POTENTIAL SOURCES AND DISTRIBUTION OF NITRATE IN THE GROUNDWATER OF WASIA AQUIFER, AL-KHARJ AREA, CENTRAL SAUDI ARABIA

BY

ABID KHOGALI

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

GEOLOGY

December 2019

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN- 31261, SAUDI ARABIA
DEANSHIP OF GRADUATE STUDIES

This thesis, written by **Abid Gasmalbari Ahmed Khogali** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN GEOLOGY.**

Dr. Abdulaziz M. Al-Shaibani
(Advisor)

Dr. Mohammad Makkawi
(Member)

B. S. Tawabini

Dr. Bassam Tawabini
(Member)

Prof. Luis A. González
(Member)

For him:

Prof. Martin Keller
(Member)

Dr. Abdullatif Al-Shuhail
Department Chairman

Dr. Salam A. Zummo
Dean of Graduate Studies

19/12/19

Date

Dedication

To my parents and brothers

To all my family members

To my fiancée

To the Sudanese community at King Fahd University of Petroleum and minerals

ACKNOWLEDGMENTS

I would like to express my gratitude to the Geosciences Department and Collage of Petroleum Engineering and Geosciences at King Fahd University of Petroleum and Minerals for giving me the opportunity to do my MSc and providing the required facilities and assistance.

Special thanks to my supervisor Dr. Abdulaziz Al-Shaibani for his guidance, assistance and continuous support. Thanks also go the other committee members, Dr. Mohammad Makkawi, Dr. Bassam Tawabini, Dr. Martin Keller and Dr. Luis A. González for their valuable help and guidance.

I am greatly thankful to Dr. Abdullatif Al-Shuhail the chairman of the Geosciences Department for his support during this research.

Sincere appreciation to my parents and brothers for their support, prayers and patience.

Much gratitude to my colleagues and friends at Geoscience Department and KFUPM.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Full Name	: ABID GASMALBARI AHMED KHOGALI
Thesis Title	: POTENTIAL SOURCES AND DISTRIBUTION OF NITRATE IN THE GROUNDWATER OF THE WASIA AQUIFER, AL-KHARJ AREA, CENTRAL SAUDI ARABIA
Major Field	: GEOLOGY
Date of Degree	: December 2019

Al-Kharj area is one of the major agricultural and dairy farms areas in the kingdom. Wasia Group contains the main aquifer that supplies drinking and irrigation water to this area. Previous studies on the geochemistry of the groundwater of the Wasia aquifer have reported elevated nitrate concentrations in Al-Kharj area but without evidentially identifying the exact sources of this nitrate contamination. The presence of nitrate concentrations in groundwater is usually attributed to the use of fertilizers. However, other sources like natural sources may exist especially when some wells are away from direct human interaction. Therefore, this study aims to investigate the possible sources of nitrate and its distribution as well as to assess the groundwater quality of the Wasia aquifer in Al-Kharj area, central Saudi Arabia. Based on the stability of the characteristics of nitrate isotopes ($\delta^{15}N–NO_3$ and $\delta^{18}O–NO_3$) from different sources, it has been used for identifying the potential sources of nitrate in this area. Tritium (^3H) is used to estimate the recent recharge date. Water quality index (WQI) is used to assess the suitability of this groundwater for drinking purposes. The suitability of the Wasia aquifer for agricultural uses is evaluated based on several assessment indices. Samples were collected from thirty-four (34) wells (4 samples each) distributed in the study area. The isotopic signatures and distribution of the $\delta^{15}N–NO_3$ and $\delta^{18}O–NO_3$ revealed that atmospheric deposition and fertilizers are the potential sources of nitrate in the north and eastern sections of the study area, while manure and wastewater are the main nitrate contributors in the western section. Only two samples show tritium rates above the detection limit of the used method (0.8 TU). This may not necessarily be an indication of the absence of recent recharge. Instead, this groundwater could be a mixture of recent and connate waters. Wasia groundwater quality in the study area generally ranges from poor to unsuitable for drinking according to WQI. According to Sodium Adsorption Ratio (SAR), Magnesium Ratio (MR) and Kelly's Ratio (KR), all groundwater samples are considered appropriate for irrigation. Moreover, as per Corrosivity Ratio (CR) and Total Hardness (TH), the studied groundwater is basically corrosive and needs attention when choosing transportation pipes. It can be concluded that in the Wasia aquifer both, natural sources such as atmospheric deposition, and anthropogenic sources like manure and fertilizers appear to increase the Wasia aquifer nitrogen content. Proper treatment is required before drinking from Wasia aquifer. Monitoring and regular checking for water quality is required in the study area.

ملخص الرسالة

الاسم الكامل: عابد قسم البارئ احمد خوجلي

عنوان الرسالة: عنوان الرسالة: المصادر المحتملة وتوزيع النترات في المياه الجوفية لخزان الوسيع الجوفي، منطقة الخرج، وسط المملكة العربية السعودية

التخصص: جيولوجيا

تاريخ الدرجة العلمية: ديسمبر 2019

تعتبر منطقة الخرج من المناطق المهمة من ناحية الزراعة وتربية المواشي في المملكة العربية السعودية. مجموعة صخور الوسيع تحتوي على خزان المياه الجوفي الذي يغذي هذه المنطقة بالمياه. أظهرت الدراسات السابقة التي أجريت على جيوكيمياء المياه الجوفية لخزان الوسيع زيادة نسب النترات عن الحد الطبيعي من غير تحديد مصادر هذا التلوث. وجود النترات بكميات كبيرة في المياه الجوفية عادة ما يعزى الى استخدام الاسمدة الصناعية. مع ذلك، يمكن ان تكون هذه النترات طبيعية المنشاة خاصه إذا كانت الآبار بعيدة من المناطق المأهولة بالسكان. لهذا، تهدف هذه الدراسة للتحقيق في مصادر هذه النترات وتقيم جودة مياه خزان الوسيع في منطقة الخرج. اعتماداً على ان نظائر النترات ($\delta^{15}N\text{–}NO_3$ and $\delta^{18}O\text{–}NO_3$) تظهر خصائص ثابته في مختلف المصادر، تم استخدامها في هذه الدراسة للبحث عن المصادر المحتملة للنترات. تم استخدام الترتيوم (^3H) لتقدير زمن اخر تغذية لخزان المياه الجوفية في المنطقة. تم استخدام مؤشر جودة المياه (WQI) لتقيم هذه المياه للشرب. تقيم هذه المياه لعمليات الري تم بناءة على عدة معاملات. توزيع ونسب نظائر النترات كشفت ان ترسب الغلاف الجوي والأسمدة الصناعية تمثل المصادر المحتملة للنترات في القسمين الشمالي والشرقي من منطقة الدراسة. في حين أن مخلفات الحيوانات ومياه الصرف الصحي هما المساهمان الرئيسيان للنترات في القسم الغربي. عينتان فقط أظهرتا نسب ترتيوم اعلى من حد كشف الطريقة المستخدمة (0.8 TU). هذا يدل على ان مياه خزان الوسيع في هذه المنطقة تمثل خليط من مياه تم تغذيتها حديثاً ومياه احفورية. تتراوح عينات المياه التي درست من سيئة الى غير

مناسبة للشرب بناءاً على مؤشر جودة المياه. بناءاً على نسبة امتصاص الصوديوم (SAR)، نسبة المغنيزيوم ونسبة كيلي، تعتبر كل عينات المياه التي درست جيدة لري المحاصيل. اما بناءاً على نسبة التآكل (CR) والصلابة الكلية (TH)، تعتبر هذه المياه ذات قابلية عالية لتآكل خطوط نقل المياه. من هذه الدراسة يبدو ان المصادر الطبيعية كترسب الغلاف الجوي والمصادر البشرية المنشأ مثل السماد الصناعي ومياه الصرف الصحي تزيد من محتوى النترات في خزان الوسيع الجوفي.

CHAPTER 1

INTRODUCTION

1.1. Overview

Nitrate (NO_3^-) contamination in groundwater is a worldwide problem. The risk on public health associated with drinking contaminated water with nitrate includes Blue-baby syndrome (methemoglobinemia), which has led to considerable studies on nitrate occurrence within the groundwater (Hem, 1985; Kendall et al., 2007; Stadler, 2006). High-level concentrations of nitrate in groundwater are usually attributed to the use of fertilizers. However, other sources, including natural, are possible. Examples of nitrate sources are leakage from disposal networks, in-situ sewage disposal, animal waste, landfills, soil nitrate, industrial waste, interaction with contaminated runoff and irrigation water, and atmospheric deposition from dry and wet precipitations (Wakida and Lerner, 2005). Nitrate may also be released from hydrothermal waters and nitrogen-bearing rocks like igneous, metamorphic and specially sedimentary and meta-sediment rocks (Holloway and Dahlgren, 2002).

The Wasia Group represents an important succession within the Cretaceous system of the Arabian platform. It is significant in terms of both hydrocarbons and groundwater resources. The clastic part of Wasia Group represents an important freshwater aquifer that supplies Riyadh, as it is one of the most prolific sources of groundwater in Saudi Arabia

(Alfaifi et al., 2017; Ministry Of Agriculture And Water, 1984; Zaidi et al., 2016). On the other hand, the hydrocarbon contents increase eastward as the same unit represents an important reservoir (Alsharhan and Nairn, 1988; El-Naggar and Al-Rifaiy, 1972; Harris et al., 1984).

Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) and Dornier Consulting (DCo) carried out a recent study on the Wasia aquifer for the Ministry of Environment, Water and Agriculture of Saudi Arabia in 2013. This study covered the Wasia groundwater geochemistry in addition to other aspects. One of the findings of this study is the high concentrations of nitrate in some wells despite being away from human activities (GTZ/DCO, 2013).

In this study, we will use the isotopes nitrogen-15 and oxygen-18 of the nitrate anion (NO_3^-) to try to identify the nitrate sources by comparing their isotopes signature with the potential sources, which are discussed later section in this thesis.

1.2. Problem Statement

Ministry of Environment, Water and Agriculture have conducted several groundwater studies. One of these studies aimed to study groundwater quality and hydrochemistry, environmental isotopes, hydrology, geophysical survey, geology, hydrogeology, and other aspects on Wasia aquifer (GTZ/DCO, 2013, 2009, 2006). In this study, the hydrochemistry of the Wasia aquifer groundwater is showing high nitrate concentrations in several wells. The fact that some of these wells are away from anthropogenic activities, raises a question about the source of nitrate in the aquifer. This unusual presence of nitrate in groundwater is not unprecedented to the Kingdom, as previous reports by the Ministry of Water and

Electricity have shown similar findings in different areas (GTZ/DCO, 2009, 2006). Alabdula'aly et al. (2010), who studied the nitrate presence in the groundwater of Saudi Arabia, also discussed this problem. He found high nitrate concentration in some wells away from possible human interaction. In response to this problem, additional studies are required to identify possible other sources of these elevated nitrate concentrations in the Wasia aquifer.

1.3. Objectives

The main targets of this study are:

- To investigate nitrate sources in the study area by analyzing the isotopes ($^{15}N\text{-}NO_3$ and $^{18}O\text{-}NO_3$).
- To assess nitrate concentrations and distribution in the study area.
- To estimate recent recharge date, based Tritium ^3H.
- Other minor objectives include assessing variations of major ion and trace element concentrations in the groundwater of the Wasia aquifer, and the water quality for domestic, and agricultural uses.

1.4. Study Area

The study area is located to the east of Al Kharj city in central Saudi Arabia within the southeastern section of the Riyadh province and situated between latitudes 24.00°N and 24.35°N and longitudes 47.40°E and 48.00°E (Fig. 1). The area has elevations between 400 m and 480 m above the sea level. Wadi As-Sahba crosses the central part and represents the lowest elevation in the study area (Zaidi et al., 2016).

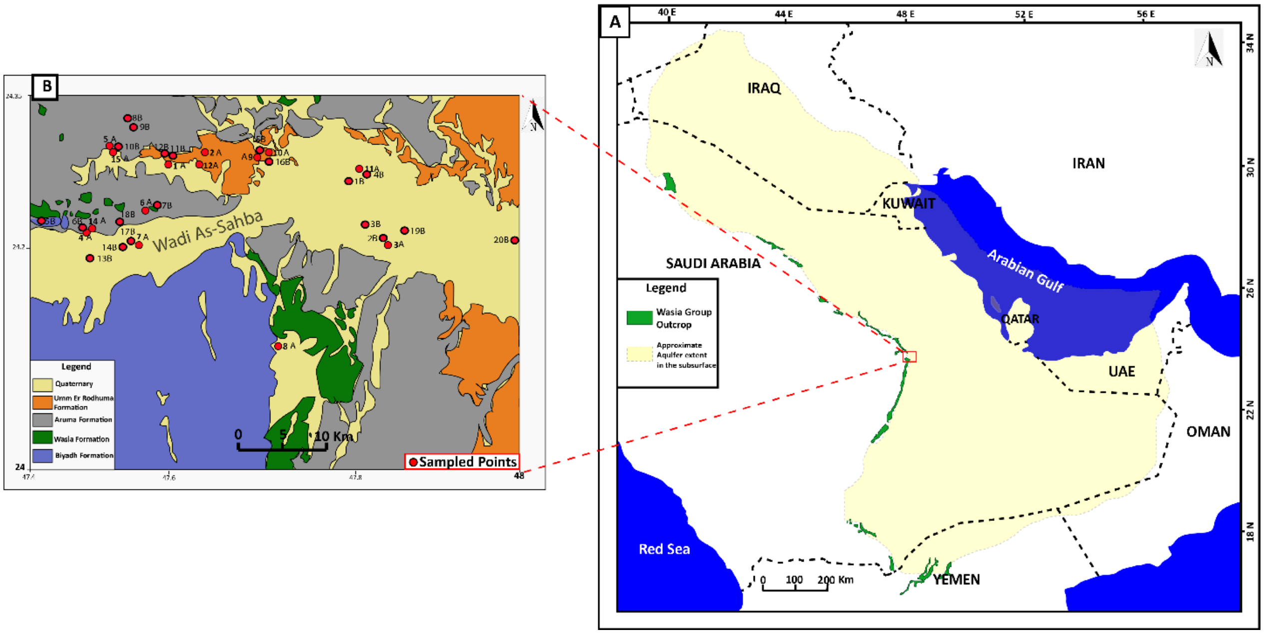


Figure 1: A) Map of the Arabian Peninsula showing Wasia group outcrop locations and the regional extent of Wasia aquifer in the subsurface (modified from Ministry of Agriculture and Water, 1979 and GTZ/DCO, 2013), B) geological map of Al-Kharj area showing the sampling points.

The study area lies within an arid climate region with a wide range of temperatures and rainfalls. The temperature ranges within a maximum of 48° C during summer to approximately 3° C during winter (Zaidi et al., 2016). The annual evaporation rates reach 2000 mm while the average annual rainfall is below 100 mm (Almazroui, 2011).

CHAPTER 2

LITERATURE REVIEW

The Arabian Plate represents one of the most significant geological places in the globe. It consists of igneous rocks in the Arabian Shield in the west, along with sedimentary rocks in the other areas that fall east of the shield.

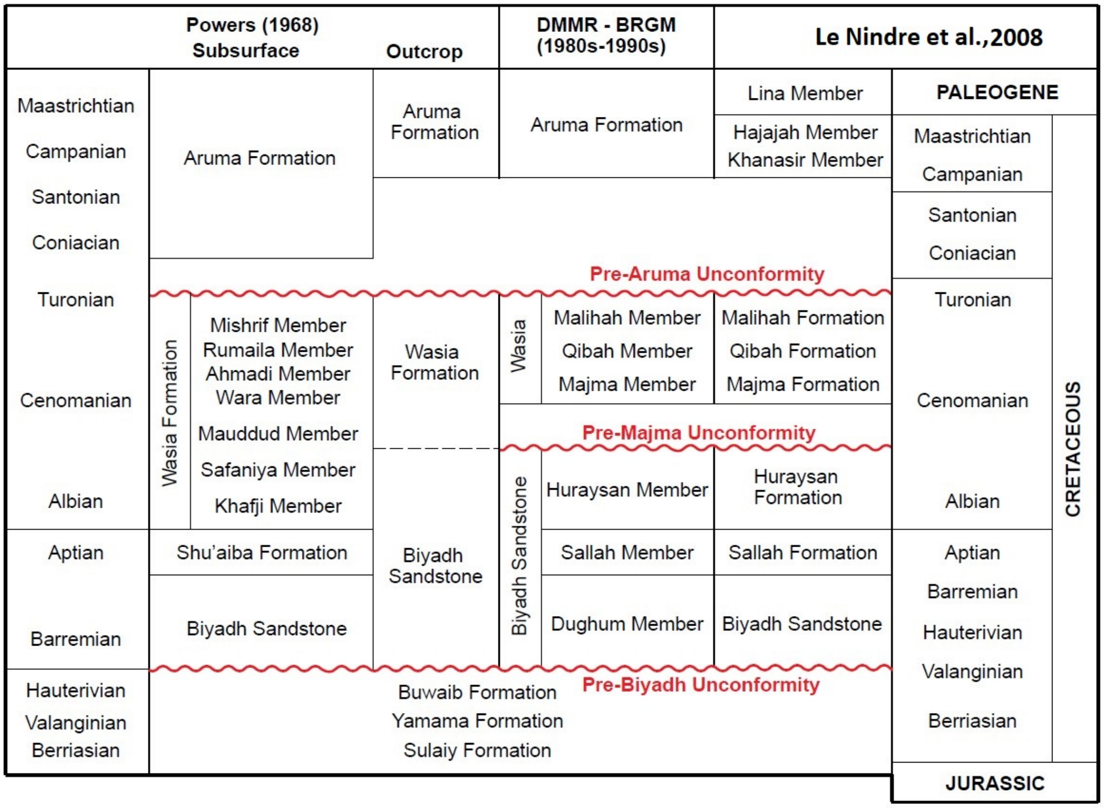
In the subsequent sections, the geological and paleogeographic settings, sedimentology, stratigraphy, and hydrogeology of the Wasia Group and the underlying (Biyadh sandstone, Sallah and Shu'aiba Formations) and the overlying units (Aruma Group) are briefly summarized. While the tritium isotopes and sources of nitrate in groundwater are briefly discussed in later sections.

