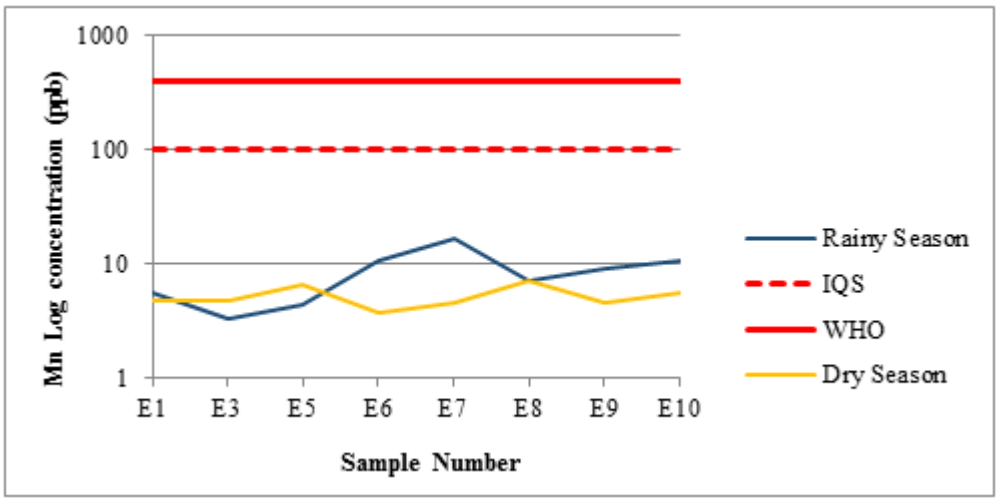

Figure 4.28. Manganese concentration in the study area

Barium (Ba)

Barium is a widespread element. It has a mean content of 425 mg kg^{-1} in the earth's crust. In the upper continental crust, its range is between 550 and 668 mg kg^{-1}. Since barium is lithophilic, it is likely to concentrate in acid igneous rocks and argillaceous sediments, varying from 250 to 1 200 mg kg^{-1} in different rocks. Due to its ionic radius being very close to that of potassium, it usually has the same fate as potassium in geochemical processes. The transportation of barium is very hard and rough during weathering because it readily precipitates as sulfates and carbonates

and is strongly adsorbed by clays (Kabata-Pendias and Mukherjee, 2007). The effects of barium on health are dependent on the compounds' water solubility. Water-soluble barium compounds can be hazardous to human health. The absorption of extremely large amounts of water-soluble barium can result in paralysis and, in some cases, death. Low concentrations of water-soluble barium may cause breathing problems in some people, muscle weakness, stomach irritation, increased blood pressure, changes in nerve reflexes, heart rhythm changes, swelling of the brain and liver, and kidney or heart damage. There is no evidence that barium can result in infertility or birth defects and cancer in humans (EU, 2004).

The concentration of barium in the samples of the study area and its maximum limit values as per Iraqi and WHO standards are tabulated and shown in (Table 4.18).

Table 4.18. Barium concentration in the study area

Sample	Sample Location	Location Type	Ba (ppb) Rainy Season	Ba (ppb) Dry Season
E1	Erbil city	Well	61.33	59.04
E3	Erbil city	Well	199.78	204.22
E5	Kani Qirzhalla village	Well	20.56	22.11
E6	Kawrgoesk Camp	Well	55.87	71.04
E7	Lajan Village	Well	97.55	90.45
E8	Sirawa Village	Well	38.63	39.71
E9	Qurshaghlu village	Well	27.04	27.31
E10	Qushtapa sub-district	Well	61.84	39.13
Iraq Standards (1996)	700 ppb			
WHO Standards (2006)	700 ppb			

For both rainy and dry seasons, the barium concentrations are found to be lower than the IQS (2010) and WHO (2011) maximum limit values (Figure 4.29).

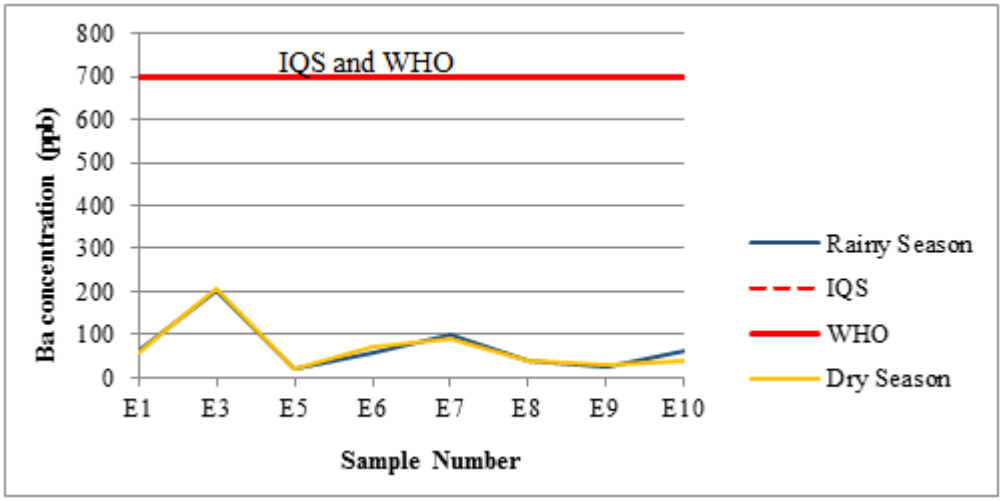

Figure 4.29. Barium concentration in the study area

Boron (B)

Boron occurs naturally in groundwater, but it is found in surface water mostly as a result of the discharge of treated wastewater, which originates from its use in some detergents, to surface waters. Boron can enter the body through fruits and vegetables, water, air, and consumer goods. Boron poisoning can cause death by infecting the stomach, liver, kidneys, and brain. When exposed to low levels of boron, irritation of the nose, throat, and eyes may occur. We consume approximately two milligrams per day regularly. Only five grams of boric acid is enough to make a person ill, and 20 grams or more to endanger their life (EU, 2004).

The concentration of boron in the samples of the study area and its maximum limit values as per Iraqi and WHO standards are tabulated and shown in (Table 4.19).

Table 4.19. Boron concentration in the study area

Sample	Sample Location	Location Type	B (ppb) Rainy Season	B (ppb) Dry Season
E1	Erbil city	Well	47.00	40.00
E3	Erbil city	Well	60.00	54.00
E5	Kani Qirzhalla village	Well	102.00	105.00
E6	Kawrgoesk Camp	Well	125.00	117.00
E7	Lajan Village	Well	37.00	38.00
E8	Sirawa Village	Well	752.00	818.00
E9	Qurshaghlu village	Well	496.00	521.00
E10	Qushtapa sub-district	Well	132.00	89.00
Iraq Standards (2010)	500 ppb			
WHO Standards (2011)	500 ppb			

For both seasons, the Boron concentrations are found to be lower than the IQS (2010) and WHO (2011) maximum limit values in all samples, except in the E8, and E9 wells are higher than the limit (Figure 4.30).

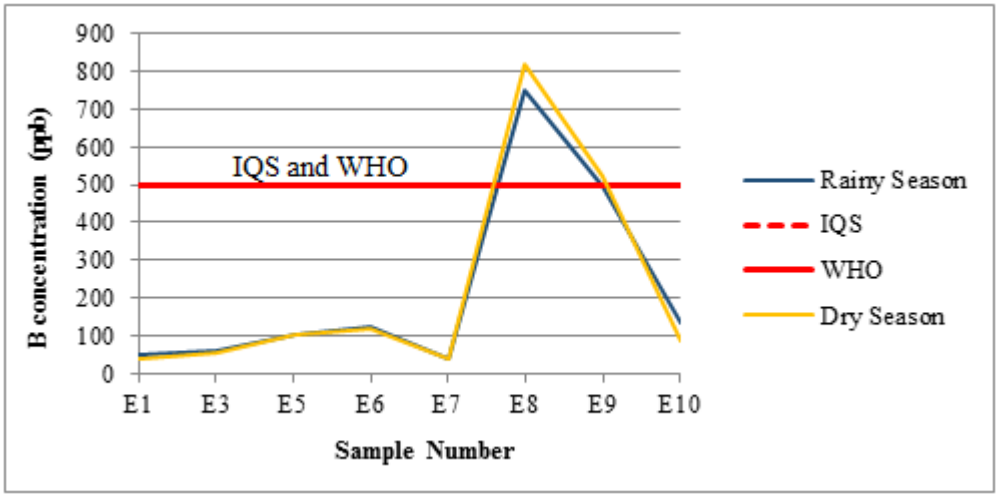

Figure 4.30. Boron concentration in the study area

vi- Cadmium (Cd)

The average cadmium content in the Earth's crust is from 0.1– 0.2 mg kg^{-1}. This metal is rarely found in its pure form in nature. Octavite (CdSe), monteponite (CdO), and Greenockite (CdS) are their most common minerals. Despite having the same valence and ionic radius as calcium, cadmium does not replace calcium in minerals (Kabata-Pendias and Mukherjee, 2007). Cadmium is regarded as one of the most environmentally hazardous metals, with negative effects on all biological processes in humans, animals, and plants. It primarily precipitates in the kidneys and has a biological half-life of 10-35 years in humans (Al-Mashaikie, 2014). This metal clearly shows its significant negative impact on the environment and food quality. Air pollution and P-fertilizers are the two most significant sources of pollution. The majority of cadmium pollution from different sources, higher than 90%, remains in the top 15 cm of soil. The application of phosphate fertilizer raises the concentration of cadmium in soil solution. Cadmium is a highly toxic metal for humans. Because of its ability to combine with sulfhydryl groups and thus disrupt the function of several SH-group enzymes, which results in protein changes. Cadmium overuse primarily harmed the skeletal structure, emphysema, hypertension, and renal damage, carcinogenic in kidney and prostate (Kabata-Pendias and Mukherjee, 2007).

The concentration of Cadmium in the samples of the study area and its maximum limit values as per Iraqi and WHO standards are tabulated and shown in (Table 4.20).

Table 4.20. Cadmium concentration in the study area

Sample	Sample Location	Location Type	Cd (ppb) Rainy Season	Cd (ppb) Dry Season
E1	Erbil city	Well	0.05	0.05
E3	Erbil city	Well	0.05	0.05
E5	Kani Qirzhalla village	Well	0.05	0.06
E6	Kawrgoesk Camp	Well	0.06	0.05
E7	Lajan Village	Well	0.05	0.05
E8	Sirawa Village	Well	0.05	0.05
E9	Qurshaghlu village	Well	0.06	0.05
E10	Qushtapa sub-district	Well	0.09	0.05
Iraq Standards (2009)	3 ppb			
WHO Standards (2008)	3 ppb			

In all of the samples examined, the concentration of cadmium is less than the maximum limit values for Iraqi Standards 2010 and WHO 2011 in both seasons (Figure 4.31).

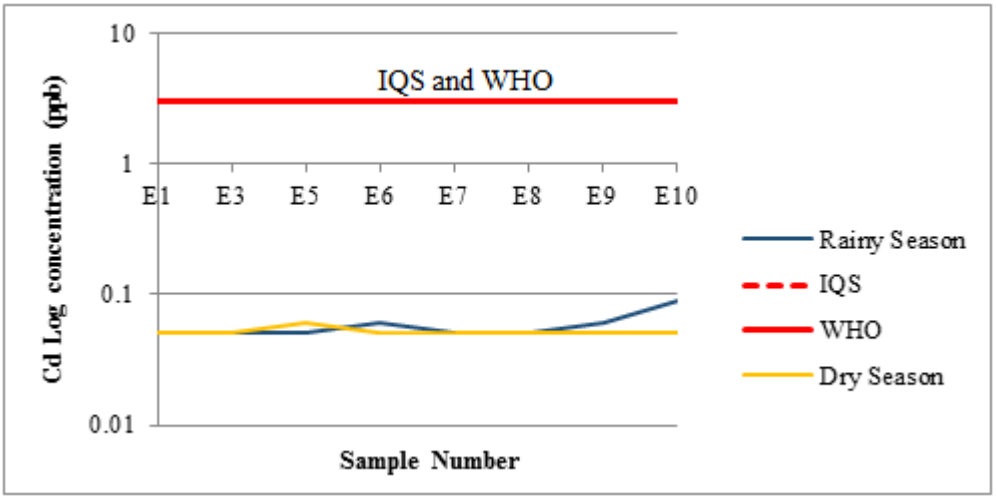

Figure 4.31. Cadmium concentration in the study area

vii- Aluminum (Al)

It is a common and abundant element occupying about 8% of the earth's crust. It is a natural constituent of soil, plant, and animal tissues as a free mineral (Al), and as a compound such as Aluminium oxide (Al_2O_3), Aluminium Chloride ($AlCl_3.6H_2O$), Aluminium Sulfate $Al_2 (SO_4)_3$, and Aluminium hydroxide ($Al_2 (OH)_3$. It is frequently found in conjunction with particulate matter or organic complexes with a high relative molecular mass (WHO, 1996).

The concentration of aluminium in the samples of the study area and its maximum limit values as per Iraqi and WHO standards are tabulated and shown in (Table 4.21; Figure 4.32).

Table 4.21. Aluminum concentration in the study area

Sample	Sample Location	Location Type	Al (ppb) Rainy Season	Al (ppb) Dry Season
E1	Erbil city	Well	48.00	35.00
E3	Erbil city	Well	26.00	35.00
E5	Kani Qirzhalla village	Well	31.00	55.00
E6	Kawrgoesk Camp	Well	98.00	28.00
E7	Lajan Village	Well	92.00	46.00
E8	Sirawa Village	Well	54.00	100.00
E9	Qurshaghlu village	Well	79.00	41.00
E10	Qushtapa sub-district	Well	65.00	53.00
Iraq Standards (2010)	200 ppb			
WHO Standards (2011)	200 ppb			

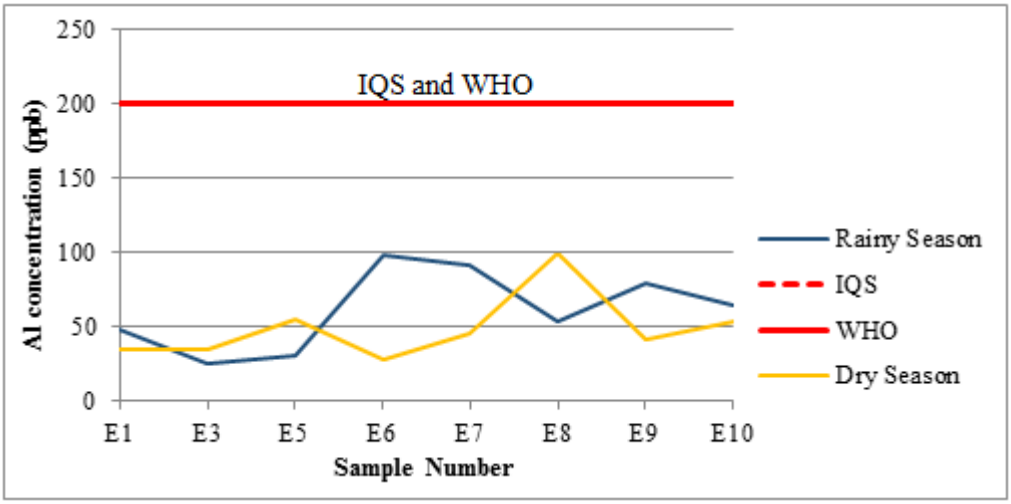

Figure 4.32. Aluminum concentration in the study area

viii- Arsenic (As)

Groundwater rich in arsenic can be found in inland basins in arid and semi-arid climates (Welch et al., 2000). Another common source of high arsenic groundwater in alluvial plain sediments, which contain highly, reduced groundwater with a high Fe^{+2} concentration. In both situations, the aquifers are located in geologically young sediments and in relatively flat, low-lying areas where groundwater flushing is minimal (Smedley and Kinniburgh, 2002). It is one of the common metals of the earth's crust usually as arsenic sulfide or as metal arsenates and arsenides. Arsenic compounds such as Arsenic trioxide (As_2O_3), Arsenic sulfide (As_2S_3), Potassium arsenate (KH_2AsO_4), and Potassium Arsenite ($KAsO_2.HAsO_2$). As per WHO, Arsenic may be essential for

most animals, but there is no proof that is essential for humans. Arsenic and organic arsenic are quickly and nearly eliminated by the kidneys (Tam et al., 1982). Arsenic poisoning can accumulate in the skin, bone, and muscles which causes skin lesions, palm and sole thickening, hardening, and cracking, as well as skin cancer and liver disease (Karim, 2000).

The concentration of Arsenic in the samples of the study area and its maximum limit values as per Iraqi and WHO standards are tabulated and shown in (Table 4.22; Figure 4.33).

Table 4.22. Arsenic concentration in the study area

Sample	Sample Location	Location Type	As (ppb) Rainy Season	As (ppb) Dry Season
E1	Erbil city	Well	9.00	5.30
E3	Erbil city	Well	8.80	7.10
E5	Kani Qirzhalla village	Well	5.30	4.70
E6	Kawrgoesk Camp	Well	7.40	5.60
E7	Lajan Village	Well	6.40	5.80
E8	Sirawa Village	Well	6.50	5.10
E9	Qurshaghlu village	Well	6.40	4.90
E10	Qushtapa sub-district	Well	6.20	5.40
Iraq Standards (2010)	10 ppb			
WHO Standards (2011)	10 ppb			

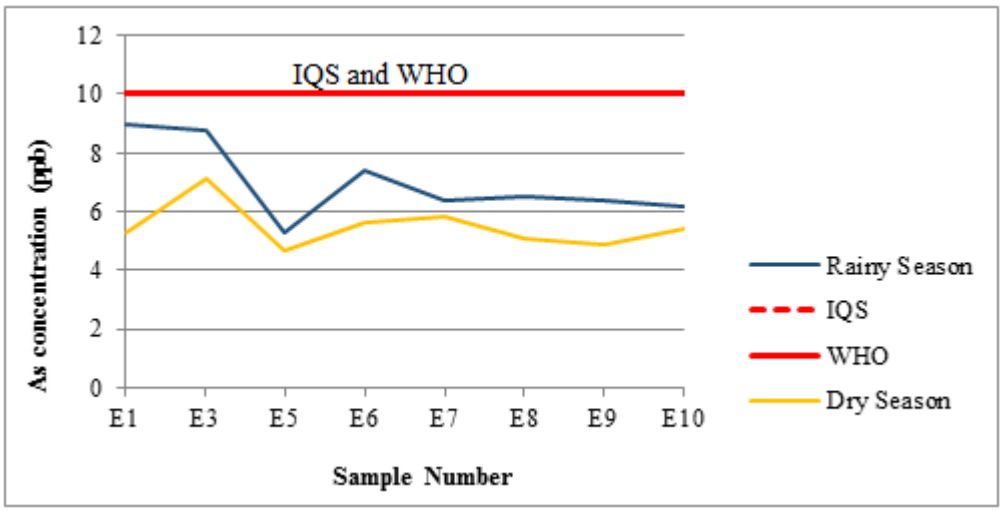

Figure 4.33. Arsenic concentration in the study area

ix- Copper (Cu)

Drinking water with dissolved copper has undesirable color and astringent taste. Copper concentrations in water that exceed one mg/l cause staining of laundry and plumbing fixtures. For

adults, the lethal oral dose ranges between 50 and 500 mg of copper salt per kilogram of body weight (WHO, 1996). Several case reports explain vomiting, diarrhea, nausea, and other acute symptoms that are thought to be caused by ingested copper ions.

The concentration of copper in the samples of the study area and its maximum limit values as per Iraqi and WHO standards are tabulated and shown in (Table 4.23; Figure 4.34).

Table 4.23. Copper concentration in the study area

Sample	Sample Location	Location Type	Cu (ppb) Rainy Season	Cu (ppb) Dry Season
E1	Erbil city	Well	3.00	3.30
E3	Erbil city	Well	1.70	2.80
E5	Kani Qirzhalla village	Well	3.30	5.10
E6	Kawrgoesk Camp	Well	5.30	1.90
E7	Lajan Village	Well	5.70	2.60
E8	Sirawa Village	Well	7.60	6.00
E9	Qurshaghlu village	Well	4.70	3.70
E10	Qushtapa sub-district	Well	5.40	3.90
Iraq Standards (2010)	1000 ppb			
WHO Standards (2011)	2000 ppb			

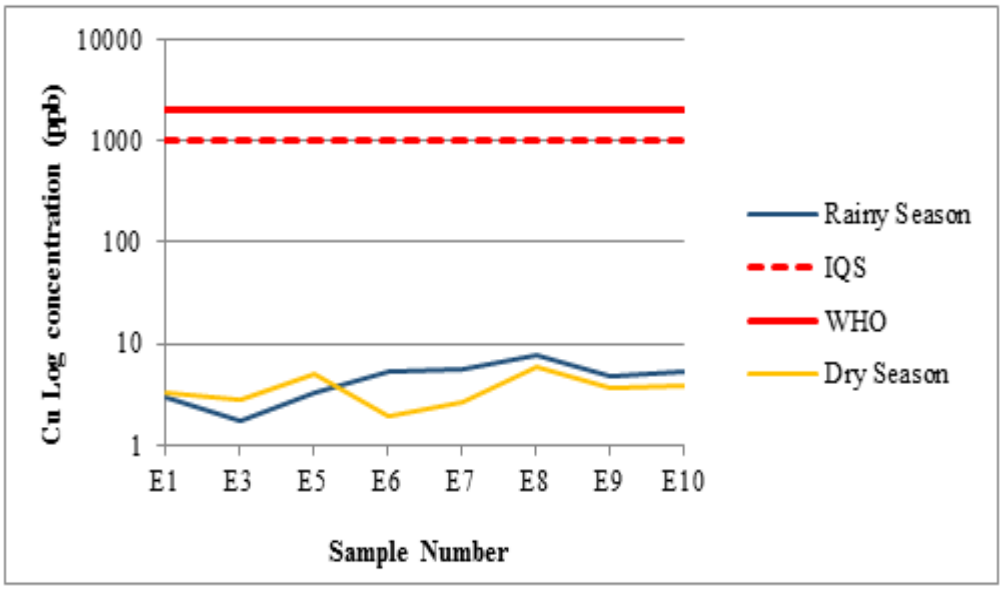

Figure 4.34. Copper concentration in the study area

x- Lead (Pb)

Is the most abundant heavy element, accounting for 13 mg/kg of the earth's crust. With the reduction in lead emissions in the atmosphere since the implementation of legislation restricting its use in fuel, water has taken on new significance as the most controllable source of lead exposure. Lead is a cumulative general poison, with the fetus, pregnant women, infants, and children under the age of six being the most vulnerable to adverse health effects (WHO, 1996). Lead is a toxic chemical that accumulates in the human skeleton and affects both the central and peripheral nervous systems, causing neurological and behavioral effects (Voudouris and Voutsa, 2012).