2.1. Biyadh Sandstone, Sallah and Shu'aiba Formations:

The Biyadh Formation was defined and separated from the Wasia sandstone by Steineke et al. (1958). Powers et al. (1966) subdivided Biyadh Formation into four units. The lower unit consists of brown, massive, coarse-grained sandstone with some shaley intercalation. The second unit composes of light-colored coarse-grained sandstone and conglomerate. The third unit was described as shale, limestone and marl unit. Unit 4 is again coarse-grained sandstone. In 1991, Vaslet et al. combined the first two units of Powers et al. (1966) into Dughum member, while the upper two units were defined as Sallah and Huraysan members. Le Nindre et al. (2008) reduced Biyadh Formation to the only first two units of Powers et al. (1966).

The Sallah Formation is a surface unit that correlated with the Shu'aiba Formation in the Subsurface (Le Nindre et al., 2008). It was first defined as a member of the Biyadh Formation by Vaslet et al. (1991). Later, upgraded to a full Formation by Le Nindre et al. (2008).

The Shu'aiba Formation is the subsurface equivalent of the Sallah Formation (Le Nindre et al., 2008). Van Buchem et al. (2002) showed a regional stratigraphic correlation for the Formation based on outcrop and subsurface data.



Powers (1968) Subsurface			Outcrop	DMMR - BRGM (1980s-1990s)		Le Nindre et al.,2008		
Maastrichtian Campanian Santonian Coniacian	Aruma Formation		Aruma Formation	Aruma Formation		Lina Member	PALEOGENE	
						Hajajah Member Khanasir Member	Maastrichtian Campanian	CRETACEOUS
							Santonian Coniacian	
	Pre-Aruma Unconformity							
Turonian Cenomanian	Wasia Formation	Mishrif Member Rumaila Member Ahmadi Member Wara Member	Wasia Formation	Wasia	Malihah Member Qibah Member Majma Member	Malihah Formation Qibah Formation Majma Formation	Turonian Cenomanian	
				Pre-Majma Unconformity				
Albian		Mauddud Member Safaniya Member Khafji Member	Biyadh Sandstone	Biyadh Sandstone	Huraysan Member	Huraysan Formation	Albian	
Aptian	Shu'aiba Formation				Sallah Member	Sallah Formation	Aptian	
Barremian	Biyadh Sandstone				Dughum Member	Biyadh Sandstone	Barremian Hauterivian Valanginian	
	Pre-Biyadh Unconformity							
Hauterivian Valanginian Berriasian	Buwaib Formation Yamama Formation Sulaiy Formation						Berriasian	
							JURASSIC	

Figure 2: Surface and subsurface stratigraphic units of the Cretaceous period in Saudi Arabia (Le Nindre et al., 2008).

2.2. Wasia group:

The Wasia Group represents a very important section within the Cretaceous system of the thick Arabian platform (Fig. 2 and Figure 3). It is significant both in terms of hydrocarbon and groundwater aspects. Closer to the outcrop, the clastic part of the Wasia Group represents an important freshwater aquifer that supplies Riyadh province. On the other hand, as you go east toward the gulf, the hydrocarbon significance increases as the same clastic part represents an important reservoir (Alsharhan and Nairn, 1988; El-Naggar and Al-Rifaiy, 1972; Harris et al., 1984).

2.2.1 Stratigraphy:

Both outcrop and subsurface of the Wasia Group have been widely studied (Alsharhan and Nairn, 1988; Cagatay, 1988; Harris et al., 1984; Le Nindre et al., 2008; Moshrif and Kelling, 1984; Powers et al., 1966; Sharief et al., 1989; Steineke et al., 1958). This may be attributed to its double significance in terms of hydrocarbon reservoir in addition to groundwater aquifer.

The Wasia Group is outcropped in an intermittent curve from approximately latitude 20.9°N to 30°N, for about 1500 km long and approximately 50 km width (Powers et al., 1966; Sharief et al., 1989). The thickness of the formation varies within this discontinuous arc from about 30 m thick in the south to almost 90m in the north (Sharief et al., 1989).

The Group was first proposed by Steineke et al. (1958), while Powers et al. (1966) were the pioneers in describing its boundaries. Depositional environments and their tectonic setting together with the subsequent diagenesis and hydrocarbon potentiality have been studied by Cagatay (1988), Harris et al. (1984), Moshrif and Kelling (1984) and Sharief et al. (1989) (Fig. 3). A detailed review of the Wasia Group stratigraphy and paleontology in the Arabian Gulf and the current terminologies was provided by Alsharhan and Nairn (1988). Le Nindre et al. (2008) revised the lithostratigraphic and biostratigraphic units in addition to the stratigraphic sequences of the Wasia Group in the outcrop and its correlation in the subsurface (**Error! Reference source not found.**). Keller et al. (2019) did an outcrop analog study on the Wasia-Biyadh and Aruma aquifers. Their study focused on the interpretation of reservoir quality by measuring porosity and permeability of 150 outcrop sample and gamma-ray measurements (Fig. 4).

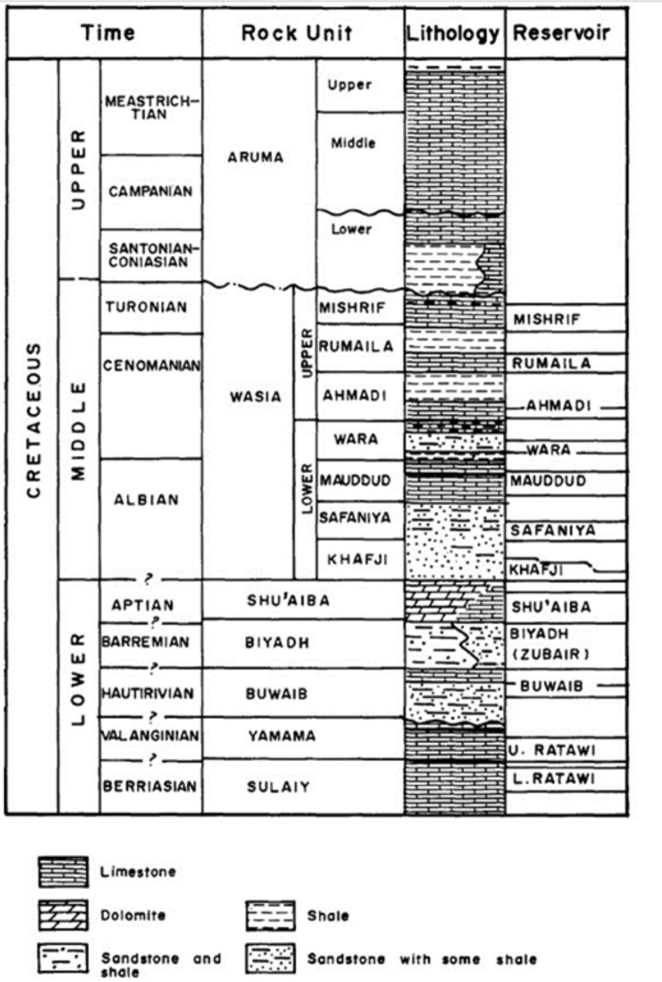


Figure 3: Cretaceous stratigraphic section, Saudi Arabia (Sharief et al., 1989).

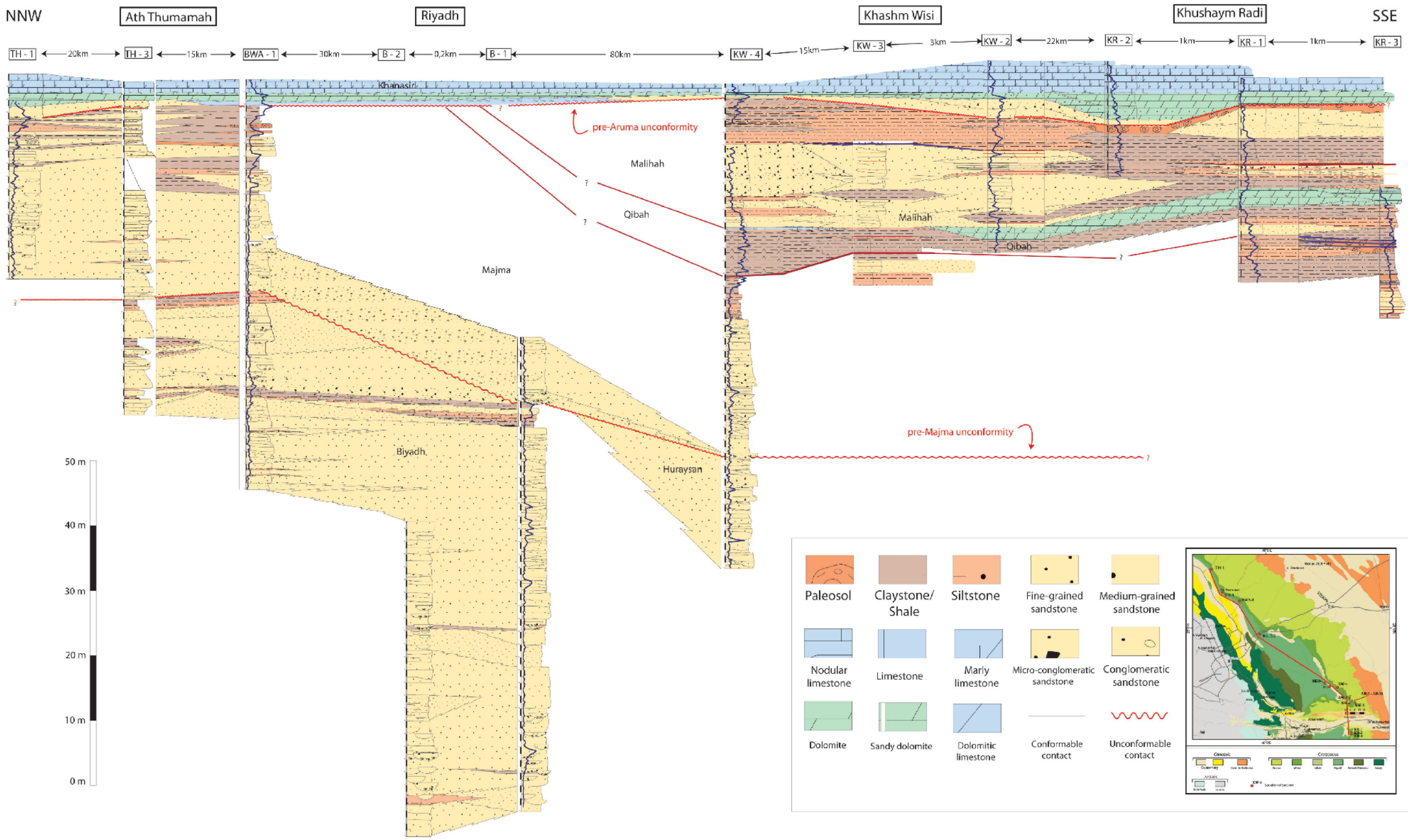


Figure 4: Craterous strata in Saudi Arabia from Ath Thumamah area to Khushaym Radi area (Keller et al., 2019)

2.2.2 Hydrogeology

The Wasia Group as a groundwater aquifer has been generally studied also. The first work on the hydraulic properties of the Wasia aquifer in the eastern province was provided by Aramco (1960). Subsequently, a study by SOGREAH (1968) on Biyadh-Wasia aquifer in the Wasia Water Wells Field (100 km east of Riyadh on Riyadh-Dammam road) and Al-Kharj area. Based on their study the transmissivity of the aquifer ranges between 0.03 and 0.01 m^2/sec.

In 1975, Sir M. Macdonald and Partners (SMMP) did a regional study to look for another freshwater source for Riyadh province. They confirmed that the Wasia is a reliable aquifer for supplying parts of Riyadh province with fresh water. According to their study, the transmissivity of the aquifer ranges from 0.007 to 0.07 m^2/sec. Bureau De Recherches Geologique et Minieres (BRGM, 1976) carried out another study for oil companies in the eastern province for using the Wasia as a major Water supply for water injection program. Later, in 1977, the United State geological survey (USGS) used SMMP data to simulate the drawdown for more 20 years (until 1997). Their results showed an expected 60 m drawdown for 34 wells with a pumping rate of 200,000 m^3/day. Another attempt to simulate the aquifer drawdown developed by Tokhais (1982). He came up with 25 m drawdown with 210,000 m^3/day pumping rate. According to the Ministry Of Agriculture And Water (1984), the Wasia Group along with the below Biyadh Formation are one hydraulic system and represents one of the most prolific aquifers in the kingdom. Subyani and Sen (1989) developed a geostatistical model for the Wasia aquifer in central Saudi Arabia. Subyani and Sen (1991) used Recharge Outcrop Relation (ROR) to estimate the water recharge amount for the Wasia aquifer. Their results showed a 4 mm/year recharge in central Saudi Arabia. Magaji (1995), made an assessment for hydrogeological parameters of the

Wasia aquifer using thin-section study through an unpublished Master thesis. Deutsche Gesellschaft für Internationale Zusammenarbeit and Dornier Consulting (GTZ/DCO, 2013, 2009, 2006) conducted regional considerable studies on the Wasia aquifer for the Ministry of Water and Electricity. These studies included groundwater quality and hydrochemistry, environmental isotopes, hydrology, geophysical survey, geology, hydrogeology. Stöckl (2010), did a Master thesis on the hydrological and hydrochemical controls on radioactivity on the Wasia aquifer with aid of the data obtained by GIZ\DCo. Zaidi et al. (2016) and Alfaifi et al. (2017), used the same data for an evaluation of the aquifer groundwater chemistry and groundwater management scenarios, respectively. Zaidi et al. (2016) also provided a piezometric surface of the Wasia aquifer in Al-Kharj area (Fig. 5). Al-Omran et al. in 2016, studied the hydrochemical properties of the groundwater of Al-Kharj area. In 2018, Alharbi and

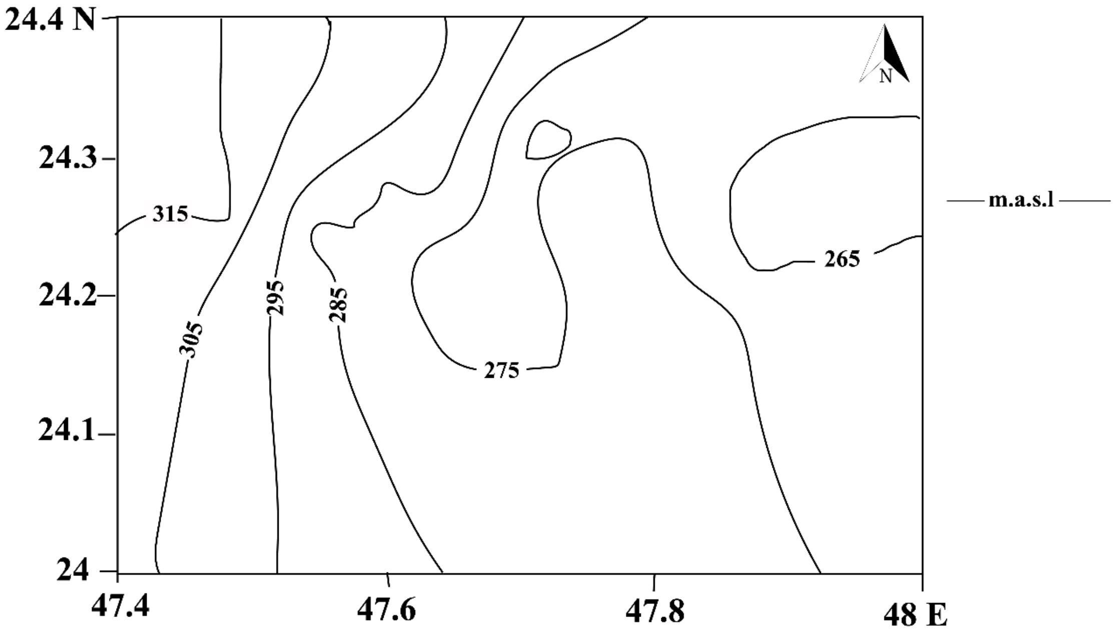


Figure 5: Water level in the study area. Modified from Zaidi et al. (2016)

Zaidi did a hydrochemical classification and cluster analysis of the groundwater of Wadi Sahba which crosses Al-Kharj area.

To date, no local scale published studies on the sources of the nitrate concentration are known to have been conducted on this hydraulic system.