The concentration of lead in the samples of the study area and its maximum limit values as per Iraqi and WHO standards are tabulated and shown in (Table 4.24; Figure 4.35).

Table 4.24. Lead concentration in the study area

Sample	Sample Location	Location Type	Pb (ppb) Rainy Season	Pb (ppb) Dry Season
E1	Erbil city	Well	275.30	239.60
E3	Erbil city	Well	189.10	166.40
E5	Kani Qirzhalla village	Well	155.60	215.10
E6	Kawrgoesk Camp	Well	314.20	206.70
E7	Lajan Village	Well	206.90	270.80
E8	Sirawa Village	Well	139.90	152.00
E9	Qurshaghlu village	Well	254.20	160.00
E10	Qushtapa sub-district	Well	234.70	189.40
Iraq Standards (2010)	10 ppb			
WHO Standards (2011)	100 ppb			

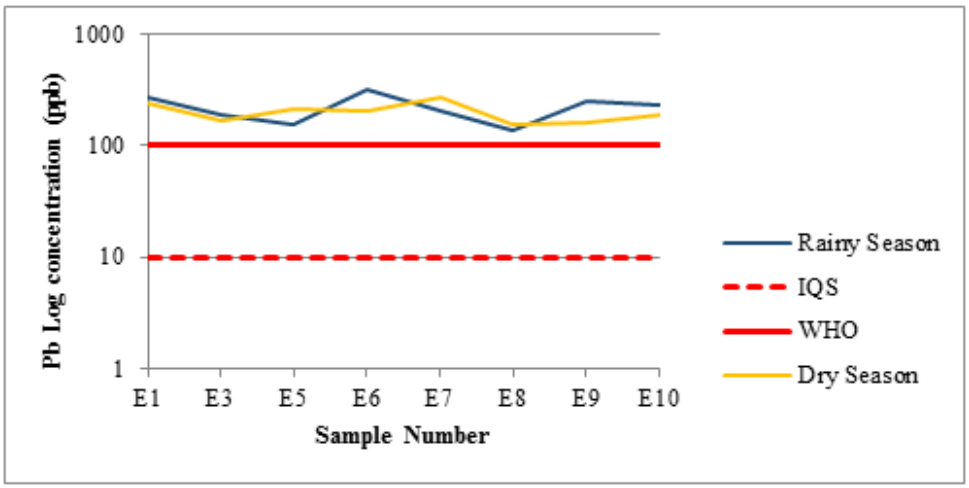

Figure 4.35. Lead concentration in the study area

xi- Selenium (Se)

It is one of the essential trace elements that occur in the earth's crust, frequently in conjunction with sulfur-containing minerals. It exists in a variety of forms, including elemental selenium, selenites, and selenates. Conditions that are acidic or reducing elemental selenium can be obtained by reducing inorganic selenites, whereas, selenates are formed more readily in alkaline and oxidizing environments. Water usually dissolves both selenites and selenates. High dietary intakes of selenite and other selenium compounds result in nausea and vomiting, abdominal pain, diarrhea, marked hair loss (Sioris et al., 1980), or acute oral doses of selenium cause gastrointestinal disturbances, discoloration of the skin, and decayed teeth (WHO,1996).

The concentration of selenium in the samples of the study area and its maximum limit values as per Iraqi and WHO standards are tabulated and shown in (Table 4.25; Figure 4.36).

Table 4.25. Selenium concentration in the study area

Sample	Sample Location	Location Type	Se (ppb) Rainy Season	Se (ppb) Dry Season
E1	Erbil city	Well	0.50	0.50
E3	Erbil city	Well	1.10	0.90
E5	Kani Qirzhalla village	Well	3.40	3.20
E6	Kawrgoesk Camp	Well	2.10	2.10
E7	Lajan Village	Well	0.50	0.60
E8	Sirawa Village	Well	3.80	4.20
E9	Qurshaghlu village	Well	4.70	4.70
E10	Qushtapa sub-district	Well	1.00	1.60
Iraq Standards (2009)	10 ppb			
WHO Standards (2011)	*			

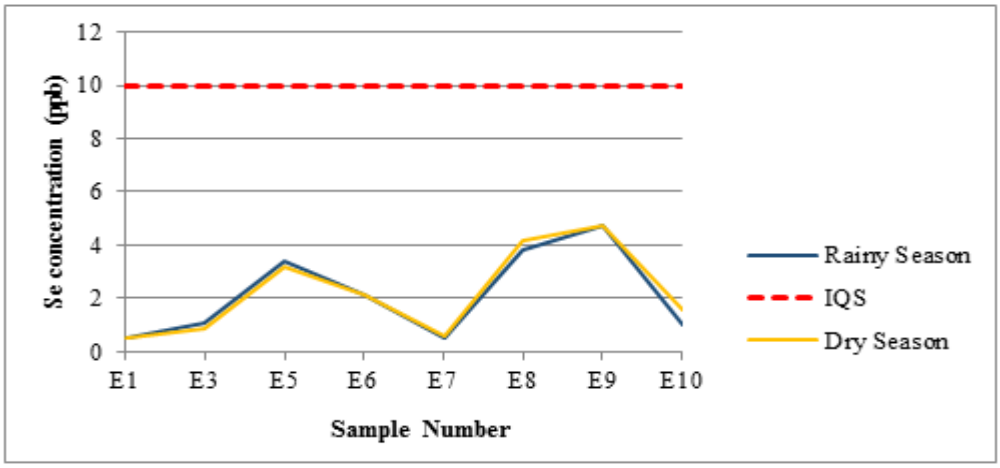

Figure 4.36. Selenium concentration in the study area

Generally, trace element contents in groundwaters in Erbil Basin are mainly sourced from rock mineral decomposition, discharge of sewage wastewater, leakage from the storage areas of domestic and industrial wastes, pesticides, and fertilizers are the primary sources of trace elements in groundwaters. The lead concentrations in all the investigated groundwaters exceed the maximum permissible limits of IQS and WHO standards. High contents of lead in groundwaters might also be due to the exhaust gases from automobiles and gases emitting from refinery stations (Fig 4.12).

4.2.5. Showing of major cation and anion contents in groundwaters on diagrams

The groundwater quality study is useful for making a preliminary determination of the relationship between aquifer mineralogy and groundwater composition. Groundwater dissolves the elements in the aquifer through which it flows. The classification of groundwater based on chemical indicators is determined by hydro-chemical parameters. Water is classified in a variety of ways, including Piper's (1944), and Schoeller's (1972) diagrams.

i- Piper Diagram

The Piper diagram is widely used to display chemical data of water to better understand the sources of dissolved components in water and it is useful to identify the characteristics of the water samples that were analyzed and the water quality effect. This technique is based on the idea that cations and anions in water are in general chemical equilibrium. In this diagram, there are two triangles, The first one on the left side is to plot cations (Ca^{+2}, Mg^{+2}, and Na^{+} plus K^{+}) and the second one on the right side is to plot anions (SO_4^{-2}, Cl^{-}, CO_3^{-2} plus HCO_3^{-}) (Piper, 1944). The diagram uses the percentage of milliequivalents (meq/L%) of the cations and anions data. The two lines drawn from cation and anion plots parallel along a line to the upper diamond-shaped edges until they intersect at a single point in one of the diamond-shaped fields. So this point represents one of the hydrogeochemical facies. These trilinear diagrams assist in determining the chemical relationships between groundwater samples (Logeshkumaran et al., 2015).

Chemical data from representative samples collected in the study area are plotted on a Piper trilinear diagram for the dry and rainy seasons (Figure 4.37; Figure 4.38; Figure 4.39).

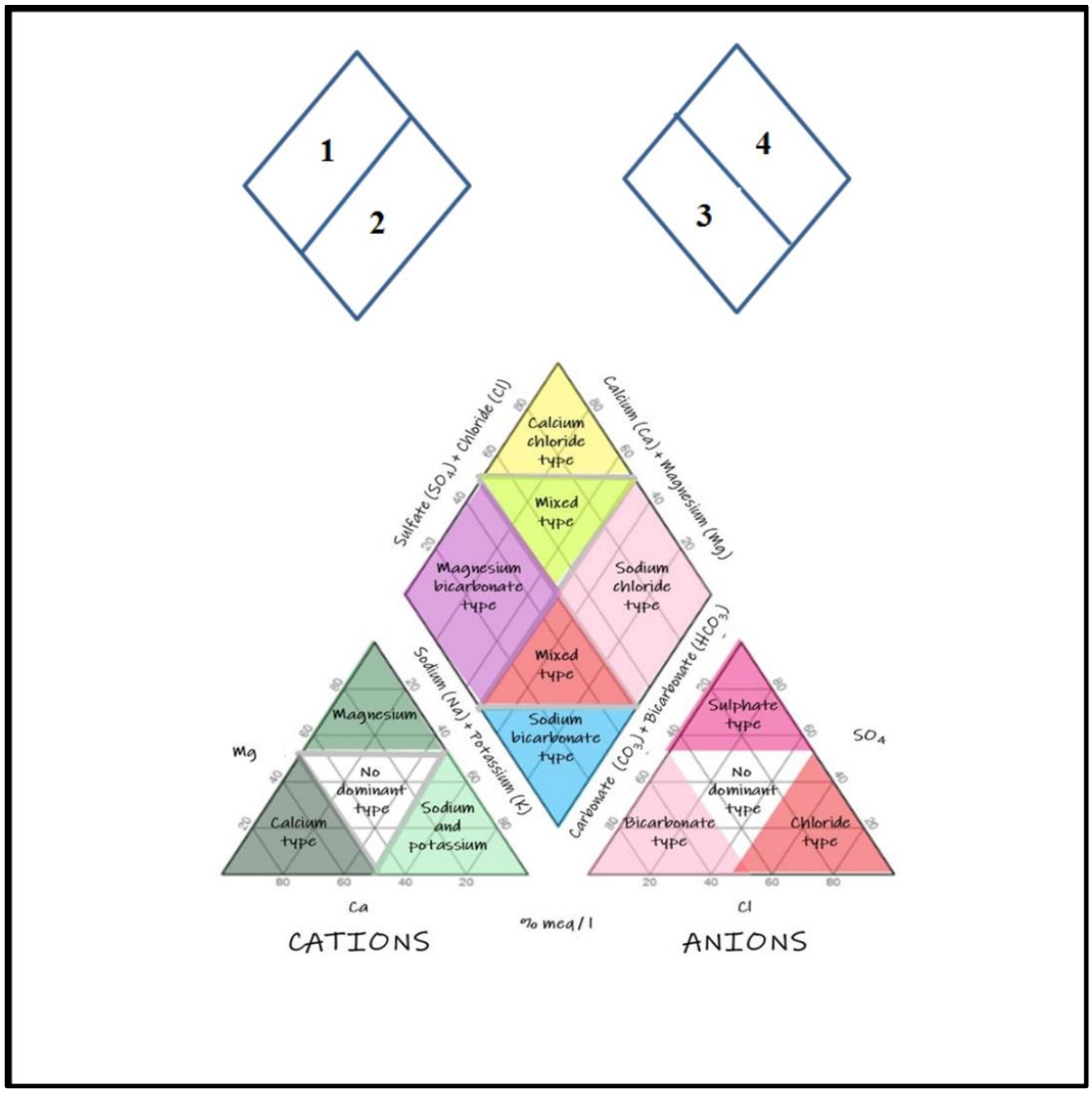

Figure 4.37. Piper diagram

1- In this region, Ca + Mg > Na+ K, Carbonate and sulfate waters (alkaline earths exceed alkalies)

2- In this region, Na + K > Ca, Mg, Salty waters (alkalies exceed alkaline earth)

3- $Ca + SO_4 > HCO_3 + CO_3$ (weak acids exceed strong acids)

4- $HCO_3 + CO_3 > Cl, SO_4$ (strong acids exceed weak acids).

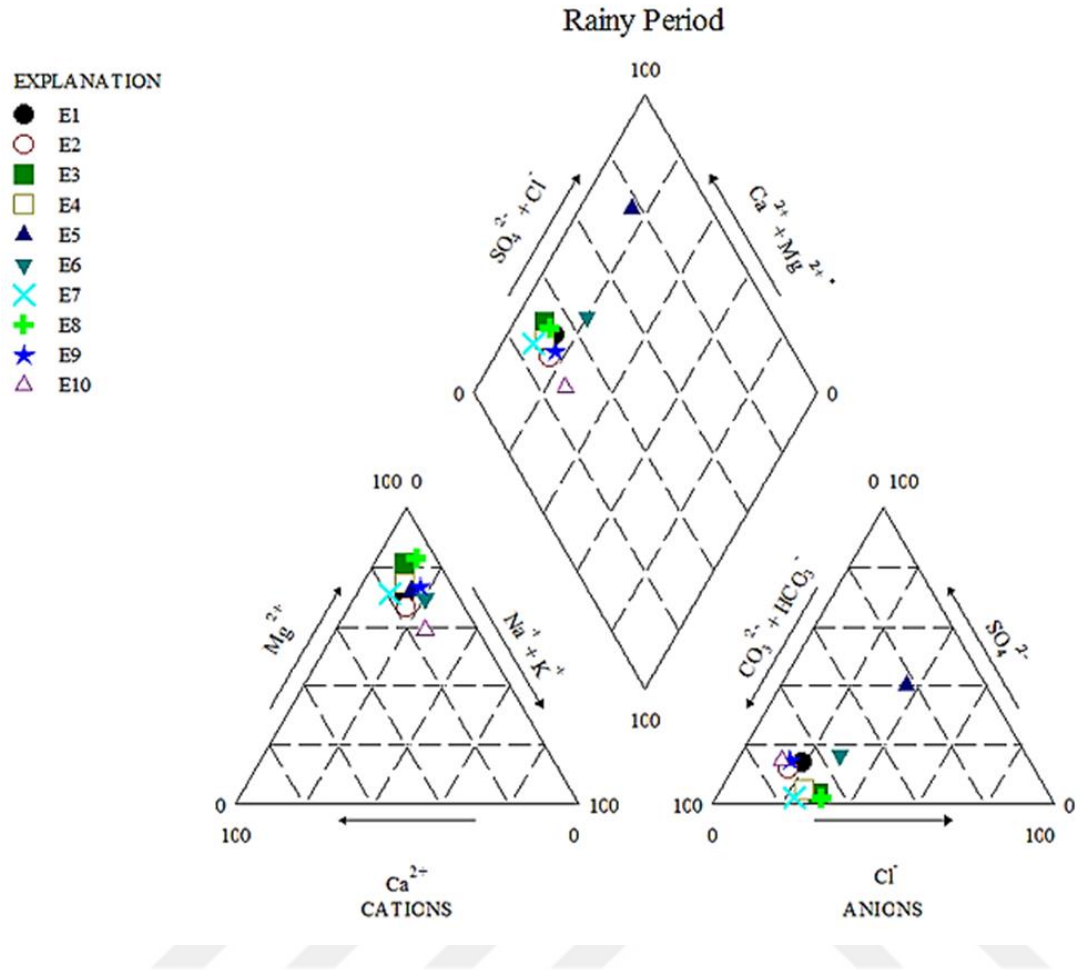

Figure 4.38. Piper diagram for water samples in the rainy season (May 2021)

According to the major cation and anion milliequivalent percentages of the studied waters, the diagrams were drawn in the rainy season (May 2021). The diagram plot demonstrates that all samples are located in the magnesium type field, which means that the Mg^{+2} ionic superiority over Ca^{2+}, Na^{+}, and K^{+} among cations, while the samples are located in the bicarbonate type field, which means that the CO_3 and HCO_3^{-} superiority over Cl^{-} and SO_4^{2-} among anions. Except for the E5 well which is situated in no dominant type, the other wells point to the Mg^{+2}- HCO_3^{-} type. The SO_4^{-2} for the E5 well = 63%, Cl^{-} = 78%, and $CO_3^{-} + HCO_3^{-}$ = 23 % (Figure 4.38; Table 4.26).

Table 4.26. Classification of water samples in the studied area by piper diagram

No.	Rainy Season		Dry Season	
	Water type	**Sample numbers**	**Water type**	**Sample number**
1	$CaCO_3$ and $MgCO_3$	E1,E2,E3,E4,E6,E7,E8,E9,E10	$CaCO_3$ and $MgCO_3$	E1,E2,E3,E4,E7,E8,E9,E10
2	$CaSO_4$ and $MgSO_4$	E5	$CaSO_4$ and $MgSO_4$	
3	NaCl, $NaSO_4$, and KCl		NaCl, $NaSO_4$, and KCl	
4	$NaHCO_3$		$NaHCO_3$	
5	Mixed type		Mixed type	E5 and E6

The waters are generally grouped in the calcium-magnesium-bicarbonate type field. In this field, carbonate hardness > non-carbonate hardness, thus the type of waters are Ca-HCO_3 and Mg-HCO_3 waters, and weak acids exceed strong acids, except the E5 well is located in the calcium chloride type and strong acids exceed weak acids. Non-carbonate hardness > Carbonate hardness in this field, thus, the type of water is Ca-Mg-Cl-SO_4 water. The SO_4^{-2} + Cl^- for E5 well = 78%, K^+ + Na^+ = 18%, CO_3^- + HCO_3^- = 22%, and Ca^{+2} + Mg^{+2} = 82%.

All samples in the rainy season are in alkaline earths exceed alkalies.

The E3 and E4 waters are located in the calcium type field on the cation's triangle in the dry season, which means that the Ca^{+2} ionic superiority over Mg^{+2}, Na^+, and K^+ among cations, whereas E8 is located in the magnesium type field, which means that the Mg^{+2} ionic superiority over Ca^{+2}, Na^+, and K^+ among cations (Figure 4.39). The E7 well is located between the magnesium and no dominant type fields. The rest of the samples are located in the no dominant field (Figure 4.39).

The E5 and E6 wells are located in the no dominant type field among the anions.

During the dry season, the diamond-shaped diagram shows that all wells are located in the magnesium bicarbonate type field. The carbonate hardness is greater than non-carbonate hardness, thus, the water type is $CaCO_3$ and $MgCO_3$ type, except for the E5 and E6 wells in the mixed type field. The E5 and E6 are located in the strong acids that exceed weak acids, and other samples are located in the weak acids that exceed strong acids.

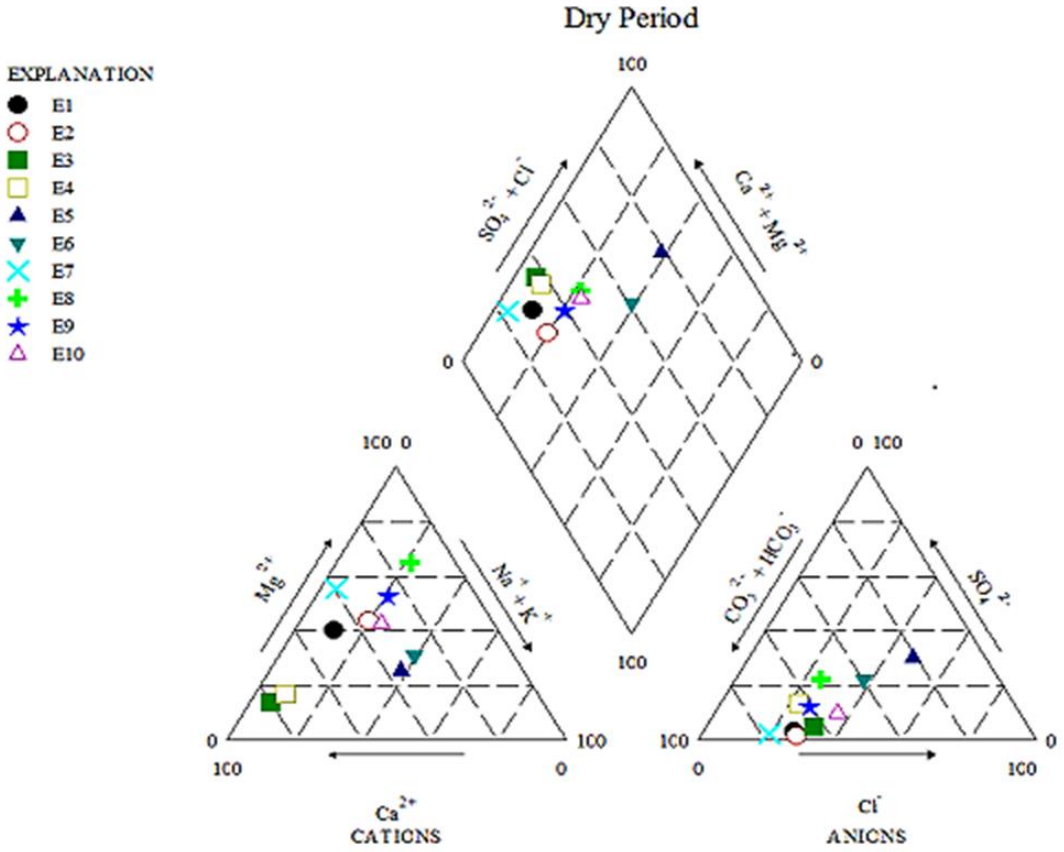

Figure 4.39. Piper diagram for water samples in the dry season (October 2021)

ii- Schoeller Diagram

Schoeller (1972) classified water based on the major cations and anions by plotting the concentrations of these ions in meq/L units on semi-logarithmic paper.The horizontal axis is arithmetic and consists of rCa^{+2}, rMg^{+2}, r ($Na^{+} + K^{+}$), rCl^{-}, rSO_4^{-2}, and $rHCO_3^{-}$, and the vertical axis is logarithmic. The concentrations are in milliequivalents per liter (meq/L).