2.3. Aruma Group:

Powers et al. (1966) made a detailed description of Aruma Formation which was defined by Steineke et al. (1958). Aruma Formation was subdivided by El-Asa'ad (1984, 1983a, 1983b) into three members, the Khanasir member, the Hajajah member, and the Lina member. Alsharhan and Nairn (1990) upgraded Aruma Formation to a Group, and so, its members to Formations. The Khanasir Formation composed of a fauna-rich limestone (Vaslet et al., 1991) and was dated based on ammonites (Le Nindre et al., 2008). The Hajajah Formation composed of limestone intercalated with shale and mudstones (Philip et al., 2002). The Lina Formation consists of shales with some alterations of dolomitic limestone (Philip et al., 2002).

2.4. Sources of nitrate in groundwater

Nitrate exists naturally in the environment as part of the nitrogen cycle. The nitrogen cycle is a complex cycle in which nitrogen is transformed into multiple chemical forms including the solid, gaseous and liquid phases (Fig. 6). The nitrogen cycle includes several processes such as nitrification, denitrification, volatilization, fixation, atmospheric deposition and ammonification (Gutiérrez et al., 2018). Nitrification refers to the oxidation of ammonium (NH_4^+) to nitrate (NO_3^-) by nitrifying bacteria. Denitrification is the reduction process of nitrate to other nitrogen oxides (N_2O, NO or N_2). Volatilization is the release of NH_3^- gas to the atmosphere. Nitrogen fixation is the process that transforms natural nitrogen gas to other chemical forms of nitrogen.

Nitrogen fixation includes fixation by bacteria, lighting or by industrial fixation for multiple uses (Cleveland et al., 1999). Ammonification or as known as mineralization refers to the transformation of organic matter to ammonium (Kendall et al., 2007). Nitrogen from atmosphere mainly occurs in the oxidized form (NO_3^-) or the reduced form (NH_4^+) (Stadler et al., 2008), which subsequently be deposited and carried by water. Anthropogenic activities (like fuel burning by vehicles and factories) and natural processes (like volatilization of ammonia, nitrification and denitrification, and lightening) release nitrogen products to the atmosphere (Kendall, 1998).

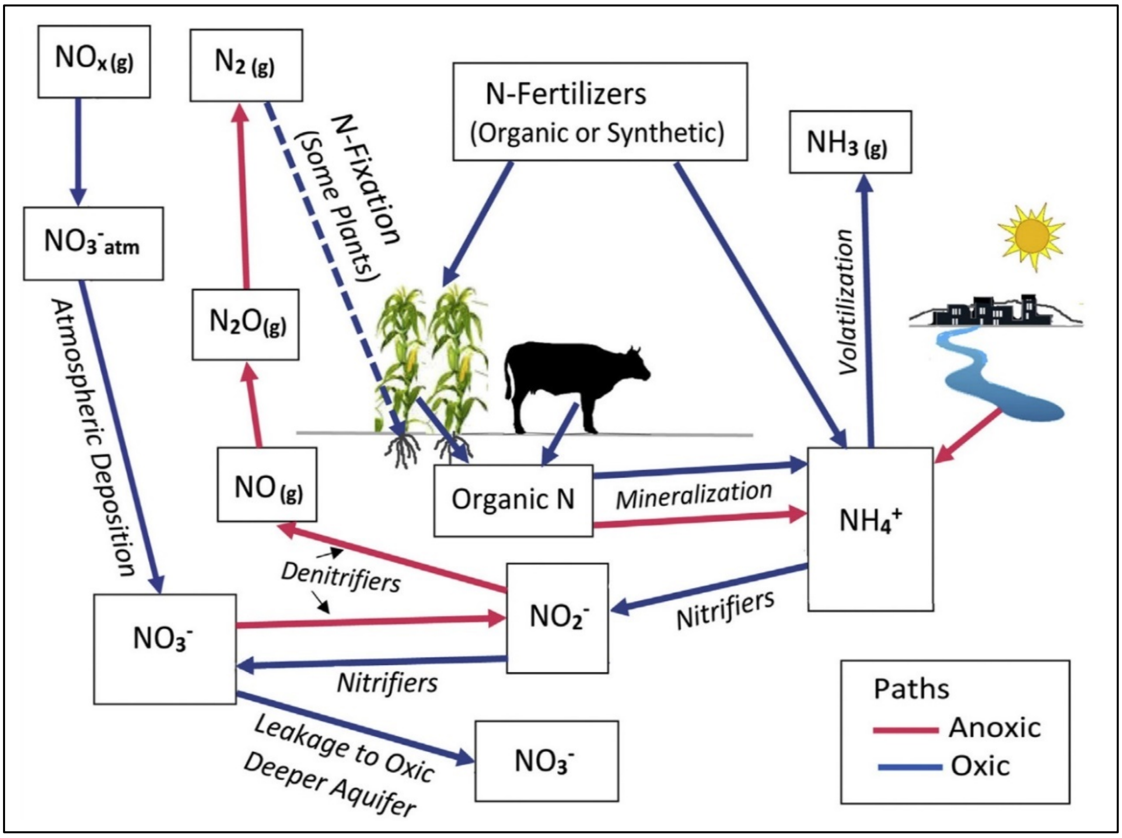


Figure 6: Simplified diagram of the processes in the nitrogen cycle (Gutiérrez et al., 2018)

The sources of nitrate are mainly atmospheric deposition, fertilizers, sewage and manure, and soil nitrification (Li et al., 2017). Fertilizers-derived nitrate is one of the significant sources of nitrate in groundwater. Using N-fertilizers increases plants output. However, extensive use of these fertilizers may result in nitrate accumulations in the soil where it might then percolate to the groundwater. Ammonium ions from wastewater and septic tanks can be oxidized to nitrate which may leach to surrounding soil and then to groundwater (Wakida and Lerner, 2005). Nitrogen in soil may exist in several forms: mineral nitrogen, fixation of atmospheric nitrogen as organic nitrogen in plants and in leguminous bacteria, or in soil biomass (Canter, 1997).

2.5. Nitrate Isotopes

Nitrate (NO_3^-) is a nitrogen oxide that consists of one nitrogen and three oxygen atoms. Nitrogen (N) has two stable isotopes that occur naturally, ^{15}N and ^{14}N. ^{14}N represents around 99.63% of the nitrogen in the atmosphere. ^{15}N composes the rest (Junk and Svec, 1958). There are three stable isotopes of oxygen (O). The common one is ^{16}O that represents around 99.76%, then ^{18}O (0.2%), and ^{17}O (0.03%) (Cook and Lauer, 1968).

Stable isotope ratio (R) is the abundance of the rare isotope compared to the abundance of the most common one in the sample:

$$R = \frac{abondance\ of\ the\ rare\ istope}{abondance\ of\ the\ abundant\ isotope}$$

For nitrate, R is $^{15}N/^{14}N$ and $^{18}O/^{16}O$.

The resulted isotopic ratio (R) is then compared to a reference material with a known isotopic signature. The difference is expressed in delta units (δ) and calculated in parts per mill or per thousand:

$$\delta_{sample} = \frac{(R_{sample} - R_{standard})}{R_{standard}} * 1000$$

$R_{standard}$ for oxygen is the Vienna Standard Mean Ocean Water (VSMOW) and the atmospheric air (AIR) for the nitrogen. If the δ is positive, the sample has heavier isotope that the standard (enrichment). When δ is negative, the sample has lighter isotope that the standard (depletion).

The chemical, physical and biological processes that affect the nitrogen cycle act differently on nitrogen from different sources, and hence, results in different N isotopic ratio. The use of the $\delta^{15}N$ of nitrate for nitrate sources discrimination was firstly introduced by Kohl et al. (1971) to estimate the contribution of fertilizers in the nitrate budget in Sangamon river, USA. Xue et al. in 2009 collected different $\delta^{15}N$ ranges from multiple studies on various nitrate source. Figure (7) shows the percentiles and outliers of $\delta^{15}N\text{-}NO_3^-$ for many nitrate sources.

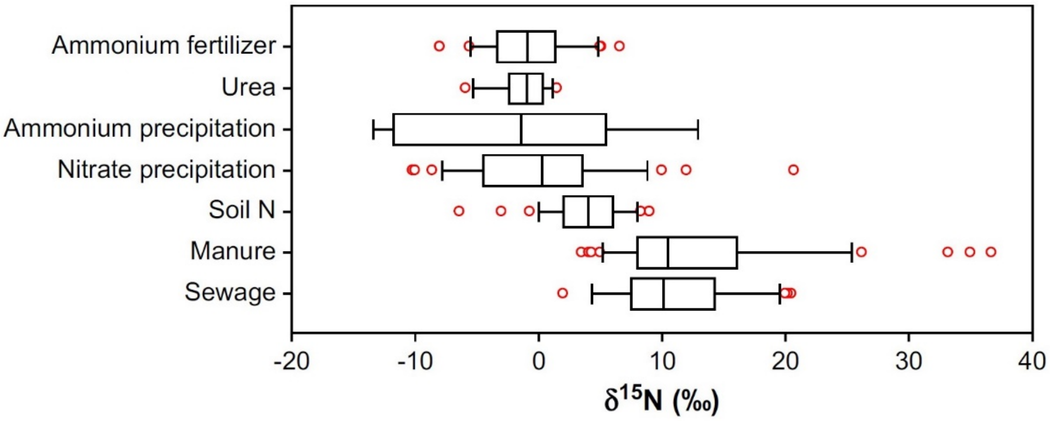


Figure 7: Boxplots of different nitrate sources based on δ15N-NO3- (Xue et al., 2009)

As shown in figure (7), sometimes it is difficult to distinguish between nitrate sources based only on $\delta^{15}N$ values because many sources may have common $\delta^{15}N$ ranges. This has directed to use of dual nitrate isotope approach ($\delta^{15}N$ and $\delta\ ^{18}O$) (Fenech et al., 2012; Xue et al., 2009). Based on the fact that isotopic characteristics of nitrate are distinct, isotope-based approaches are used to identify the possible sources of nitrate (Mayer et al., 2002; Wells and Krothe, 1989). Different ranges of nitrate isotopic signature are reflected between different sources (Fig. 8). Kendall (1998) has mentioned three benefits of using the approach of dual nitrate isotopes: (i) oxygen isotope has a wider range of isotopic compositions from different sources, and thus, a higher resolution when using $\delta^{15}N$ and $\delta\ ^{18}O$ together. (ii) nitrate sources that have common $\delta^{15}N$ ranges may be distinguished when having $\delta\ ^{18}O$ values (e.g. soil nitrate and atmospheric nitrate) and (iii) theoretically, nitrate sources contributions can be determined even in the cases of enormous denitrification. This is attributed to that $\delta^{15}N$ and $\delta\ ^{18}O$ of nitrate changes systematically during denitrification (Fenech et al., 2012).

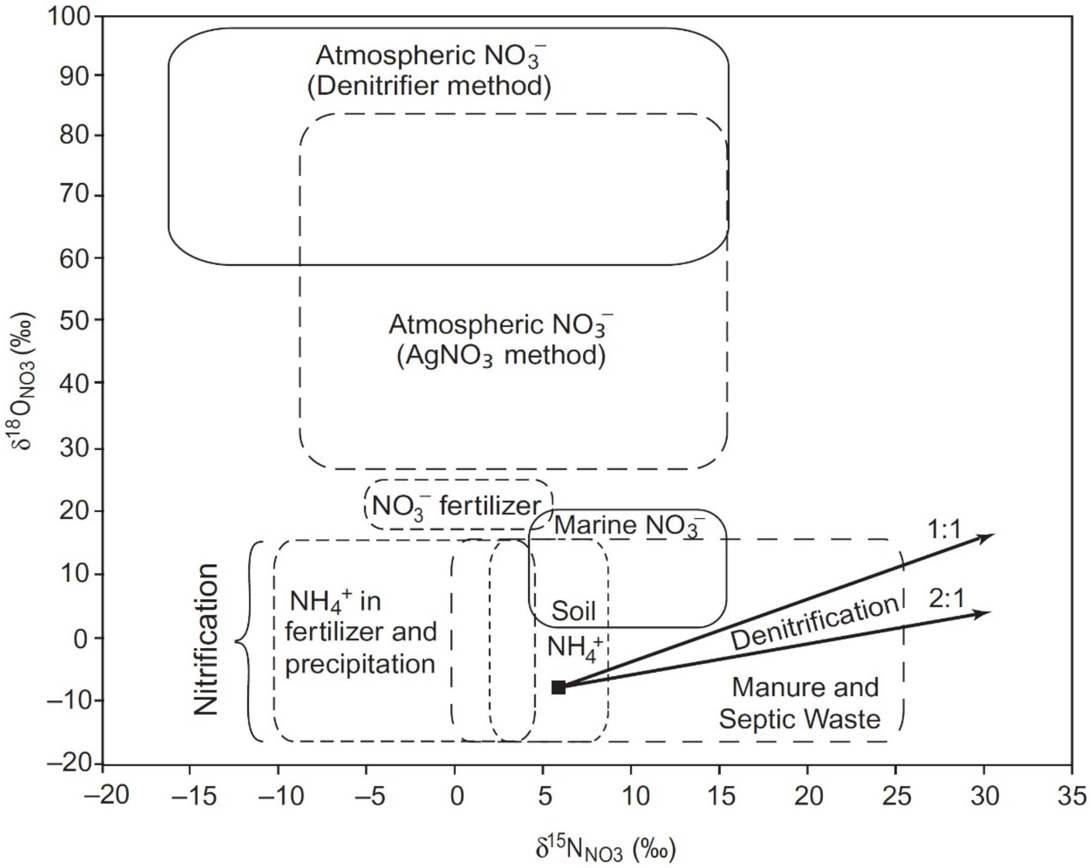


Figure 8: Ranges of nitrate isotopic composition for deferent nitrate sources (Kendall et al., 2007)

2.6. Tritium for recent recharge assessment:

The radioactive isotope of hydrogen Tritium "^{3}H" can be used for tracing recent groundwater recharges based on its relative geochemical stability (Hem, 1985)(Kendall and Doctor, 2003). Tritium content has increased dramatically in the atmosphere since the testing of nuclear bombs in 1952. After 1963, tritium rate in the atmosphere has declined due to its decay, precipitation and the termination of atmospheric nuclear testing. Tritium has a half-life of approximately 12.3 years and usually expressed in tritium units (TU) (C. W. Fetter, 2014; Clark and Fritz, 1997). Approximate recharge date of groundwater can simply be determined by correlating the measured tritium concentrations in the groundwater to the recorded tritium content in the atmosphere since 1952.

CHAPTER 3

Methodology

This study had three phases: hydrogeological field investigations, laboratory analysis, and data integration and interpretation. Figure (9) shows a flowchart that illustrates a summary of individual tasks and methods used in this study, which are discussed briefly in the following paragraphs:

3.1. Hydrogeological Field investigations:

In this study, we conducted three field trips to Al-Kharj area, central Saudi Arabia. The first visit to the study area was a reconnaissance field trip on May 2018. Fourteen “14” groundwater samples and seventeen “17” outcrop rocks samples were collected in this field trip. As expected, the groundwater samples have shown high nitrate concentrations after laboratory analysis. Later, we conducted two more visits to collect more samples.

3.1.1 Groundwater:

The studied groundwater was collected from thirty-four (34) wells tapping Wasia Aquifer in Al-Kharj area from May 2018 to January 2019 (Fig. 10). Four samples (1 liter each) from each well were picked in polyethylene bottles for nitrate isotopes, tritium, ionic concentrations, and trace metals analysis (Fig. 11). The sampled wells were mainly used for irrigation and cattle watering purposes. The polyethylene bottles were washed three times with deionized water before sampling to avoid contamination. The wells were purged for almost one hour (more than five times the well’s volume) before sampling to collect fresh and representative samples.

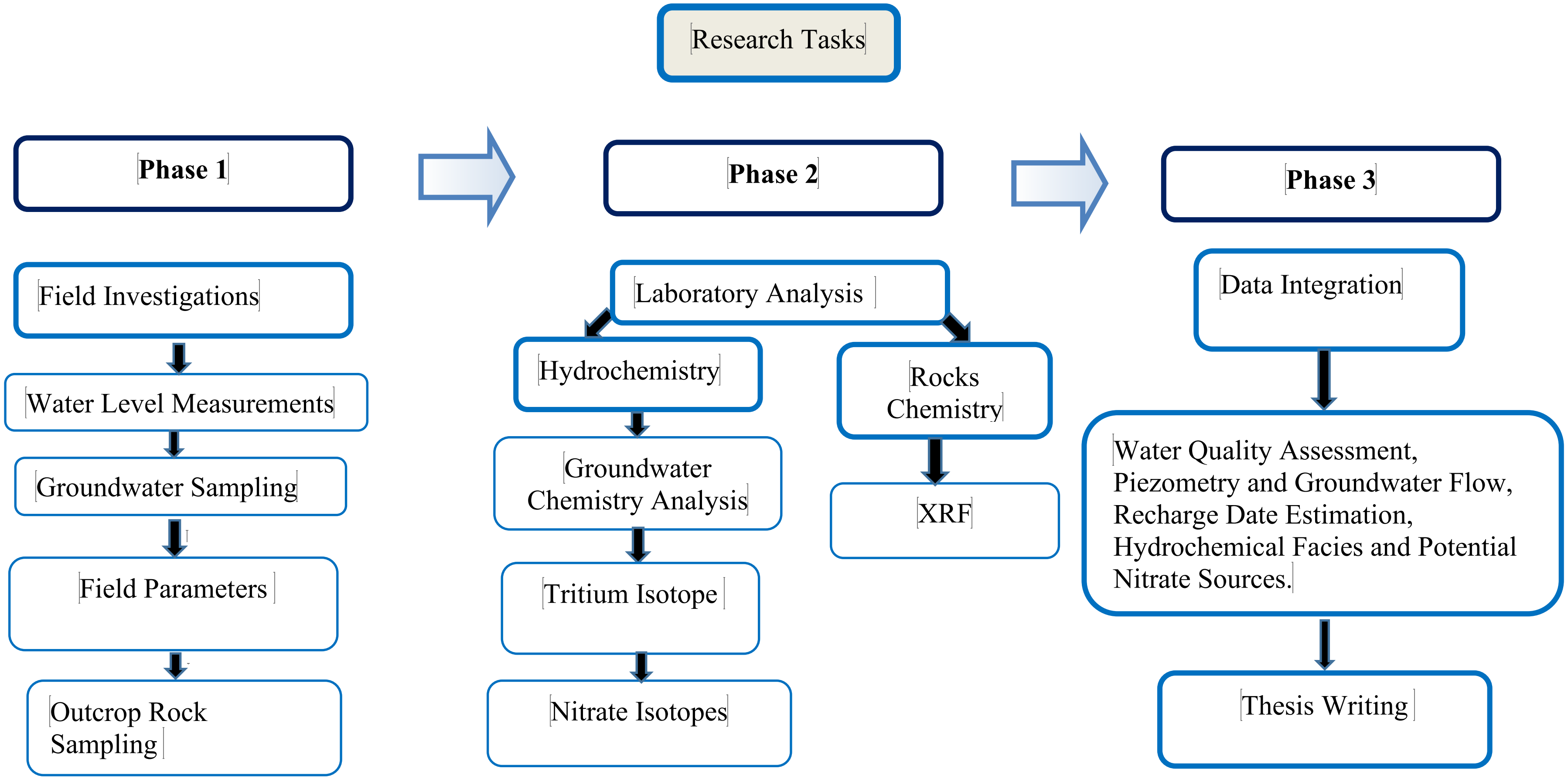


Figure 9 : Flow chart showing the tasks and methods of the study

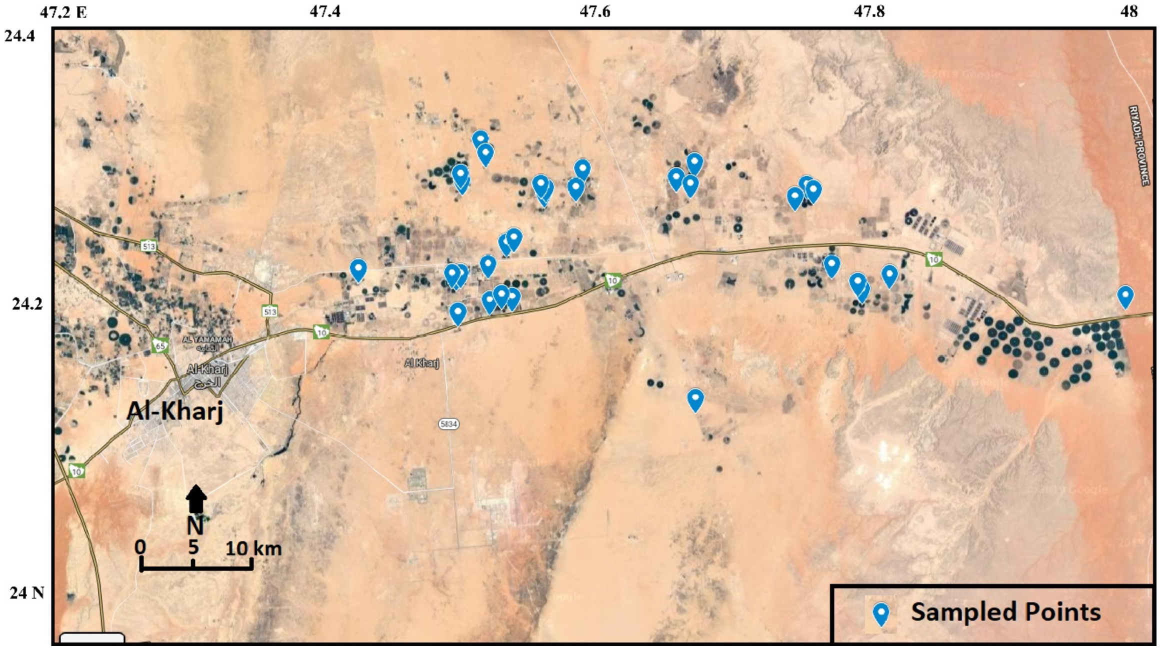


Figure 10: Google map showing the locations of the sampled wells in the study area.

Water-level, pH, EC, and temperature were measured in-situ using water level meter and multi-parameter meter (Hanna HI 9828), respectively.Samples were filtered (0.45 µm) to decrease the groundwater microbial activity and then kept in a cooling box below 4° C for ions concentrations, trace elements, nitrate isotopes, and tritium analysis. HNO_3 is added to samples of the trace metals concentrations analysis for two purposes. First, to reduce pH <2 at the time of sample collection. When pH <2, precipitation, adsorption to container wall and microbial degradation are minimized. Though any acid will serve the purpose, HNO_3 is preferred because of its oxidizing nature. Secondly, adding HNO_3 converts metal ions into their nitrate salts, which are highly soluble.

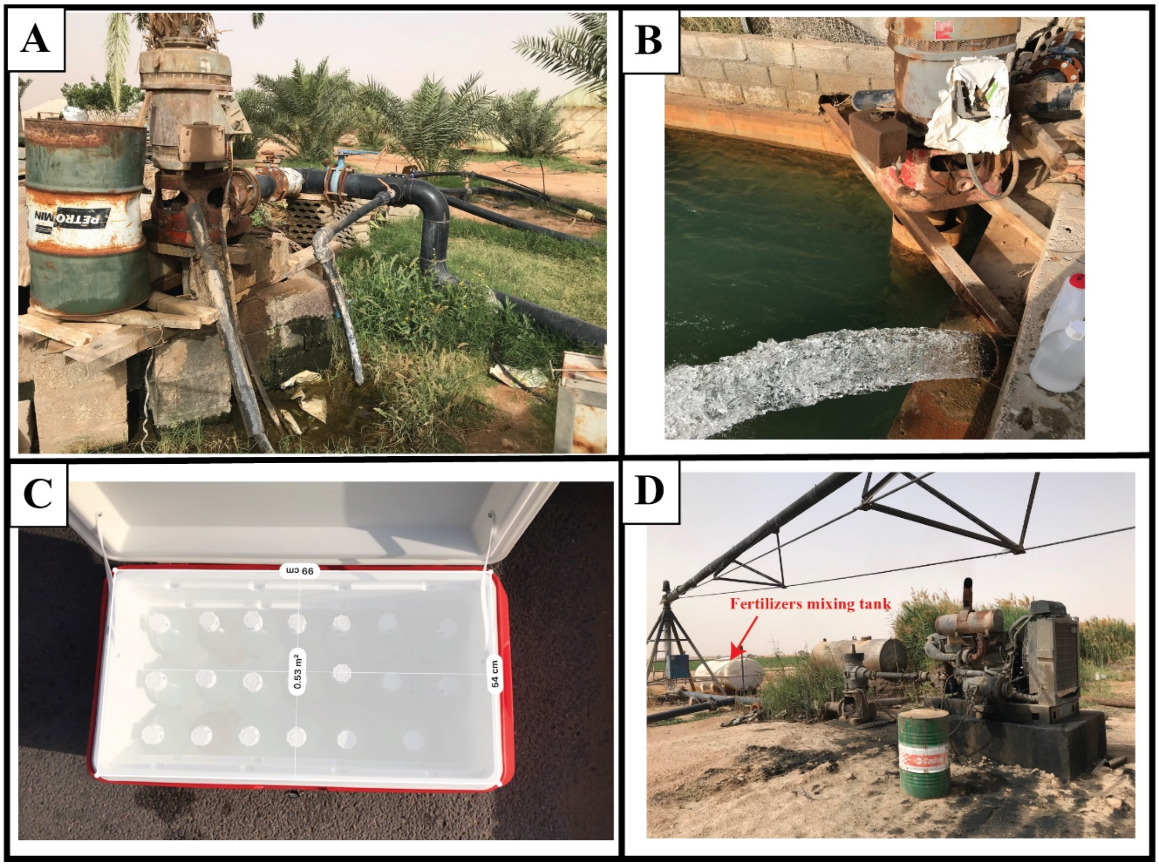


Figure 11: A) Collecting groundwater samples from irrigation wells in Al-Kharj area. B) Purging water from the well for almost one hour to avoid sampling stagnant water. C) Preserving the samples in the field in a cooling box and adding ice cubes to keep it below 4° C. D) Fertilizers mixing tanks near the well.

3.1.2 Outcrop:

The geological field investigations of the Wasia outcrop have started with looking for the best exposure of the Group on the study area. Topographic map was used to locate the targeted outcrops. Description of the composition, color, texture, thicknesses, and sedimentary structures are included in the outcrop description. Global Positioning System (GPS) was used for determining the position of the described profiles. Geological hammer for getting fresh rock samples, while meter tape was used for measuring beds thickness.

The rocks sampling approach depended on bed thicknesses. For thick beds (more than 30 cm), one sample every 30 cm was taken. On the other hand, for thinner beds (less than 30 cm), the single sample was considered representative. This strategy was to ensure the coverage of the full outcrop for subsequent analysis.

3.2. Laboratory Analysis:

The laboratory analysis is divided into two parts: groundwater analysis and rocks analysis.

3.2.1 Groundwater :

Groundwater analysis was conducted in the Environmental and Hydrology Laboratory at King Fahd University of Petroleum and Minerals (KFUPM). Ionic concentrations in mg/l were measured using Ion Chromatograph Dionex ICS-6000 (IC) using the EPA 9056A standard method including Sodium (Na^+), Magnesium (Mg^{2+}), Potassium (K^+), Calcium (Ca^{2+}), Chloride (Cl^-), Fluoride (F-), Nitrite (NO_2^-), Bromide (Br), Phosphate (PO_4^{3-}), Nitrate (NO_3^-), and Sulphate (SO_4^{2-}). Total Dissolved Solids (TDS) concentration was measured by the gravimetric method. Bicarbonates (HCO_3^-) were measured using the titration method. Inductively coupled plasma mass spectrometry iCAP RQ ICP-MS with EPA 6020A method was used to measure trace metals in µg/l.

Isotopes analysis were conducted at Environmental Isotope Laboratory, University of Waterloo, Ontario, Canada (^3H, $^{15}N–NO_3$ and $^{18}O–NO_3$). For nitrate isotopes, NO_3^- is converted to NO_2^- using a cadmium catalyst then chemically converted to N_2O which is then analyzed on a Trace Gas - GVI IsoPrime-IRMS (TG-IRMS). Tritium measurements were conducted using liquid scintillation counting (LSC) technique. To higher the precision and lower the limit of detection, samples were counted after being enriched 15 times by electrolysis. This process gives a detection limit of 0.8 ± 0.8 TU.

3.2.2 Rock samples:

For rocks analysis, X-ray Fluorescence Spectrometry (XRF) technique was used on the finely grained rock powder for getting the elemental rock chemical composition. M4 Tornado, Bruker µXRF was used at 50 kV and 200 µA.

3.3. Data Analysis:

Ionic concentrations analysis results were verified by computing ion balance errors for each sample using the following equation (Appelo and Postma, 1994):

$$Ion\ balance\ error = \frac{\sum Cations - \sum Anions}{\sum Cations + \sum Anions} \times 100$$

All parameters were calculated in meq/l. The results show that 85% of the samples fall within the permissible range (± 3).

Hydrochemical facies and ionic relationships were discussed using two variables plots and Piper's diagram (Piper, 1944). Using the groundwater of Wasia aquifer for drinking was assessed based on the Water Quality Index (WQI) and by comparing the results to international and local water quality standards. Salinity hazard (EC), Magnesium Ratio (MR), sodium percent (Na%), Sodium Adsorption Ratio (SAR), Corrosivity Ratio (CR), Permeability Index (PI), Total Hardness (TH), and Kelly's Ratio (KR) were calculated to evaluate the suitability of the sampled groundwater for agricultural uses.

Surfer 14, RockWorks 16, Aquachem 4.0, Microsoft Excel 2013, Adobe Illustrator CC 2018 and OriginPro 2016 were the main software for processing and plotting the data, and for drawing the maps.

3.4. Statistical Analysis:

Statistical analyses including correlation, factor analysis, and cluster analysis were performed to recognize the relationship between hydrochemical constituents, to define groups of clusters that show similar characteristics, and identify the chemical parameters that were responsible for most of the data variability.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Hydrogeology and Hydrochemical classification

A fall in the groundwater level has been noticed in the study area compared to Zaidi et al. (2016) study in 2010 as shown in figure (12). This drop ranges between 0 m to 15 m where over-extraction in the city centre and local farms is probably the main cause of this decline. However, a little increase in water level is also noticed in the south-eastern part of the study area, which is mainly due to the decrease of private wells in this section.

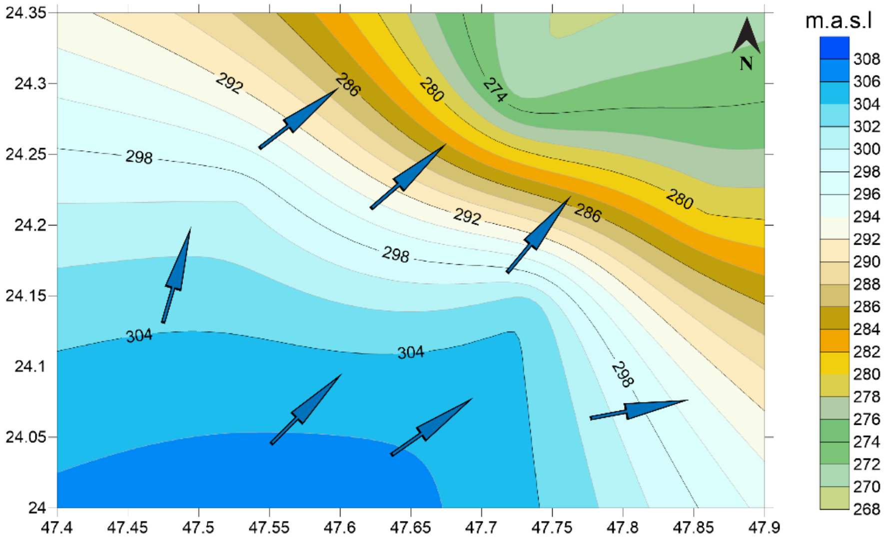


Figure 12: Map showing the water level and groundwater flow directions.

4.1.1 Hydrochemistry

Descriptive statistical analysis of the physicochemical parameters, international and local drinking water standards (WHO 2011, EPA 2012, and SASO 2000), and the percentage of the physicochemical parameters that exceeded the permissible limits by those standards are shown in table (1). The average pH value is 7.6 in the analyzed samples and ranges from

6.8 to 8.0 implying that 100% of this groundwater lies within the permissible limits by local and international standards. The temperature of the studied groundwater ranges between 27.6°C to 36.7°C. The average TDS value in these samples is 3032 mg/l with a minimum of 1100 mg/l and a maximum of 7712 mg/l. 100% of this groundwater went above the permissible TDS value for drinking by the standards. The TDS average value is however lower than the value in 2010 where it was around 3764.75 mg/l (Zaidi et al., 2016) and higher than the value in 2014 where it was almost 2000 mg/l from generally both Biyadh and Wasia aquifer in the study area (Al-Omran et al., 2016). The average measured total hardness is 1165.2 mg/l indicating that this groundwater is very hard where all the samples are above the allowable drinking standard limits. Ca^{2+} represents the dominant cation with an average of 310.1 mg/l, then Na^+ (216.1 mg/l), followed by Mg^+ (95 mg/l) and finally K^+ (5.2 mg/l). Among the anions, SO_4^{2-} (767.3 mg/l), Cl^- (483.5 mg/l) and HCO_3^- (146.5 mg/l) are the dominants. NO_3^- reached up to 395.2 mg/l in some wells within an average of 68.2 mg/l. B, Li, and Fe are the most dominant metals in this groundwater with an average of 444.6 µg/l, 24.5 µg/l and 963 µg/l respectively. Boron (B), Manganese (Mn) and Iron are the only heavy metal that exceeded the permissible limits for drinking in this groundwater.

Table 1: Descriptive statistical analysis of the physicochemical parameters, international and local drinking water standards and the percentage of the physicochemical parameters that exceeded the permissible limits by those standards in the study area.