The Schoeller diagram was drawn according to chemical analyses of water samples in May 2021(Rainy Season) (Figure 4.40). The lines connecting the ions in the water samples are parallel or close to each other on the Schoeller diagram and show that these waters are fed from aquifers of similar lithology.

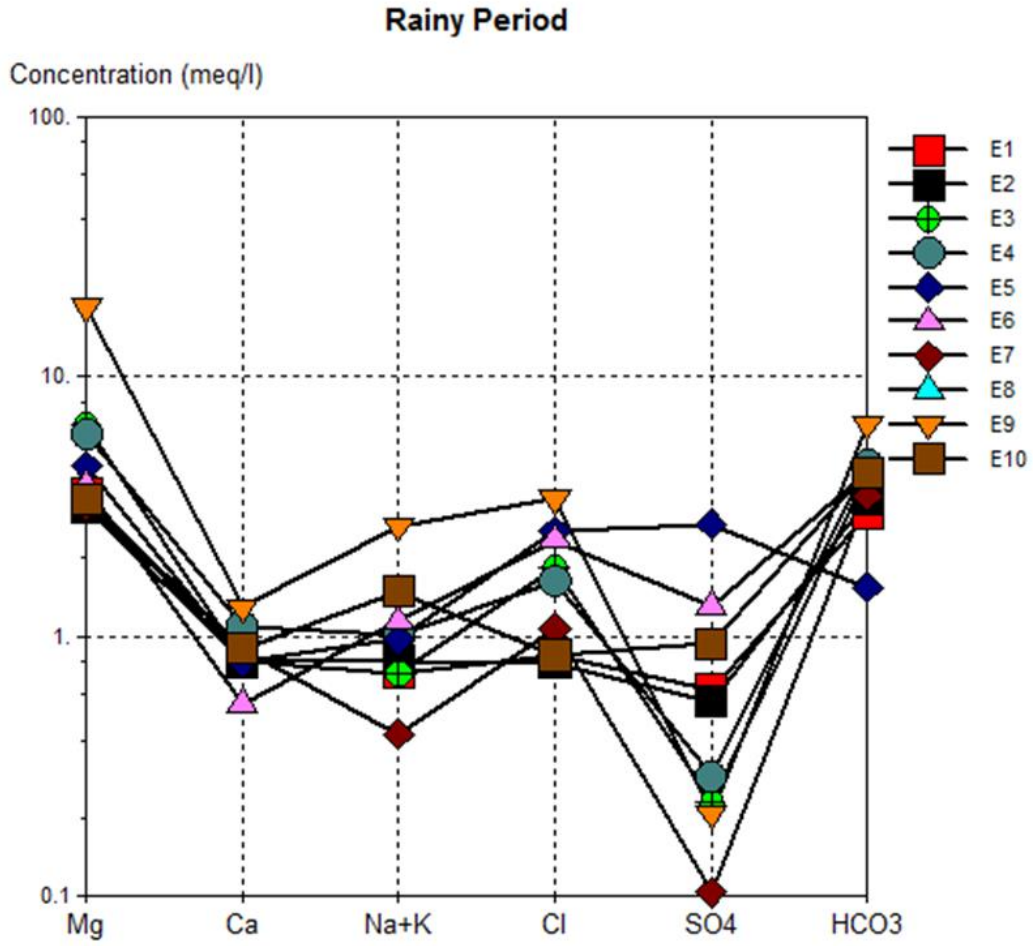

Figure 4.40. Schoeller diagram for water samples in the rainy season (May 2021)

The Schoeller diagram was drawn according to chemical analyses of water samples in October 2021(Dry Season) (Figure 4.41).

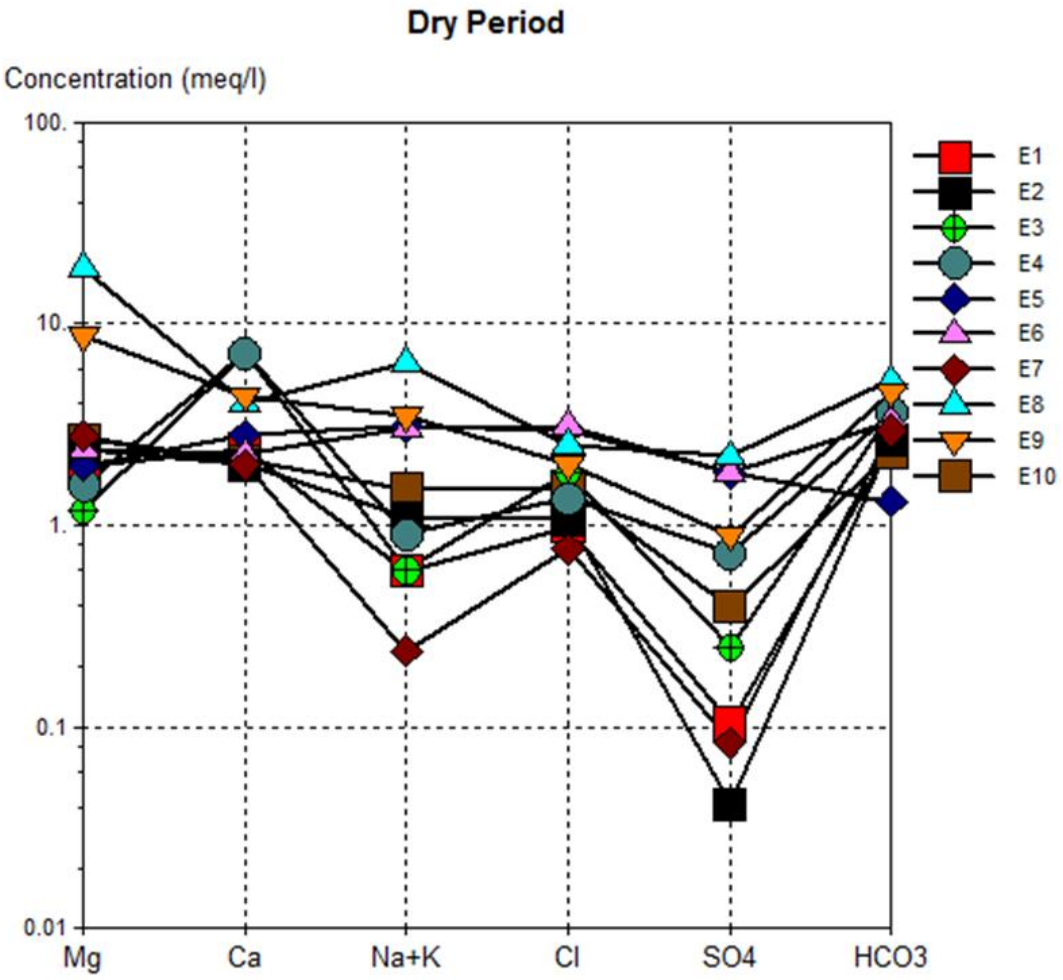

Figure 4.41. Schoeller diagram for water samples in the dry season (October 2021)

The water types were determined by using AquaChem software. Seasonal changes were determined in the water types of investigated groundwaters. The dominant water type is Mg-HCO_3, in the rainy season, whereas variable water types are observed in the dry season (Table 4.27). The effect of precipitation, type of aquifer (confined or unconfined), residence time in the aquifer, and groundwater fluctuation may be the sources of the seasonal changes in water types in the study area. The main source for Mg^{2+} in groundwaters in the rainy season reflects the high degree dissolution process of dolomites by the rainfall in sedimentary rocks and basin deposits.

Table 4.27. Water type of investigated groundwaters

Sample Number	Water Type	
	Rainy Season	Dry Season
E1	Mg-HCO_3	Ca-Mg-HCO_3-Cl
E2	Mg-Na-HCO_3	Mg-Ca-Na-HCO_3-Cl
E3	Mg-HCO_3	Mg-Ca-Na-HCO_3-Cl
E4	Mg-HCO_3-Cl	Ca-HCO_3-Cl
E5	Mg-HCO_3-Cl	Ca-Mg-HCO_3
E6	Mg-SO_4-Cl-HCO_3	Na-Ca-Mg-Cl-SO_4
E7	Mg-HCO_3-Cl	Na-Mg-Ca-HCO_3-Cl
E8	Mg-HCO_3-Cl	Mg-Ca-HCO_3
E9	Mg-HCO_3-Cl	Mg-Na-Ca-HCO_3
E10	Mg-Na-HCO_3	Mg-Ca-Na-HCO_3

iii- Gibbs Diagram

Based on chemical analysis data from water samples, the three principal mechanisms affecting water chemistry could be identified as atmospheric precipitation, rock dominance, and the evaporation-crystallization process(Gibbs, 1970). The Gibbs diagram is commonly used to create a relation between the composition of water and aquifer lithological properties. This diagram displays three separate areas, including precipitation dominance, evaporation dominance, and rock–water interaction dominance (Logeshkumaran et al., 2015). The Gibbs ratio (I) for anion (Cl^-, HCO_3^-) (Equation 4.5) and Gibbs ratio(II) for cation (Na^+, K^+, Ca^+) (Equation 4.6) for the groundwater samples in different wells were determined and plotted on the X-axis and the TDS values on the Y-axis in Gibbs diagram.

$$\text{Gibbs ratio (I) for anion} = \frac{Cl^-}{(Cl^- + HCO_3^-)} \quad (4.5)$$

$$\text{Gibbs ratio (II) for cation} = \frac{(Na^+ + K^+)}{(Na^+ + K^+ + Ca^{+2})} \quad (4.6)$$

where all ionic concentrations are represented in meq/l.