Variable	Units	Minimum	Maximum	Median	Mean	Standard deviation (n)	WHO	EPA	SASO	Samples exceeding the WHO permissible drinking limits (%)
pH	pH unit	6.8	8.0	7.6	7.6	0.31	6.5-8.5	6.5-8.5	6.5-8.5	0
T	°C	27.6	36.9	31.8	31.8	31.7	-	-	-	0
Conductivity	µS/cm	1307.5	8672.6	2939.7	3500.2	1903.15	1500	1500	2300	94.1
TDS	mg/L	1100.0	7712.0	2476.0	3032.0	1714.63	500	500	1000	100
Total-Hardness	mg/L	449.4	2889.9	1005.1	1165.2	618.43	250	250	500	100
Na+	mg/L	66.9	551.6	193.0	216.1	114.98	200	200	-	47
K+	mg/L	1.1	11.5	5.0	5.2	2.60	12	12	-	0
Mg^{2+}	mg/L	36.7	244.2	80.2	95.0	50.09	50	50	-	88.2
Ca^{2+}	mg/L	119.4	755.5	267.6	310.1	165.68	75	75	75	100
HCO_3^-	mg/L	68.3	193.2	149.3	146.5	29.23	500	500	-	0
F-	mg/L	0.7	1.9	1.2	1.3	0.33	1.5	2	1.5	32.3
Cl-	mg/L	136.1	1837.2	322.7	483.5	430.79	250	250	250	64.7
NO_2^-	mg/L	0.0	0.2	0.0	0.0	0.06	3	1	3	0
Br-	mg/L	0.0	6.0	2.2	2.3	1.57	10	10	10	0
NO_3^-	mg/L	0.1	395.2	23.3	68.2	107.41	50	45	50	35.3
PO_4^{3-}	mg/L	0.0	8.7	0.0	0.5	1.92	-	-	-	0
SO_4^{2-}	mg/L	236.5	1625.9	682.0	767.3	397.66	250	250	250	97
Li	µg/L	0.0	86.8	0.5	24.5	31.82	-	-	-	0
B	µg/L	133.7	1426.7	390.7	444.6	254.94	500	-	-	20.5
Co	µg/L	0.1	3.6	0.5	0.8	0.79	-	-	-	0
Mn	µg/L	-1.4	88.2	2.5	8.1	16.21	50	50	100	2.9
V	µg/L	0.1	4.0	1.8	1.8	1.19	-	-	-	0
Zn	µg/L	0.0	48.8	0.0	4.5	12.02	3000	3000	5000	0
Fe	µg/L	18.3	4123.2	641.3	963.0	1128.69	300	300	300	58.8
As	µg/L	0.0	0.4	0.1	0.1	0.11	10	10	10	0
Ni	µg/L	0.0	1.7	0.3	0.4	0.49	20	100	100	0
Cu	µg/L	0.1	11.2	0.9	1.3	1.90	2000	1000	1000	0
Mo	µg/L	0.9	18.9	4.5	5.1	3.07	70	-	-	0

4.1.2 Hydrochemical Classification

Piper diagram can be used to classify different groundwater hydrochemical facies (Piper, 1944) as seen in figure (13). On the cation's triangle, all the samples from the present study lie within the no-dominant type with some samples within the Ca-dominant zones. The previous study by Zaidi et al. (2010) shows the same cation types. This concludes that, no dominant cation type in Wasia aquifer in the study area. The anion's triangle reflects that most of the studied groundwater samples fall within SO_4^{2-}-dominant and Cl+SO4 types where five samples fall inside the Cl type zone and only one inside the no-dominant type zone. However, in 2010's analysis, most of Wasia aquifer samples take place within the Cl-dominant and Cl-SO_4 types (Zaidi et al., 2016). This show that, there is an increase of SO_4^{2-} concentration since 2010 where the gypsum layers and pyrite cement within Wasia group are the main suspects (Çağatay et al., 1996; Hakimi et al., 2012; Zaidi et al., 2016). The diamond shape of piper diagram reveals that alkaline earth exceeds alkalies and strong acids surpass weak acids. However, the studied groundwater samples can be classified into three groups. Group 1 (WB02, WB03, WB05, WB06, WB07, WB13, WB14, WB17, WB18, WB19) is a Ca-SO4-Cl water type and characterized by higher salinity range (1584 - 7712 mg/l). Most of the water samples belong to the second group (WB01, WB04, WB08, WB09, WB10, WB11, WB12, WB15, WB16, WB20, WA03, WA04, WA06, WA07, WA08, WA14) which is a (Ca-SO4 water type) and has a salinity range of 1240 mg/l to 6256 mg/l. The third group (WA01, WA02, WA05, WA09, WA10, WA11, WA12, WA15) is less saline than the other two groups (1100 – 2400 mg/l) and displays a Ca-Na-SO4-Cl water type. Generally, the groundwater of Al-Kharj area is rich in Ca, Mg, SO4, and Cl (Al-Omran et al., 2016).

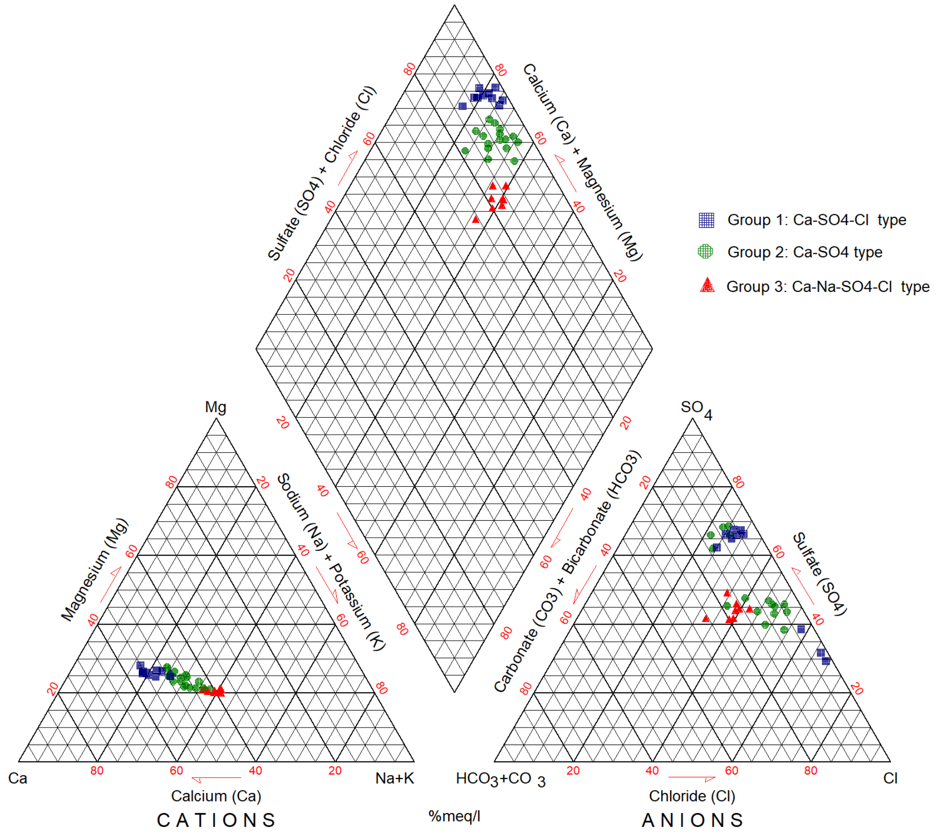


Figure 13: Hydrochemical facies classification of Wasia aquifer in the study area using Piper diagram.

4.2.Drinking and Irrigation water quality

4.2.1 Drinking-Water Quality

Water quality for human drinking uses is assessed based on Water quality index (WQI) which depends on the impact of the various hydrochemical parameters on the total water goodness (Horton, 1965). Ten parameters have been selected to calculate WQI in this study (TDS, pH, Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, NO_3^-, HCO_3^-, and SO_4^{2-}). The permissible limits for drinking water by WHO (2011) are used.

WQI was calculated in five steps. First, a weight to each parameter has been assigned out of 5 based on its relative influence on overall water quality and human health (Table 2).

Secondly, the relative weight of any parameter is assigned using the next formula:

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

In this formula, Wi is the relative weight of each parameter, wi refers to the assigned weight for every parameter while the total number of parameters is n. The assigned weight (wi) and relative weight (Wi) for every chemical parameter are shown in table (2).

Thirdly, the quality rating scale (qi) of every parameter is calculated by dividing its concentration (Ci) by its corresponding standard (Si) and then multiplied by 100 as follow:

$$qi = \frac{Ci}{Si} \times 100$$

The sub-index (SI_i) is determined in the fourth step by the formula:

$$SI_i = Wi \times qi$$

The last step involves calculating WQI using the following equation:

$$WQI = \sum_{i=1}^{n} SI_i$$

According to the resulted WQI values, the groundwater can be classified into five types describing its suitability for drinking purposes as seen in the table (3). Since 2010, the Wasia aquifer groundwater ranged between poor to unsuitable for drinking (Al-Omran et al., 2016; Zaidi et al., 2016). However, in this study, one sample is considered good for drinking whereas the rest fall within poor to unsuitable classes (Table 3).

Table 2: Assigned weights, relative weights, and WHO 2011 standards.

Variable	WHO Standards (2011)	Weight (wi)	Relative weight (Wi)
pH	6.5-8.5	**3**	0.1
TDS	500	**5**	0.166
Na^+	200	**3**	0.1
K^+	12	**1**	0.034
Mg^{2+}	50	**2**	0.066
Ca^{2+}	75	**3**	0.1
HCO_3	500	**1**	0.034
Cl^-	250	**3**	0.1
NO_3^-	50	**5**	0.166
SO_4^{2-}	250	**4**	0.134
Total		30	1

Table 3: Groundwater classification according to WQI.

WQI Range	Type of Water	Percentage of each type (%)
<50	Excellent	0
50-100	Good	2.9
100-200	Poor	47
200-300	Very Poor	26.5
>300	Unsuitable for drinking purposes	23.6

4.2.2 Irrigation Water Quality

Suitability of Wasia groundwater in Al-Karj region for agricultural uses was evaluated based on salinity hazard (EC), sodium percentage (%Na), sodium adsorption ratio (SAR), corrosivity ratio (CR), Kelly's ratio (KR), magnesium ratio (MR), total hardness and permeability index (PI). These parameters are discussed separately below and shown in table (4).

Salinity Hazard (EC)

Electrical conductivity (EC) is an important element to measure the suitability of the groundwater for crops irrigation. In this study, 26.4% of the analyzed samples are considered permissible for irrigation. Whereas, the rest is considered unsuitable (Table 4).

Sodium Adsorption Ratio (SAR)

This ratio reflects the sodium amount or alkalinity hazard and it is good to assess groundwater usability for irrigation purpose. The SAR in this study was calculated using the formula:

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

SAR refers to Sodium Adsorption Ratio, where all ion concentrations are expressed in meq/l. Groundwater with SAR less than 10 is excellent for irrigation, 10–18 is good, 18–26 is permissible, while more than 26 is considered unsuitable (Richards, 1954). All the samples fall within the excellent category in this study (Table 4).

U.S. Salinity Laboratory (USSL) diagram is used to explain the dual effect of salinity and alkalinity hazards (Richards, 1954). In this diagram, the salinity hazard is divided into C1, C2, C3, and C4 areas, while the sodium adsorption ratio is divided into S1, S2, S3, and S4 areas (Fig. 14). In this plot, all the values of the studied groundwater fall within C4-S1, C3-S1and C4-S2 which means generally that this groundwater has a very high to high salinity and medium to low alkalinity. Compared to Zaidi et al. (2016) study, the Wasia aquifer reflected a higher alkalinity ratio. Regardless of the high salinity hazard of this groundwater, it can be used for irrigation in most cases under proper use and awareness.

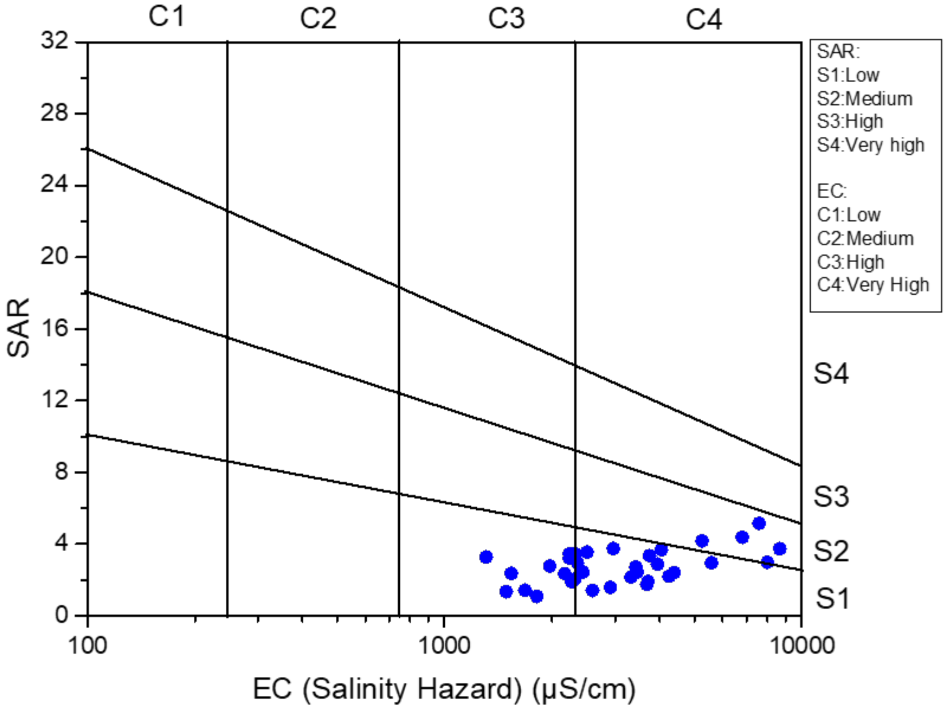


Figure 14: Classification of irrigation water salinity and alkalinity by USSL (Richard, 1954) of 34 samples from Wasia aquifer.

Sodium Percent (Na %)

Sodium concentration percentage is vastly used for determining the appropriateness of groundwater quality for irrigation (Wilcox, 1948). The sodium percent has been calculated using the following formula:

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

Where all ion concentrations are expressed in meq/l. Groundwater sample with Na% value less than 20 is considered excellent, 20–40 is good, 40–60 is still permissible, 60-80 is doubtful, while values more than 80 are assigned unsuitable for irrigation. Based on Na% values, 11.7% of the studied groundwater are classified as excellent, 79.4% are good and the rest are permissible (Table 4). Since 2010 Wasia groundwater is within the permissible zone (Zaidi et al., 2016).

Magnesium ratio (MR)

Magnesium ratio can be used to classify groundwater suitability for irrigation purpose (Paliwal, 1972). Generally, groundwater with MR less than 50% is considered suitable based on the following equation:

$$MR = \frac{Mg^{2+}}{(Mg^{2+} + Ca^{2+})} \times 100$$

Based on magnesium ratio (MR), all the samples are considered suitable for irrigation purposes (Table 4).

Corrosivity ratio (CR)

Based on corrosivity ratio (CR), groundwater can be classified as safe for transportation, when CR is less than 1 (Tripathi et al., 2012). Where all concentrations are in mg/l, CR is calculated based on:

$$CR = [\frac{\frac{Cl^-}{35.5} + 2\left(\frac{SO_4^{2-}}{96}\right)}{2\left(\frac{HCO_3 + CO_3}{100}\right)}]$$

Wasia aquifer groundwater in the study area is considered 100% corrosive based on CR (Table 4), and so carefulness is required for choosing the proper pipes for transportation.

Kelly's Ratio (KR)

It is expressed as:

$$KR = \frac{Na^+}{Ca^{2+} + Mg^{2+}}$$

Where all ion concentrations are expressed in meq/l. Groundwater with KR more than 1 is considered unsuitable for agricultural use (Richards, 1954). All Wasia aquifer groundwater in the study area is considered suitable for irrigation (Table 4).

Total Hardness

This parameter has been determined using the following formula (Todd and Mays, 1980):

$$TH\ as\ CaCO_3 = 2.5\ (Ca^{2+}) + 4.1\ (Mg^{2+})$$

TH refers to Total Hardness and calculated as $CaCo_3$ in mg/l. When TH is between 0-75 the groundwater is considered soft, 75-150 classified as mediumly hard, 150–300 as hard, while more than 300 is considered very hard. As shown in table (4), the groundwater of Wasia aquifer in the study area is classified as very hard water.

Permeability Index (PI)

The soil permeability is influenced by the continuing use of groundwater for irrigation, as it is impacted by Ca^{2+}, Mg^{2+}, $Na^{+,}$ and HCO_3^- ratios in the water. Doneen (1964) used PI to assess the appropriateness of water for irrigation usage. PI was determined in this study by the as follows:

$$PI = \frac{Na + \sqrt{HCO_3}}{Ca + Mg + Na} \times 100$$

Where all parameters are calculated in meq/l. When PI is less than 25% the groundwater is regarded suitable for irrigation and when it is more than 25% it is graded as unsuitable for irrigation. In this study, 82.4% of the analyzed waters fell within the unsuitable classification according to PI (Table 4).

Table 4: Classification of the studied groundwater for irrigation uses.