It is figured out that the majority of the samples are located in the rock–water interaction dominance area, except for two groundwater samples. The E8 and E9 numbered groundwaters are located in the evaporation dominance area of the Gibbs diagram (Figure 4.42; Figure 4.43).

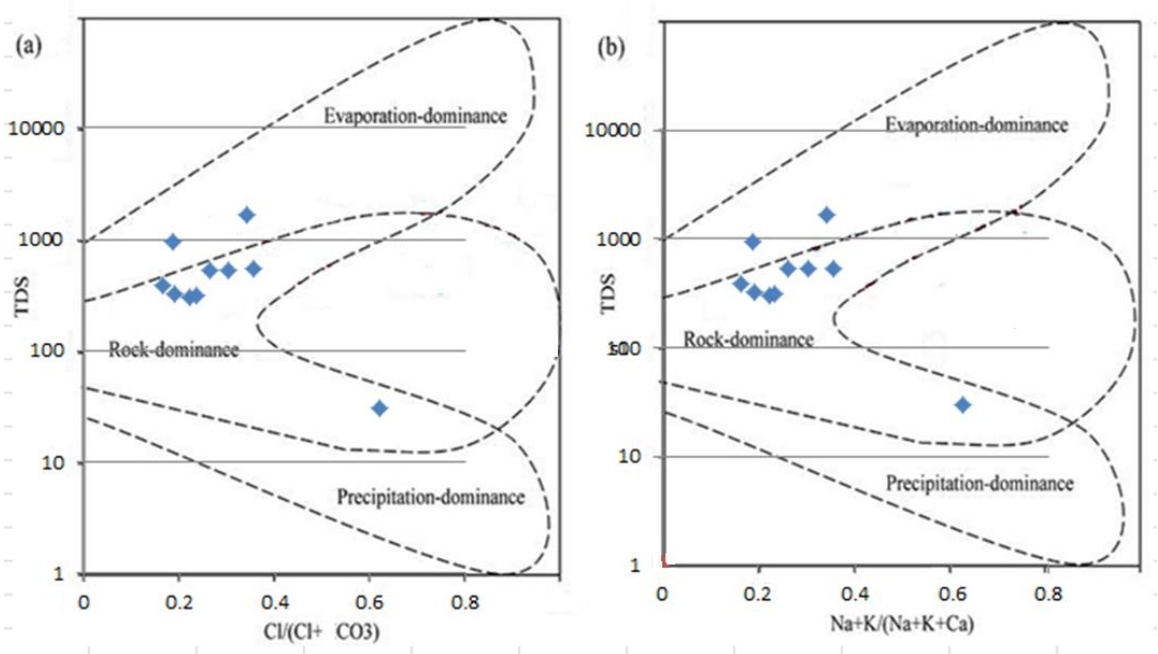

Figure 4.42. Gibbs Diagram for water samples in the studied area in the rainy season (May 2021)

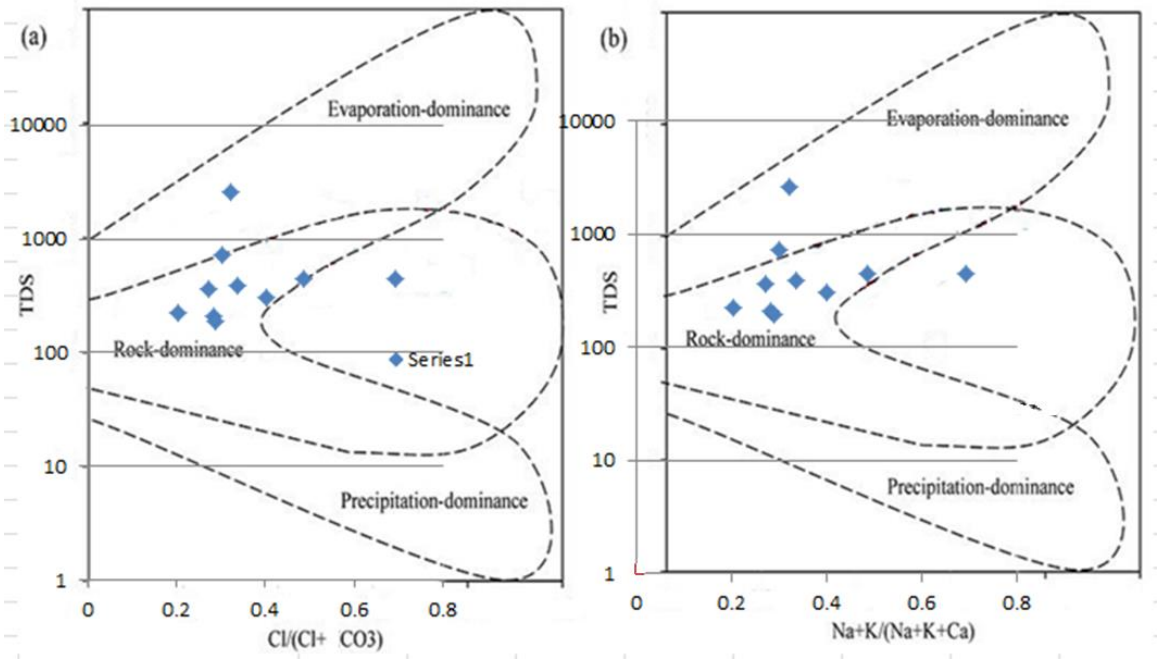

Figure 4.43. Gibbs Diagram for water samples in the studied area in the dry season (October 2021)

The distribution of groundwater sample locations on Gibbs diagrams shows that chemical weathering of rock-forming minerals has affected the quality of groundwaters in the area, and indicates that the interactions between groundwater and rocks, and sediments are the main source

of chemical compositions of groundwaters. According to the data points on the Gibbs diagram, as mentioned in the previous sentences, E8 and E9 groundwaters were plotted in the "evaporation dominance" area because of their higher TDS values. This is to be expected, because evaporation considerably increases the amounts of ions generated by chemical weathering of the rock, resulting in increased salinity and thus poor groundwater quality (Nazzal et al., 2014). However, the groundwater depths range from 52.00 m to 77.50 m and from 69.60 m to 80.10 m in E8 and E9 wells, respectively. The groundwater depths from the surface reflect that these groundwaters are not circulating in shallow aquifers. The higher TDS values in these wells' groundwaters are related to the long residence time in confined aquifers.

4.2.6. Groundwater uses for irrigation purposes:

Irrigation water quality is important for crop yield, soil productivity maintenance, and environmental protection (Wanda et al., 2013). Excess dissolved ions in irrigation water, such as Na, HCO_3, and CO_3, have a physical and chemical impact on plants and agricultural soil, reducing productivity. These ions' physical effects include decreasing osmotic pressure in plant structural cells; as a result, water cannot reach the leaves and other parts of the plant (Dara, 2011).

Plant metabolism is disrupted as a result of the chemical effects. Plant development is influenced by the concentration of specific ions, such as sodium and boron, rather than the total salt concentration (Arumugam and Elangovan, 2009).

The Food and Agriculture Organization (FAO) suggested indices for determining and evaluating the quality of irrigation water, such as sodium adsorption ratio(SAR), and percent sodium ion (Na%).

The USA salinity laboratory and Wilcox diagrams were used to determine the suitability of the groundwaters in the study area for irrigation purposes.

USA salinity laboratory diagram

The USA Salinity Laboratory diagram is used to classify water to be used for agricultural irrigation according to Na^+ ion content. US Salinity Laboratory diagrams were prepared by calculating the electrical conductivity and sodium adsorption rates (SAR) of the waters. Electrical conductivity (EC) is a good indicator of crop salinity because it reflects the TDS in groundwater. The United States Salinity Laboratory (1954) classified ground waters based on electrical conductivity (Table 4.28).

Table 4.28. Classification of water according to USA Salinity Laboratory (1954)

Salinity hazard classes	EC in (micromohs/cm)	Remark on quality
C1	100-250	Excellent
C2	250-750	Good
C3	750-2250	Doubtful
C4	> 2250	Unsuitable

The sodium adsorption ratio (SAR) value was calculated with the following formula:

$$\text{Sodium Adsorption Ratio (SAR)} = \frac{Na^{+}}{\frac{\sqrt{(Ca^{+2}+Mg^{+2})}}{2}} \quad (4.7)$$

where the concentrations are expressed in meq/l.

The SAR of investigated groundwaters was given in Table 4.29 and Table 4.30

Table 4.29. SAR for investigated groundwaters in the rainy season

Sample Number	EC	SAR
E1	610	0.32
E2	650	0.52
E3	1050	0.34
E4	1060	0.46
E5	60	0.56
E6	1090	0.73
E7	630	0.27
E8	3310	0.81
E9	1910	0.91
E10	780	0.95

Table 4.30. SAR for investigated groundwaters in the dry season

Sample Number	EC	SAR
E1	422	0.38
E2	380	0.70
E3	786	0.28
E4	736	0.41
E5	880	1.94
E6	878	1.91
E7	444	0.14
E8	5178	1.86
E9	1422	1.34
E10	614	0.93

The waters are classified into four groups (S1, S2, S3, and S4) related to their SAR values on the USA laboratory diagram (Table 4.31).

Table 4.31. Classification of waters according to salinity and sodium content

Subclasses by salinity		Subclasses according to the amount of sodium	
C1	Slightly salty water. It can be used as irrigation water for most plants.	S1	Low sodium water. Suitable for all kinds of agriculture except for plants sensitive to sodium.
C2	Medium salinity water. It can be used for plants that need moderate salt.	S2	Moderate sodium water. Suitable for gypsum soil with good permeability.
C3	High salty water. It can be used for some plants.	S3	High sodium water. In rare cases, it can be used as irrigation water.
C4	Very high salty water. Not suitable for irrigation water.	S4	Very high sodium water. It is not used as irrigation water except in very low salinity situations.

In the US salinity laboratory diagram drawn according to the analysis results for the groundwaters examined within the scope of the study, in the rainy season, E5 is grouped in C1-S1class (Figure 4.44), this class is characterizing slightly salty and low sodium water, it can be used

as irrigation water and suitable for all kinds of agriculture except for plants sensitive to sodium. E8 is grouped in the C4-S1 class; this class is characterized by the highest salty and low sodium water. This kind of water is not suitable for irrigation and not suitable for sensitive to sodium plants. E1, E2, and E7 are grouped in the C2-S1 class, which means these groundwaters have medium salinity and low sodium; they can be used for plants that need moderate salt and are suitable for all kinds of agriculture except for plants sensitive to sodium. E3, E4, E6, E9, and E10 are grouped in the C3-S1 class, these groundwaters are highly salty and low sodium water, they cannot be used for some plants and are not suitable for plants sensitive to sodium (Table 4.31; Figure 4.44).

In the dry season, the E1, E2, E4, E7, and E10 groundwaters are grouped in the C2-S1 class, groundwaters in this class are medium salinity and low sodium water, they can be used for plants that need moderate salt and are suitable for all kinds of agriculture except for plants sensitive to sodium. E3, E5, E6, and E9 are grouped in the C3-S1 class, groundwaters in this class are characterized by too much salt and low sodium water, they cannot be used for plants without drainage and they can be used for some plants, suitable for all kinds of agriculture except for plants sensitive to sodium (Table 4.31; Figure 4.44).

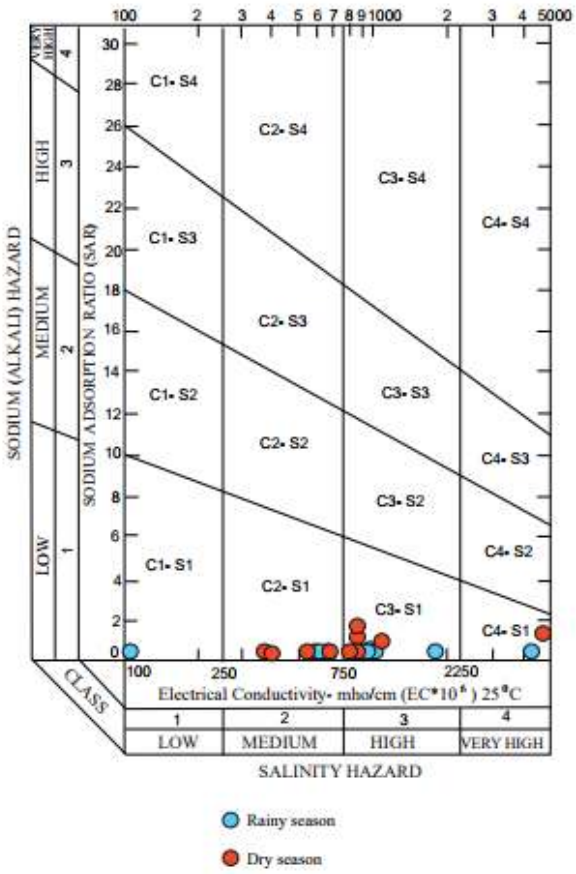

Figure 4.44. USA Salinity diagram for investigated groundwaters in Erbil Basin

Wilcox diagram

Wilcox (1955) categorized groundwater for irrigation uses using sodium percentage and electrical conductivity. Using Equation 4.8, the percent sodium was calculated with respect to the relative proportions of main cations present in water, where ion concentrations are represented in meq/l.

$$\%Na^{+} = \left[\frac{(Na^{+} + K^{+})}{(Ca^{+2} + Mg^{+2} + Na^{+} + K^{+})}\right] \times 100 \qquad (4.8)$$

%Na of the investigated groundwaters are calculated and given in Table 4.32 and Table 4.33

Table 4.32. Sodium percent for investigated groundwaters in the rainy season

Sample Number	EC	%Na
E1	610	14.18
E2	650	16.81
E3	1050	8.87
E4	1060	12.31
E5	60	15.42
E6	1090	20.59
E7	630	9.21
E8	3310	11.68
E9	1910	16.88
E10	780	25.63

Table 4.33. Sodium percent for investigated groundwaters in the dry season

Sample Number	EC	%Na
E1	422	11.84
E2	380	19.92
E3	786	6.63
E4	736	9.28
E5	880	39.14
E6	878	39.29
E7	444	4.72
E8	5178	21.67
E9	1422	20.94
E10	614	23.86

Wilcox (1955) identified waters with an EC of 750 µs/cm as excellent to good water that may be used for agriculture irrigation with little risk of dangerous amounts of exchangeable sodium. According to Wilcox, good permitted irrigation water is water that can be utilized to irrigate salt-tolerant and semi-tolerant favorable drainage situations (Wanda et al., 2013). Because sodium produces an increase in the hardness of soil as well as a decrease in its permeability, the concentration of sodium is a significant factor in determining groundwater quality for irrigation.

The observed groundwaters are grouped in "very good to good", "good to permissible" and "unsuitable" classes related to sodium percent and EC values on the Wilcox diagram (Figure 4.45). Related to the EC values and sodium percent of investigated groundwaters, only the E8 well is unsuitable for irrigation purposes, whereas the other wells are grouped in very good to good and good to permissible classes on the Wilcox diagram (Figure 4.45).

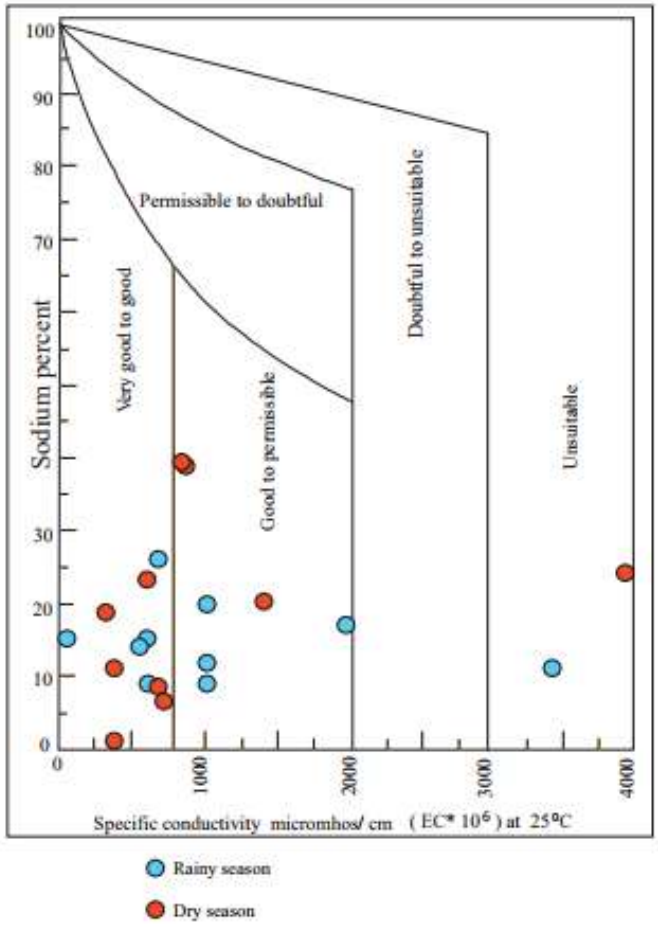

Figure 4.45. Wilcox diagram (1955) of investigated groundwaters in Erbil Basin

4.2.7. Isotope Hydrology

Isotopes are different numbers of neutrons in the same element. Isotopes are classified into two types; stable isotopes and unstable (radioactive) isotopes. Although stable isotopes change their

concentrations by physicochemical processes such as evaporation and condensation, are isotopes that do not change with time. Unstable (radioactive) isotopes are isotopes that undergo radioactive decay such as alpha–decay, beta decay, and nuclear fission. Unstable isotopes are commonly used in radiometric age measurements (Altınkale, 2004). Any non-radioactive element apart from radioactive isotopes when the nucleus is made radioactive by artificial effects, artificial radioactive isotopes are formed (Öztekin, 2000). In environmental isotopes, the hydrogen (H), which is widely used in groundwater studies, has two stable (^{1}H and ^{2}H (D) (deuterium)), a radioactive (^{3}H (tritium)); tri-stable of oxygen (O) (^{16}O, ^{17}O, and ^{18}O); carbon (C) has two stable (^{12}C and ^{13}C) and one radioactive (^{14}C) isotopes.

Isotope geology plays an important role in geological research, development, and monitoring studies. In general, isotopes are susceptible to temperature and water-rock interactions. Therefore, it is used as an effective aquifer monitoring method in groundwater surveys. Oxygen ($\delta^{18}O$), Deuterium ($\delta^{2}H$), and Tritium (^{3}H) isotopes are used to estimate the origin, age, recharge area, altitude, and underground residence time of groundwater (Aydınoğlu, 2019).

The isotopic composition of the groundwater samples for 10 wells in the study area during the dry season (October 2021) is summarized in Table 4.34. The isotopic composition of groundwater is affected by sea level, temperature, amount of precipitation, and evaporation. The $\delta^{18}O$ values of the waters vary between -4.65 ‰ and -7.02 ‰, while the $\delta^{2}H$ (Deuterium) values range from -25.98 ‰ to - 42.68 ‰. The tritium contents vary between 0.27 TU and 2.77 TU in investigated groundwaters.

Table 4.34. Isotope analysis results of groundwaters in the study area

Well Name	Location	Altitude (m)	$\delta^{2}H$ (‰)	$\delta^{18}O$ (‰)	^{3}H (TU)	Deuterium excess (d)	EC (µS/cm)
E1	Erbil City	616	-31.02	-6.05	2.19	17.38	422
E2	Erbil city	444	-36.38	-6.74	-	17.54	380
E3	Erbil city	405	-34.53	-6.41	2.77	16.75	786
E4	Erbil city	407	-33.85	-6.36	-	17.03	736
E5	Kani Qirzhalla village	440	-42.68	-7.02	0.27	13.48	880
E6	Kawrgoesk Camp	313	-31.84	-5.50	1.44	12.16	878
E7	Lajan Village	330	-30.05	-6.02	1.32	18.11	444
E8	Sirawa Village	315	-28.37	-5.52	0.29	15.79	5178
E9	Qurshaghlu village	359	-25.98	-4.65	0.38	11.22	1422
E10	Qushtapa sub-district	394	-38.64	-6.95	0.70	16.96	614

(- : not analysed)

$\delta^{18}O$ – $\delta^{2}H$ relationship

In this study, the global meteoric water line with equation y = 8x +10, east Mediterranean water line with equation y = 8x + 22, and local meteoric water line with equation y = 8x + 20 are used as reference precipitation lines. The calculated value for the deuterium excess in precipitation of Erbil city and the surrounding area is somewhat smaller than the calculated value for the Eastern Mediterranean Sea region, and the equation is $\delta^2H = 8x\ \delta^{18}O + 20$ (Mawlood and Mamand, 2021). The water's isotopic composition (Deuterium and Oxygen-18) results are measured in per mil deviations from the Vienna standard mean ocean water (VSMOW) and given as δ (‰). (Figure 4.46)