Parameters	Range	Classification	Samples (%)
Salinity Hazard (EC)	<250	Excellent	0
	250-750	Good	0
	750-2250	Permissible	26.4
	>2250	Unsuitable	73.6
Alkalinity Hazard (SAR)	<10	Excellent	100
	10-18	Good	0
	18-26	Permissible	0
	>26	Unsuitable	0
Sodium Percent (%Na)	<20	Excellent	11.7
	20-40	Good	79.4

	40-60	Permissible	8.8
	60-80	Doubtful	0
	>80	Unsuitable	0
Kelly’s Ratio (KR)	<1	Suitable	100
	>1	Unsuitable	0
Permeability Index (PI)	<25	Suitable	17.6
	>25	Unsuitable	82.4
Total Hazard (TH)	0-75	Soft	0
	75-150	Moderate	0
	150-300	Hard	0
	>300	Very Hard	100
Magnesium Ratio (MR)	<50	Suitable	100
	>50	Unsuitable	0
Corrosivity Ratio (CR)	<1	Safe	0
	>1	Unsafe	100

4.3.Statistical Analysis

Statistical analyses on the physiochemical parameters including correlation, cluster analysis, and factor analysis were made to describe the relationship between different hydrochemical constituents, to define groups of clusters that show comparable characteristics, and recognize the chemical parameters that oversaw most of the data variability.

4.3.1 Correlation Analysis

The mean values of physicochemical variables (pH, Temperature, EC, TDS, Total Hardness, Na^+, Ca^{2+}, Mg^{2+}, K^+, F^-, HCO_3^-, Cl^-, NO_2^-, Br^-, SO_4^{2-}, PO_4^{3-} and NO_3^-) were calculated and plotted in correlation matrix as shown in Table (5). Using Person’s correlation coefficient (r), the relationship between different parameters can be categorized as strong when $r > 0.7$. moderate $r = 0.5\text{-}0.7$, and weak when $r < 0.5$. A noticeable strong relationship between TDS and conductivity is detected reflecting that the dissolved solids are the mean contributors the EC values in Wasia aquifer. A strong relationship is spotted between TDS and Na^+, Mg^{2+}, Ca^{2+}, F^-, NO_3^-, SO_4^{2-} Cl^-, and Br^- revealing that those ions are the main contributors to the high TDS values. The influence of the gypsum weathering can be noticed from the strong relationship between Ca^{2+} and SO_4^{2-}. Halite weathering is also expected as the strong correlation between Na^+ and Cl^-.

Table 5: Correlation matrix of physicochemical parameters of Wasia aquifer groundwater in the study area.

Variables	pH	T	Conductivity	TDS	Total-Hardness	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	F-	Cl-	NO_2^-	Br-	NO_3^-	PO_4^{3-}	SO_4^{2-}
pH	1																
T	-0.289	1															
Conductivity	0.051	-0.338	1														
TDS	0.023	-0.374	**0.993**	1													
Total-Hardness	0.060	-0.483	**0.965**	**0.980**	1												
Na+	-0.262	-0.194	**0.871**	**0.855**	**0.794**	1											
K+	-0.371	0.208	0.169	0.147	0.125	0.455	1										
Mg^{2+}	0.071	-0.470	**0.972**	**0.985**	**0.996**	**0.805**	0.121	1									
Ca^{2+}	0.055	-0.488	**0.959**	**0.976**	**0.999**	**0.786**	0.127	**0.992**	1								
HCO_3^-	-0.142	0.331	-0.235	-0.322	-0.390	-0.013	0.213	-0.383	-0.392	1							
F-	0.252	-0.693	0.686	**0.717**	**0.763**	0.508	-0.156	**0.753**	**0.765**	-0.396	1						
Cl-	0.060	-0.171	**0.959**	**0.955**	**0.902**	**0.811**	0.128	0.915	**0.892**	-0.324	0.582	1					
NO_2^-	-0.351	0.246	-0.344	-0.338	-0.338	-0.134	0.607	-0.349	-0.331	0.045	-0.501	-0.304	1				
Br-	0.117	-0.232	**0.938**	**0.931**	**0.881**	**0.779**	0.087	**0.891**	**0.875**	-0.250	0.654	**0.940**	-0.351	1			
NO_3^-	0.089	-0.153	**0.862**	**0.856**	**0.795**	0.675	0.043	**0.816**	**0.783**	-0.333	0.545	**0.924**	-0.222	**0.879**	1		
PO_4^{3-}	-0.293	0.004	-0.160	-0.162	-0.142	-0.130	0.344	-0.154	-0.135	0.085	-0.164	-0.185	0.485	-0.206	-0.039	1	
SO_4^{2-}	0.162	**-0.737**	**0.721**	**0.734**	**0.801**	0.621	0.109	**0.794**	**0.802**	-0.193	**0.811**	0.534	-0.323	0.623	0.451	-0.083	1

4.3.2 Cluster Analysis

Groups of clusters that show similar characteristics have been defined based on dendrogram analysis as shown in figures (15) and (16). Four groups were identified. Group 1 which consists of 13 samples is characterized by lower TDS, EC, TH, and ions concentration compared to other groups. Group 2 (consists of 3 samples) characterized by higher pH and relatively high SO_4^{2-}. Group 3 is featured with its higher values. Group 4 has higher values than Group 1 though it has lower values than the other two groups (Fig. 16).

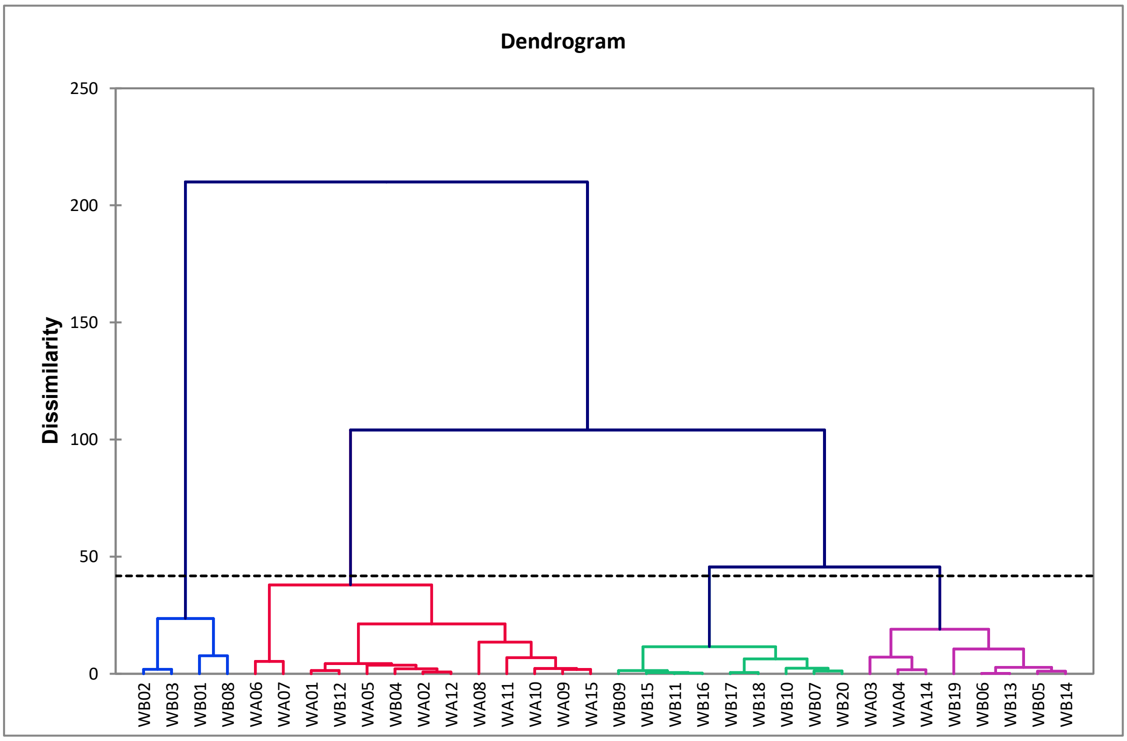


Figure 15: Dendrogram of the physiochemical parameters of 34 groundwater samples from Wasia aquifer.

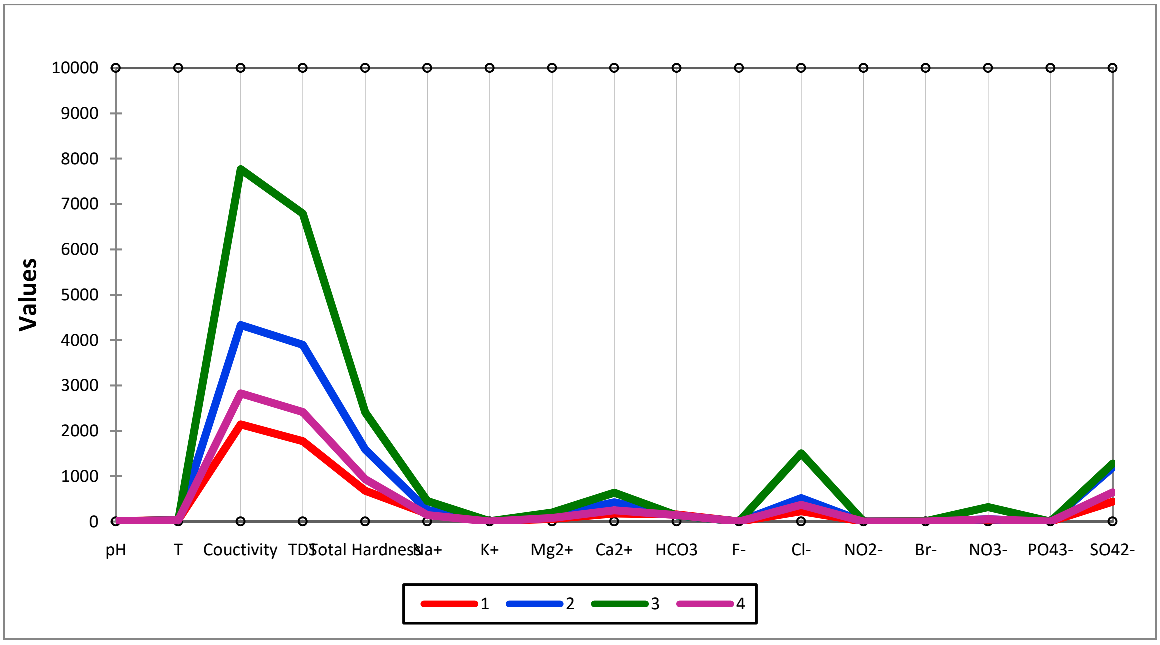


Figure 16: Line chart showing the relation between the four clustered groups based on the physiochemical parameters of the analyzed groundwater.

4.3.3 Factor Analysis

The principal components analysis (PCA) was applied onto the physiochemical parameters of the studied samples to recognize the parameters that oversaw most of the data variability. The results showed that two factors components explain 72.35% of the dataset variability as shown in figure (17). In the final factors model, factors with eigenvalue more than 1.0 were only involved (table 6)(Kaiser, 1960). Factor 1 which is responsible of 57.46% of the overall data variability, showed a significant positive loading for TDS, EC, TH, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, F^-, Br^-, SO_4^{2-}, and NO_3^- (Fig. 17-B). on the other hand, Factor 2 has a significant positive loading for K^+ and NO_2^-. As shown in Figure (17-A), the Wasia aquifer groundwater samples are grouped into four groups same as in the cluster analysis. Group 1 which consists of 13 samples lies in the negative axes of the Factor 1 and show no clear significance of any parameter except the NO_2^-. Group 2 which consists of the three samples, falls in the positive axis of Factor 1 indicating that hydrochemistry of this group is most probably controlled by the dissolution of calcite and evaporites. The third group “Group 3”, falls in the positive axis of Factor 1 and affected by most of the parameters except K$^+$ and NO_2. The samples of the last group lie in the negative axes of both factors and show no clear contribution of specific parameters in the water chemistry.

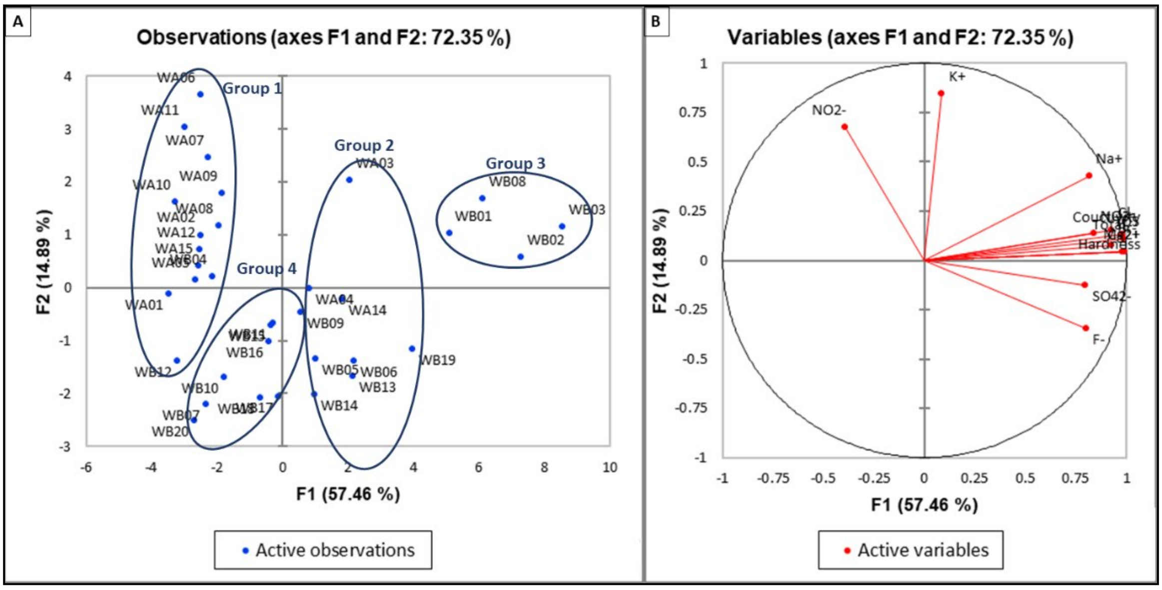


Figure 17: Distribution of the studied samples (A), and its physicochemical parameters (B) as defined by factor analysis.

4.3.4 Spatial Distribution Analysis

Spatial distribution maps have been constructed using Surfer 14 software in order to assess the lateral variations in the hydrochemical characteristics of the analyzed groundwater (Fig. 18). Generally, the TDS, Na$^+$, Cl$^-$, Ca^{2+}, Mg^{2+}, and NO_3 (Fig. 18-A, B, C, D, G, H) are increasing eastward away from the outcrop which makes sense as it's with the direction of the regional groundwater flow. In the SO_4^{2-} distribution map (Fig. 18-E), Wasia aquifer in the study area is showing high sulfate concentrations in the western part (>1400 mg/l), whereas it decreases toward the east direction (<

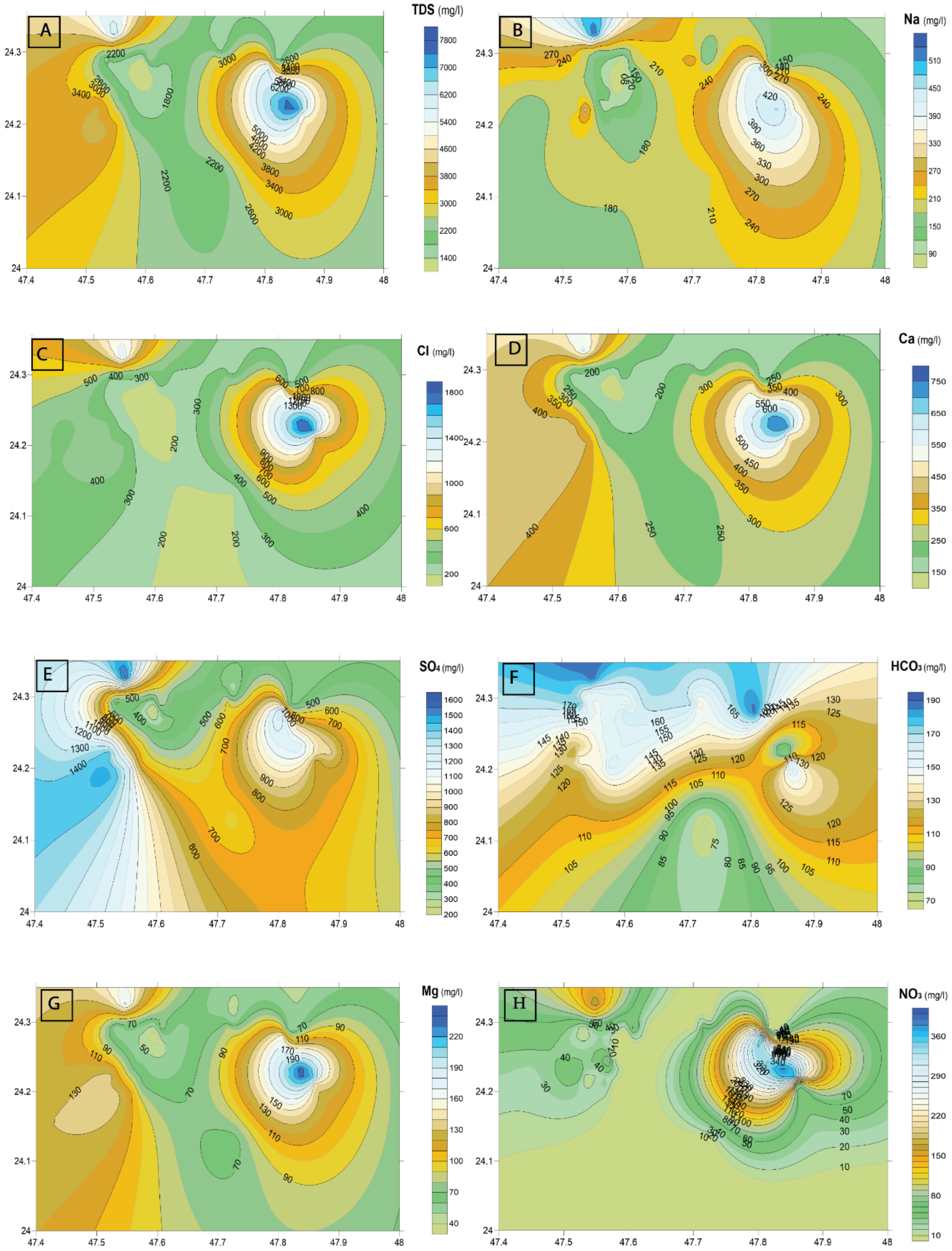


Figure 18: Spatial distribution of TDS, Na^+, Cl^-, Ca^{2+}, SO_4^{2-}, HCO_3^- , Mg^{2+} and NO_3^- in the groundwater of Wasia aquifer in the study area.

200mg/l). In contrast, the HCO_3^- is showing a different trend as it increases toward the north and the northwest directions while it decreases southward (Fig. 18-F).

4.4.Tritium Isotopes

As no detailed record of tritium concentrations exists for precipitation in Saudi Arabia, reference values for the present abundance of ^{3}H data are not available. This means we can only decide whether a recharge has occurred after 1952 or not.

^{3}H concentrations below 0.8 TU could imply the absence of recent recharge with a residence time beyond the ‘50s or ‘60s. More likely is the occurred mixture of a recent surface water source with fossil groundwater.

The samples “WB03” and “WB08” with highest tritium concentrations (0.98 TU and 0.82 TU, respectively, Table 6) are characterized by relatively high salinity (7712 and 6256 mg/l), which may be due to the influx of higher saline irrigation water used in this area. Moreover, these two samples showed high boron concentrations (783 and 1427 µg/l, respectively). Which might confirm the infiltration of recent water to these two wells. As the underling Triassic Jilh aquifer has been recharged during the late Pleistocene age (Birkle, 2016), the Wasia aquifer is most likely to be recharged during the same age.

As a result, the Wasia aquifer groundwater is most likely to be of mixed origin. Samples with tritium below 0.8 TU are supposed to be fossil water that has recharged during the Late Pleistocene, while the samples “WB03” and “WB08” seem to be recharged recently.

As the applied LSC technique is limited to a detection limit to 0.8 TU, more advanced techniques like helium (^{3}He) ingrowth may be needed to reach higher precision. The helium ingrowth method depends on measuring helium concentrations that decay from tritium after storing the groundwater sample for several months and then normalized to a reference date to reconstruct the tritium content. This method can reach a detection limit of up to 0.005 TU (Stadler et al., 2008).

4.5. Possible sources of nitrate

Stable isotopes of nitrate of selected samples from the groundwater of the Wasia aquifer in the study area are summarized in table (6). From the analysis of the studied groundwater, three main sources were given as potential sources of nitrate contamination. This includes (i) nitrogen inputs by precipitation/ atmospheric deposition (ii) nitrogen contribution from ammonium fertilizers, and (iii) manures or animal wastes. Figure (19) illustrates the possible nitrate sources in the study area.

4.5.1 Fertilizers

As the study area is dominated by agricultural use, several fertilizer types were added to the land. It is critical to differentiate between synthetic nitrate fertilizers by industrial fixation of atmospheric nitrogen, and nitrate resulting from ammonium fertilizers. The former generally have δ15N range of -5 to +8‰, and high δ18O of +17 to +25‰ as it is derived from atmospheric oxygen. While the latter has a wider range of δ15N due to its various sources (-10 to +5‰), and a lower range of δ18O (-15 to +15‰) (Kendall et al., 2007).

The investigation on the studied groundwater suggested that synthetic fertilizers are the main contaminator to this groundwater. This is inferred from the values of the δ15N and δ18O of nitrate ion these samples (Fig. 20). Where ammonium fertilizers generally have a lower range of δ18O, 63% of the studied samples fall within the area of the isotopic composition of synthetic nitrate fertilizers (-5.3 to +7.99‰, and +16.74 to +25.8‰ for δ15N and δ18O, respectively).

Groundwater samples with high δ18O values are mainly distributed in the north-eastern part of the study area which is dominated by crop irrigation (Figs. 22).

This is also supported by the tritium measurements. Two of the potential fertilizers-contaminated samples have relatively high tritium concentrations which suggest the infiltration of recent water to this aquifer.

Table 6: Stable isotopes of nitrate and tritium measurements for selected samples from the groundwater of the Wasia aquifer in the study area.

Well	E^3H	$\delta^{15}N$	$\delta^{18}O$
Units	± 0.8 T.U.	AIR ± 0.5‰	VSMOW ± 1‰
WB01	<0.8	5.89	25.81
WB02	<0.8	7.12	24.23
WB03	0.98	5.77	24.61
WB04	<0.8	-	-
WB05	<0.8	10.68	11.20
WB06	<0.8	6.60	9.51
WB07	<0.8	6.99	16.74
WB08	0.82	7.55	21.89
WB09	<0.8	6.54	23.43
WB10	<0.8	6.95	19.87
WB11	<0.8	6.96	17.39
WB12	<0.8	9.69	13.46
WB13	<0.8	10.82	13.49
WB14	<0.8	9.92	12.97
WB15	<0.8	5.51	18.49
WB16	<0.8	5.92	20.61
WB17	<0.8	7.88	13.18
WB18	<0.8	8.46	8.69
WB19	<0.8	5.72	21.73
WB20	<0.8	7.86	17.80

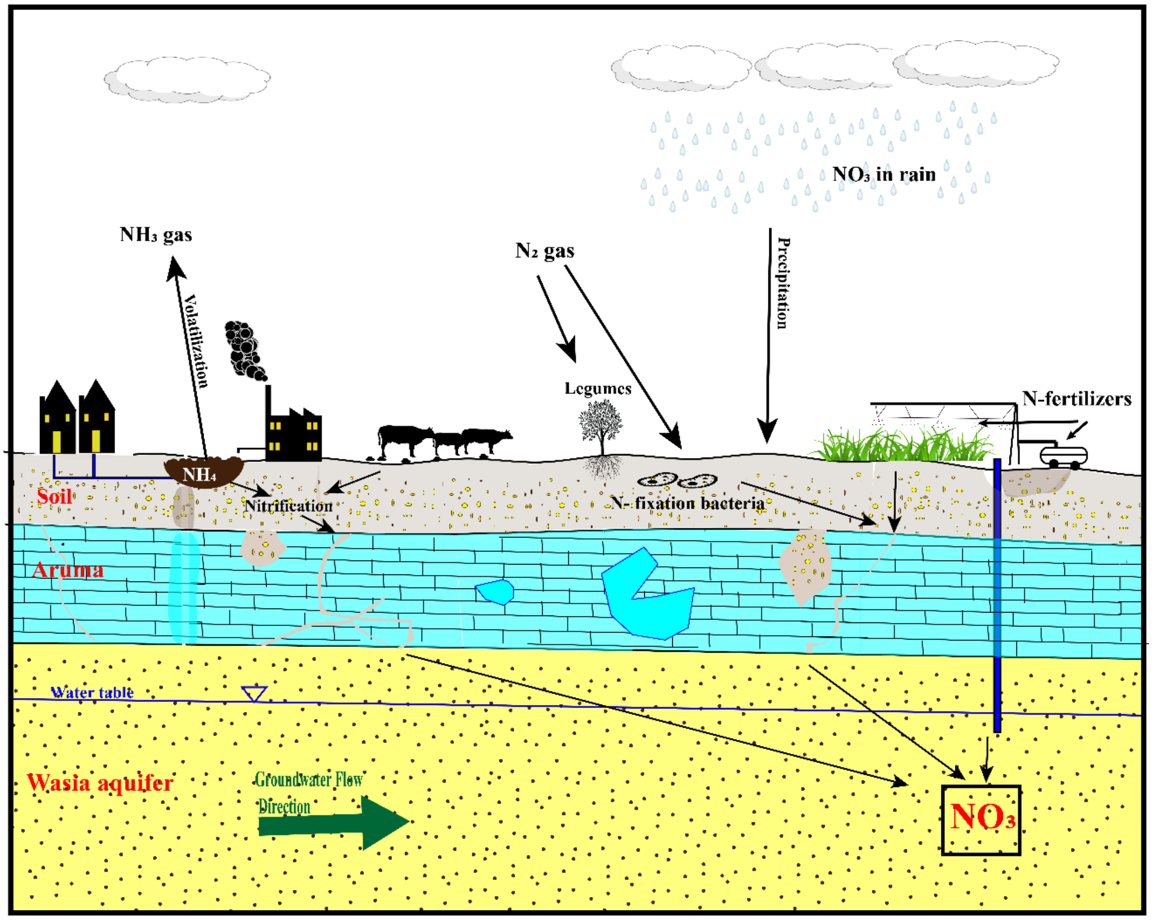


Figure 19: Simplified figure of the potential sources of nitrate in Al-Kharj area.

4.5.2 Atmospheric deposition

Rainwater analysis in the study region showed average values of NO_3- (4.26 mg/l) and Cl- (17.39 mg/l; Alabdula'aly and Khan, 2000). With a precipitation rate of 75 mm/a (GTZ/DCO, 2013), this would deposit around 3.2 kg/ha of NO_3- annually, which possibly be taken by vegetation, soil bacteria or might percolate to the water table. With regard to mass balance, this calculated nitrate amounts alone do not account for the entire nitrate as calculated in section 4.4. With a recharge of only 5 to 10 mm/a (GTZ/DCO, 2013) and high evaporation rates (Almazroui, 2011), evaporation is anticipated to play a major role in nitrate accumulation in this aquifer. Considering only evaporation, and bearing in mind recharge rates as above, and assuming 75 mm/a as average rainfall in this area (GTZ/DCO, 2013), 86.67-93.34% of evaporation is required to decrease the precipitated rainwater quantity to the recharge amounts. If only Cl- is considered as a measure for the rate of evaporation, the Cl- concentrations in this groundwater (136.1-1837.2 mg/l) could result from 87.2-99% evaporation of the rainwater that contains 17.39 mg/l of Cl-. 33-426 mg/l of nitrate might be resulted by this rate of evaporation. Which may justify the measured nitrate concentrations in the studied samples. However, in this case (when evaporation is the only contributor of Cl- and NO3- enrichments), a linear relationship between Cl- and NO_3- concentrations is expected. A strong correlation between Cl- and NO_3 was found (Fig. 21). This may indicate that evaporation played a major role to elevate the studied groundwater with nitrate.

On the other hand, according to the stable isotopes of nitrate ($^{15}N–NO_3$ and $^{18}O–NO_3$) in the studied groundwater, 58% of these nitrate concentrations are related to atmospheric deposition (Fig. 20).

Atmospheric deposition is apparently a major contributor to the elevated nitrate concentrations in the Wasia aquifer, though, reduced amounts by vegetation, fixation bacteria, and other factors cannot be predicted.

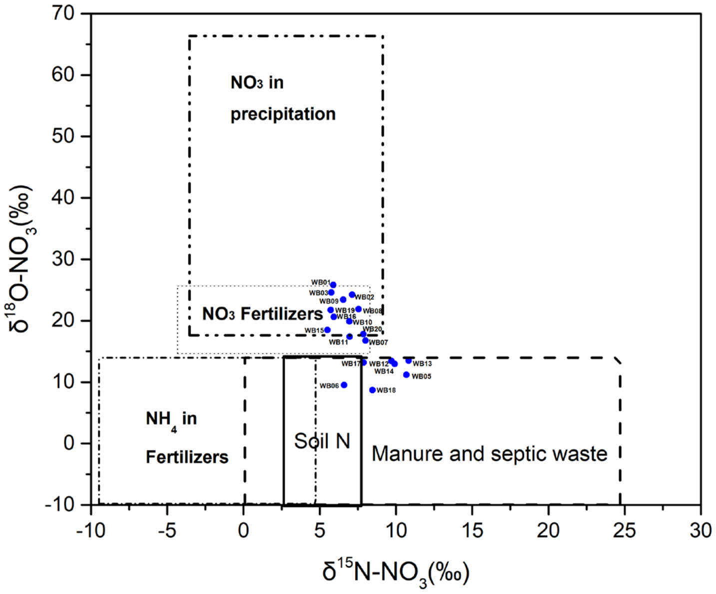


Figure 20: Relationship between δ15N and δ18O isotopes of nitrate in the studied samples. Ranges of isotope compositions for the nitrate sources are adapted from Kendall et al. (2007).

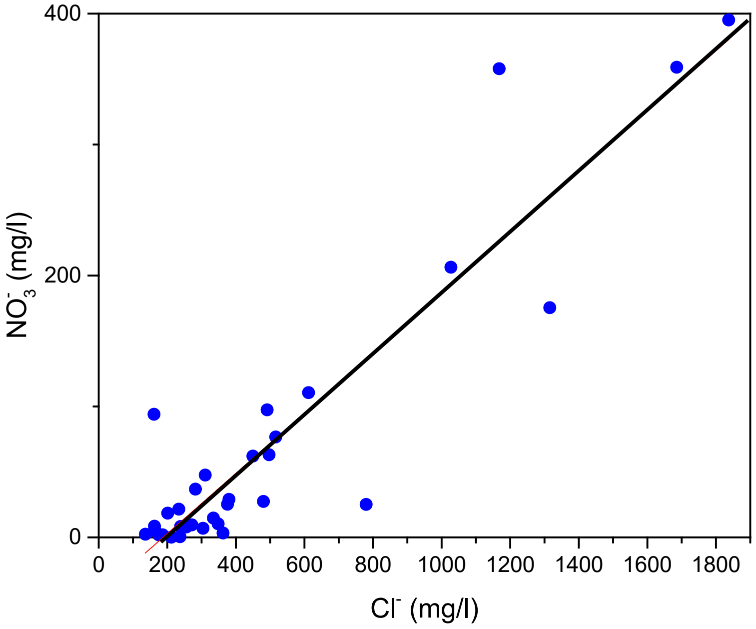


Figure 21: NO_3^- vs Cl^- for 34 groundwater samples from Al-Kharj area.

4.5.3 Nitrogen from contamination by animal and human wastes (manures)

The dominant nitrogen compound in the animal and human wastes is urea. The enzyme urease hydrolyzes the urea to ammonium and then to nitrate in the vadose zone where it can percolate down to the water table (Stadler et al., 2008). The hydrolysis of urea results in a momentary increase in pH that helps the transformation to NH_3 gas, which is simply released to the atmosphere.

The studied groundwater samples have no or undetectable concentrations of ammonia. Depending on the availability of oxygen, NH_4^+ may be oxidized and detected only as NO_3^-. Hence, N input as an animal or human waste may not be detected as ammonium.

The presence of iron in the groundwater also helps nitrifying bacteria in ammonia oxidization to nitrite and then to nitrate (Meiklejohn, 1953; Qian et al., 2017).

Besides the elevated nitrate, groundwater affected by manures usually has high Cl- and K+ amounts (Stadler et al., 2008). While K+ is basically low (>11.5 mg/l) in the studied groundwater, a strong correlation between Cl- and NO_3- was found as mentioned earlier.