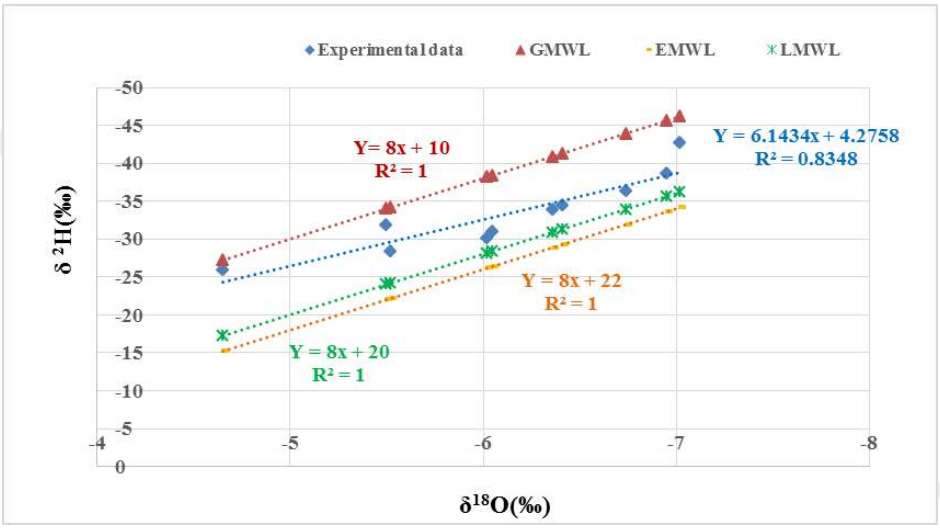

Figure 4.46. Relationship between $\delta^{18}O$ and δ^2H contents in Erbil Basin groundwaters

The investigated groundwaters are on the Mediterranean and Erbil local meteoric water lines and they are of meteoric origin since they are located nearby. In general, deviation from the meteoric water line may be due to different processes such as evaporation, condensation, and rock-water interaction. Generally, the geothermal waters have higher $\delta^{18}O$ values than meteoric waters, the reason for this is that the waters interact with the host rocks during their underground circulation and enter their structures rich in heavy isotopes. So they are enriched by taking $\delta^{18}O$ from the rocks. Higher $\delta^{18}O$ values in E6, E8, and E9 groundwaters reflect a long groundwater-rock interaction process in the aquifer (Figure 4.46).

The altitude effect also plays an important role in hydrological studies. As the altitude increases, the heavy isotope content in precipitation decreases. It means that from the oceans and seas to the inland, precipitation with poorer isotope content is observed (Yang et al., 2009). Lower $\delta^{18}O$ content in E2, E5, and E10 groundwaters indicates recharging from higher altitudes compared to others.

The value of deuterium excess (d) varies with climate; warmer locations have higher d values.

The d can be explained as below:

$$d = \delta D - 8\,\delta^{18}O \qquad (4.9)$$

For the study area, the d is more than 10‰ (Table 4.34). This is typical for the Mediterranean Sea region. The deuterium excess was less than 15‰ from E5, E6, and E9. These results are most likely the result of isotopic enrichment caused by evaporation impacts. The larger deuterium excess was found to be around 18‰ at higher altitude sampling stations. The high d in the study area is due to low relative humidity moving from the Mediterranean Sea towards the Erbil province.

δ^2H - ^3H diagram

The tritium is an unstable isotope, it undergoes radioactive decay in proportion to the residence time of groundwater in the reservoir. Tritium isotope is used in the isotope evaluation of waters. The ^3H content of groundwater decreases with increasing circulation time. Therefore, the ^3H isotope is one of the most important parameters in determining the relative ages of groundwater. In general, higher tritium and $\delta\,^2H$ contents in water indicate shallower circulating waters, while lower tritium and $\delta\,^2H$ contents indicate deep circulating waters (Görür and Genc, 2012).

In Figure 4.47, where the relationship between δ^2H - tritium is shown graphically, waters numbered E1 and E3 are younger waters with shallower circulation than other samples. High values of tritium contents were observed in waters numbered E1and E3, so the waters are younger. This means a faster recharging rate and precipitation influence at these locations. Low tritium contents were observed in waters numbered E5, E8, E9, and E10, this means the waters are deep circulating, and their aquifer residence time is longer than that of the other groundwaters (Okan and Güven, 2019).

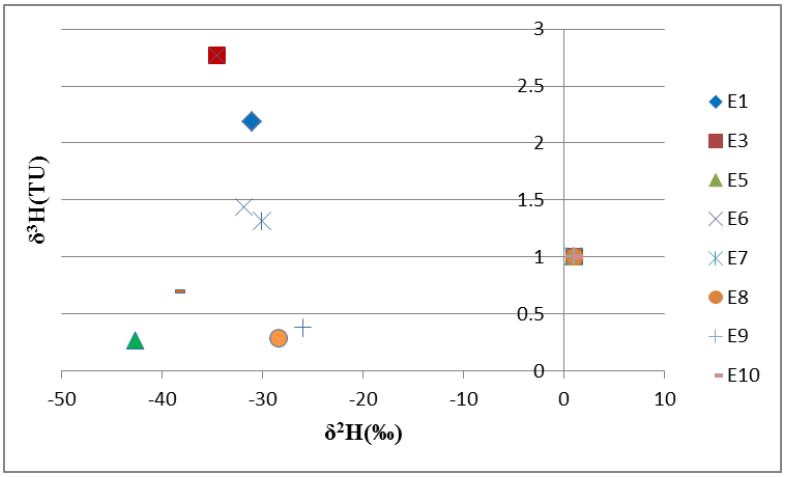

Figure 4.47. Relation between tritium and deuterium contents of groundwaters in the study area

Tritium - EC relation

While the groundwaters decrease by continuing the ^3H halving in the reservoirs during their stay and/or their movement along the flow path, their EC values also increase by taking various

ions into their bodies at different rates by interacting with the rock or rocks that make up the aquifers. Graphical evaluation of these two parameters together is used to describe groundwater circulation systems (Yüce, 2001). In the graph that shows the relationship between ^{3}H and electrical conductivity, the wells of E5, E8, and E9 represent older and deeply circulating groundwaters with low ^{3}H and high EC contents, while E1 and E3 groundwaters with high ^{3}H and low EC values, they are younger and shallower circulating waters compared to other groundwater samples (Figure 4.48).

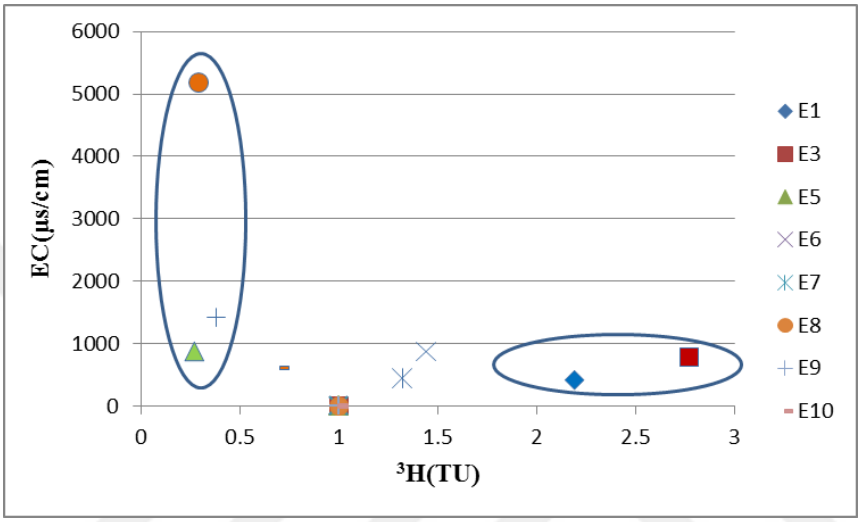

Figure 4.48. Relation between tritium and electrical conductivity of groundwaters in the study area

In the graph that shows the relationship between tritium and electrical conductivity, the wells of E5, E8, and E9 represent older and deeply circulating waters with low ^{3}H and high EC contents, while groundwater with high tritium and low EC values. E1 and E3, are younger and shallower circulating waters compared to other water samples (Figure 4.48).

5. CONCLUSIONS AND RECOMMENDATIONS

The basin is comprised of Pliocene Bakhtiary Formation and Pleistocene recent deposits formed from terrestrial deposits containing coarse pluvial, fine interpluvial pebbly sand and silt deposits.

Groundwater flow in the basin occurs in two different directions. A portion of groundwater flow is from the northeast towards the Greater Zab River, and another portion of the groundwater flows to the south and southwest towards the Lesser Zab River.

The hydrogeochemical analysis of groundwaters for rainy and dry seasons revealed that the type of groundwaters changes seasonally. The main factors affecting the general hydrogeochemistry of groundwaters are; i) groundwater- rock interaction process, ii) type of the aquifers (confined or unconfined), iii) residence time of groundwaters in the aquifers, iv) pH of groundwaters, and v) anthropogenic. The anthropogenic factors include urbanization, the use of insecticides and fertilizers in agriculture, storage of wastes, and refinery stations.

Some groundwaters were polluted with nitrate due to the impact of anthropogenic factors. The major reasons for high nitrate contents in groundwaters were the seepage from the wastewater disposal, landfills, manure, and fertilizer applications on agricultural land, and also sourced gases from oil refineries.

The trace element contents (especially Boron and lead) of some groundwaters are above the detection limit allowed by WHO and Iraqi drinking water standards. It has been determined that these metals, which are found in high concentrations in the waters, are related to the interaction mechanisms between groundwater-rock, groundwater-clay/alteration minerals, industrial processes, discharge of treated wastewater, and the exhaust gases from automobiles and gases emitting from refinery stations.

The waters examined according to their $\delta^{18}O$ and $\delta^{2}H$ contents are of meteoric origin. Low levels of tritium (^{3}H) content and high electrical conductivity in waters numbered E5, E8, E9, and E10 mean the waters are deep circulating, and their aquifer residence time is longer than that of the other waters studied. High values of tritium content and low electrical conductivity in groundwaters numbered E1, and E3 wells, indicate younger ones with short residence time in the aquifer.

Drainage network and treatment station construction for all wastewaters. A secure database has to be established to conclude all missing information about groundwater. Establishing a new water quality control center, providing it with the latest high-efficiency devices, and operating this center with a modern system to improve the accuracy of analyzes and reduce the error rate. Establishing water quality monitoring stations as a reference to the contaminated water for other areas. Monthly monitoring of physicochemical parameters and trace elements of groundwaters should be carried out in the area. Drilling a sufficient quantity of observation wells in various

locations throughout the basin to monitor hydrogeological parameters. To face drought issues and better water management, dams and ponds are needed to be built in the Erbil Basin's recharge area. To maintain groundwater quality in the basin, less organic/inorganic fertilizers should be used in agricultural activities. Organic/inorganic fertilizers, and domestic and human wastes should be stored on the impermeable concrete ground. Environmental education is required to raise awareness about the damage to irrigation and health caused by poor groundwater quality. Preventing wastewater from being dumped uncontrollably in nearby fields and wadis. Preventing uncontrolled solid waste disposal and developing infrastructure for environmentally safe solid waste disposal (i.e. of central sanitary landfills). Construction of a new sewage system in the area to reduce municipal water infiltration into groundwater

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