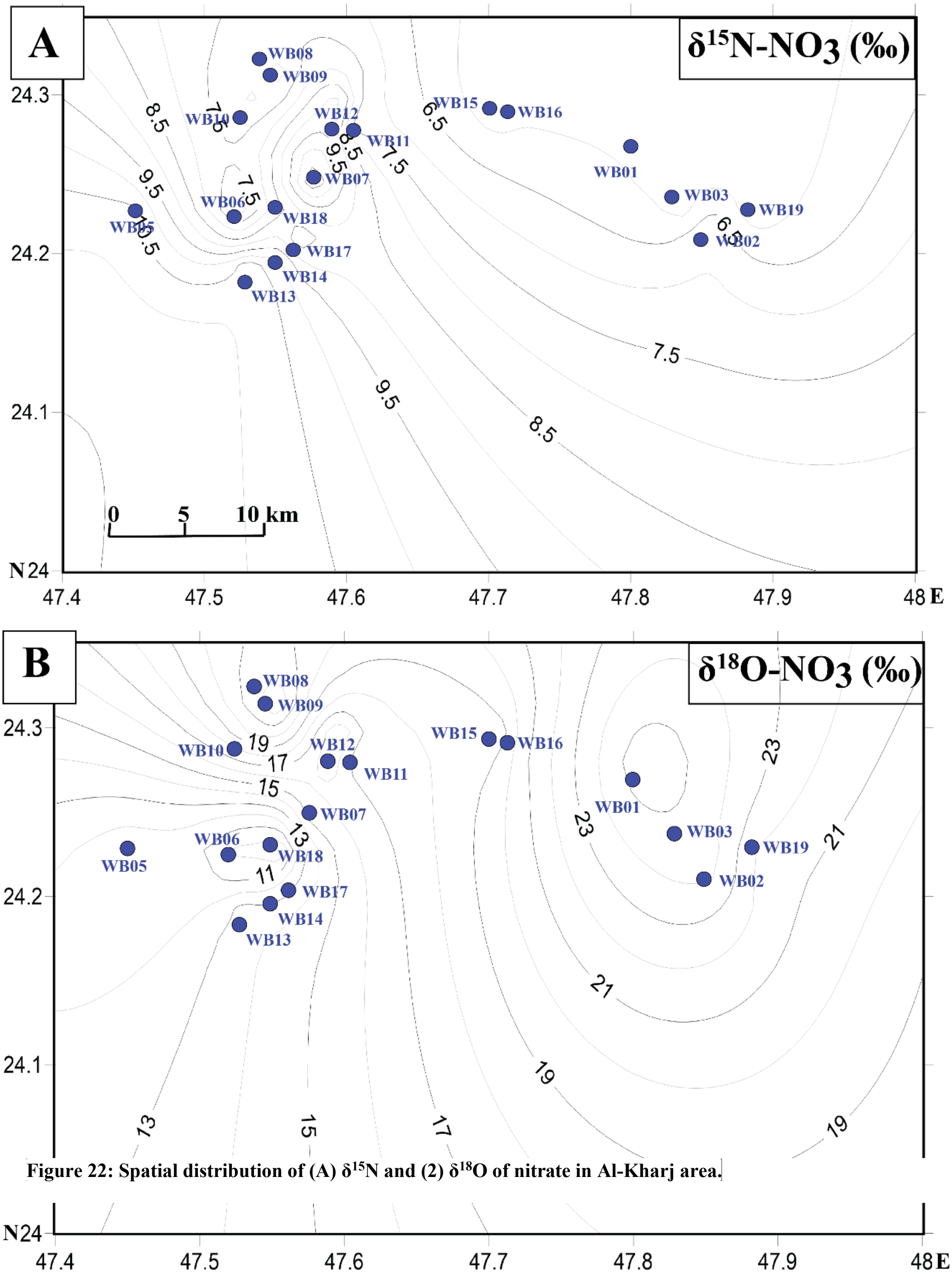


Figure 22: Spatial distribution of (A) δ^{15}N and (2) δ^{18}O of nitrate in Al-Kharj area.

Boron (B) occurs naturally in groundwater. However high levels of boron may indicate wastewater infiltration to the groundwater as it is used in soaps and for several industries. Seven samples (WB01, WB03, WB08, WB09, WB11, WB13, and WB19) from the studied groundwater exceeded the recommended level (0.5 mg/l by WHO 2011 standards).

The effect of manure and wastewater on the studied samples is confirmed by the isotopic composition of nitrate in the groundwater. About 35% of the samples (WB05, WB06, WB12, WB13, WB14, WB17, WB18) fall within the manure area as shown in Figure (20).

Spatially, these samples are distributed in the south-western part of the study area, close to the city center, have a considerable number of dairies and about only a 3 kms from Al-Kharj wastewater treatment plant.

4.5.4 Nitrogen from rocks

Elevated nitrogen in rocks has been measured in igneous, metamorphic, and especially in sedimentary deposits and metasediments (Holloway and Dahlgren, 2002). Nitrogen is easily weathered under surface conditions and it can be discharged as a solution in the saturated zone due to the high solubility of nitrate salts (Stadler et al., 2008). The Wasia Group, which represents the main aquifer in Al-Kharj area, generally consists of sandstone, conglomerate and shalely layers (Keller et al., 2019; Le Nindre et al., 2008; Powers et al., 1966). Analysis of outcrop rock samples from the Wasia group showed no or undetectable nitrogen content by x-ray fluorescence (XRF)(Fig. 23).

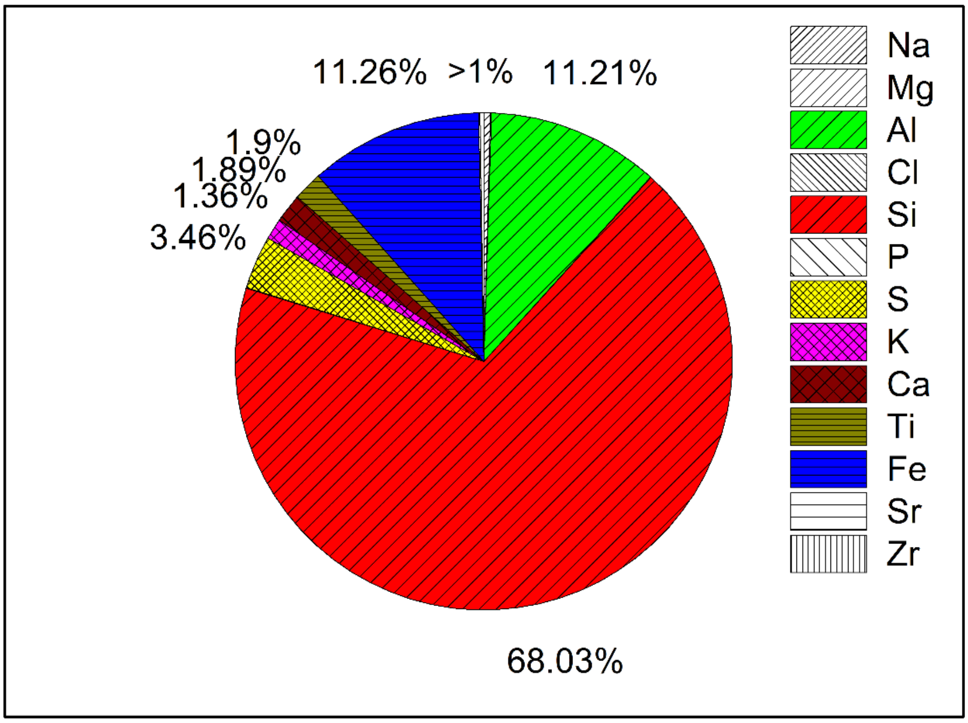


Figure 23: X-ray fluorescence of the elemental data concentrations [in %] from a Wasia outcrop in the Al-Kharj area.

4.5.5 Soil nitrogen

Nitrogen may exist naturally in the soil as some symbiotic soil bacteria do fix atmospheric nitrogen. Nitrogen also occurs in plants like the legume family (Keeney and Olson, 1986). These processes take part in the nitrogen cycle. This accumulation of nitrate in the unsaturated zone can form a large nitrate pool which may infiltrate to the saturation zone during recharge periods. Although one of the studied samples (WB06) lie within the soil nitrogen area (Fig. 5), it is less likely that soil nitrogen has contributed to the nitrogen content in the studied samples. This sample has possibly been affected by manure and waste-water nitrogen.

4.6. Estimating N Fluxes

In order to evaluate whether the rates of nitrate percolation to the aquifer and recharge amounts fit to justify present nitrate content in the studied samples, the estimated nitrate fluxes were compared to a calculated aquifer exchange time. Considering an average thickness of 100 m, a 30% effective porosity, and 5 to 10 mm/a recharge rate for the aquifer in the study area (GTZ/DCO, 2013), a direct water budget calculation gives 3000 to 6000 years needed for water exchange assuming steady-state conditions. The average nitrate concentration measured in the groundwater of this study (68.2 mg/l) would give around 20000 kg/ha of overall nitrate at 100 m aquifer thickness. Based on the time required to exchange the groundwater of the aquifer, an average 3.34 to 6.67 kg/(ha a) of nitrate flux would be required to match the overall nitrate in the aquifer.

This calculated amount cannot be explained by one source. Thus, synthetic fertilizers, atmospheric deposition, and wastewater together are most likely to be responsible for this nitrate concentration.

4.7. Statistical T-test and F-test

In order to evaluate whether the nitrate concentrations of the samples that related to fertilizers and atmospheric deposition are statistically different or related to the manure-related samples, we used the statistical t-test and F-test to compare the means and variances of the two groups, respectively. As seen in Table (7), the t-statistic and F-statistic are greater than t-critical and F-critical, respectively. This implies that the nitrate concentrations of the two groups are statistically different and hence support the results of the isotopes that they are coming from different sources.

Table 7: T-test and F-test for the fertilizers-related and wastewater-related groups in the study area.

Groups	Mean	Variance	t-stat	t-critical	F-stat	F-critical
Fertilizers/ Atmospheric deposition	159	19625	3.16	2.18	72.08	4.02
Manure/ Wastewater	30	272				

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1.Conclusion

Source-related signatures of 15N–NO3 and 18O–NO3 were measured in groundwater samples from the Cretaceous Wasia aquifer in central Saudi Arabia. The eastern and northwestern section of the study area are characterized by atmospheric and fertilizers-derived nitrate as inferred from 15N–NO3 and 18O–NO3 signatures, and distinguished by adjacent areas by elevated salinity, B, NO3 and δ18ONO3 values. The high salinity of 4,940 to 7,332 mg/L could be an influx of evaporated irrigation water, connate water or a mixture of both sources. Nitrate from the southwestern section is most likely to be of manure and wastewater origin, based on depleted salinity (1,100 – 3,928 mg/L), NO3 (3.3 – 110.5 mg/L), and 18O-NO3 (8.7 – 20.6 ‰) values, but highest 15N-NO3 ratios (up to 10.8‰).

The low tritium (3H) concentration of the Wasia groundwater, however, might indicate the absence of recent recharge, or the mixture of recent influx with fossil waters. The samples “WB03” and “WB08” with the highest tritium concentrations may indicate the influx of recent surface water. Tritium concentrations below the detection limit of 0.8 TU could be correlated to a late Pleistocene recharge event of the Wasia aquifer, as stated for the underlying Triassic Jilh aquifer using the radiocarbon method. As only 0.8 TU detection limit was reached using the enriched liquid scintillation counting (LSC) technique, more advanced methods like helium (^{3}He) ingrowth technique are needed to reach higher precisions. During the years 2010 to 2018, Wasia aquifer have witnessed an almost 15 m drop in water level in the western part of the study area. Spatial distribution of most of the hydrochemical parameters (TDS, Na^+, Ca^{2+}, Mg^{2+}, NO_3^- and Cl^-) shows an eastward increment with the regional groundwater flow but not including HCO_3 which shows a northward increment. Previous studies and analysis from the present study revealed that Wasia aquifer is generally not suitable for drinking. However, only one well has shown a good water type for drinking according to WQI. Though Wasia aquifer is good for agricultural use based on most of the used assessment indices, caution is required when planting salinity-sensitive crops due to the high salinity. Attention is also needed when choosing water transportation pipes as the water is highly corrosive. Moreover, soil permeability is going to be negatively impacted by continuing use of Wasia groundwater for irrigation.

As a conclusion, within the Wasia aquifer, natural sources such as atmospheric deposition, as well as anthropogenic sources like manure and fertilizers contribute to the nitrogen budget of the Wasia aquifer. Proper water treatment is required when using Wasia aquifer for drinking purposes although it's generally considered good for irrigation. Monitoring and frequent time interval checking for water quality is necessitated in the study area.

5.2. Recommendations

At the end of this work, I would like to recommend the following points:

- Wasia aquifer groundwater should be treated properly before using it for direct human drinking.
- Frequent checking and monitoring of groundwater quality are needed in Al-Kharj area.
- Attention is required when choosing water transportation pipes due to the high corrosivity of the Wasia groundwater.
- The near waste-water treatment plant should be investigated for probable leakage.
- Private wells should be monitored or closed as they can be a short pathway for contamination.

References

Al-Omran, A.M., Aly, A.A., Al-wabel, M.I., 2016. Hydrochemical characterization of groundwater under agricultural land in arid environment : a case study of Al-Kharj , Saudi Arabia. Arab. J. Geosci. https://doi.org/10.1007/s12517-015-2136-5

Alfaifi, H.J., Abdelfatah, M.S., Abdelrahman, K., Zaidi, F.K., Ibrahim, E., Alarifi, N.S., 2017. Groundwater Management Scenarios for the Biyadh-Wasia Aquifer Systems in the Eastern Part of Riyadh Region , Saudi Arabia. J. Geol. sociaty India 89, 669–674.

Alharbi, T.G., Zaidi, F.K., 2018. Hydrochemical classification and multivariate statistical analysis of groundwater from Wadi Sahba area in central Saudi Arabia. Arab. J. Geosci. 11. https://doi.org/10.1007/s12517-018-3955-y

Alsharhan, A.S., Nairn, A.E.M., 1990. A review of the Cretaceous Formations in the Arabian Peninsula and Gulf: part III. Upper Cretaceous (Aruma group) stratigraphy and paleogeography. J. Pet. Geol. 13, 247–266. https://doi.org/doi:10.1111/j.1747-5457.1990.tb00846.x

Alsharhan, A.S., Nairn, A.E.M., 1988. A review of the Cretaceous Formations in the Arabian Peninsula and Gulf: Part II. Mid-Cretaceous (Wasia Group) Stratigraphy and Paleogeography. J. Pet. Geol. 11, 89–112. https://doi.org/10.1111/j.1747-5457.1988.tb00803.x

Aramco, 1960. A Study of Wasia Aquifer in Eastern Saudi Arabia 128.

Birkle, P., 2016. Geochemical fingerprinting of hydraulic fracturing fluids from Qusaiba Hot Shale and formation water from Paleozoic petroleum systems, Saudi

Arabia. Geofluids 16, 565–584. https://doi.org/10.1111/gfl.12176

BRGM, 1976. Hydrogeological Investigation of the Al Wasia Aquifer in the Eastern Province of Saudi Arabia. Riyadh.

C. W. Fetter, J., 2014. Applied Hydrogeology, Fourth. ed. Pearson Education, Inc., Harlow.

Cagatay, M.N., 1988. Clay mineralogy and chemistry of some argillaceous rocks in central and eastern Saudi Arabia. Arab. J. Sci. Eng. 13, 47–63.

Çağatay, M.N., Saner, S., Al-Saiyed, I., Carrigan, W.J., 1996. Diagenesis of the Safaniya sandstone member (mid-Cretaceous) in Saudi Arabia. Sediment. Geol. 105, 221–240.

Clark, I.D., Fritz, P., 1997. Environmental isotopes in hydrogeology. CRC press.

Cleveland, C.C., Townsend, A.R., Schimel, D.S., Fisher, H., Howarth, R.W., Hedin, L.O., Perakis, S.S., Latty, E.F., Von Fischer, J.C., Hlseroad, A., Wasson, M.F., 1999. Global patterns of terrestrial biological nitrogen (N2) fixation in natural ecosystems. Global Biogeochem. Cycles 13, 623–645. https://doi.org/10.1002/(ISSN)1944-9224

Cook, G.A., Lauer, C.M., 1968. Oxygen. In: Clifford, A.Hampel (Ed.), The Encyclopedia of the Chemical Elements. Reinhold Book Corporation. Newyork.

Doneen, L.D., 1964. Water quality for agriculture. Department of Irrigation, University of California, Davis, p 48. Google Sch.

El Asa’ad, G.M.A., 1984. The paleobiogeographic distribution of the late Cretaceous fauna of Arabia and surroundings areas. Arab Gulf J. Sci. Res. 2, 105–121.

El Asa'ad, G.M.A., 1983a. Lithostratigraphy of the Aruma Formation in Central Saudi Arabia, in: Proc 1st Jordanian Geol Conf Spec Publ. pp. 72–86.

El Asa'ad, G.M.A., 1983b. Bio-and chronostratigraphy of the Aruma Formation in central Saudi Arabia, in: Proc 1st Jordanian Geol Conf Spec Publ. pp. 87–111.

Fenech, C., Rock, L., Nolan, K., Tobin, J., Morrissey, A., 2012. The potential for a suite of isotope and chemical markers to differentiate sources of nitrate contamination: A review. Water Res. 46, 2023–2041. https://doi.org/10.1016/j.watres.2012.01.044

GTZ/DCO, 2013. Detailed Water Resources Studies of Wasia-Biyadh and Aruma Aquifers – Groundwater Model and Water Management. Gesellschaft fur Technische Zusammenarbeit, Dornier Consulting. Riyadh.

GTZ/DCO, 2009. Detailed Water Resources Studies of Wasia-Biyadh and Aruma Aquifers - Phase I Completion Report. Gesellschaft fur Technische Zusammenarbeit, Dornier Consulting. Riyadh.

GTZ/DCO, 2006. Investigations of Updating Groundwater Mathematical Model(s) for the Umm Er Radhuma and Overlying Aquifers – Review of Monitoring Network. Riyadh.

Gutiérrez, M., Biagioni, R.N., Alarcón-Herrera, M.T., Rivas-Lucero, B.A., 2018. An overview of nitrate sources and operating processes in arid and semiarid aquifer systems. Sci. Total Environ. 624, 1513–1522. https://doi.org/10.1016/j.scitotenv.2017.12.252

Hakimi, M.H., Shalaby, M.R., Abdullah, W.H., 2012. Diagenetic characteristics and reservoir quality of the Lower Cretaceous Biyadh sandstones at Kharir oilfield in the western central Masila Basin, Yemen. J. Asian Earth Sci. 51, 109–120.

Harris, P.M., Frost, S.H., Seiglie, G.A., Schneidermann, N., 1984. Regional Unconformities and Depositional Cycles: Cretaceous of the Arabian Peninsula. In, J. Schlee (Ed.), Interreg. Unconformities Hydrocarb. Accumulations. Am. Assoc. Pet. Geol. Memoir 36, 67–80.

Hem, J.D., 1985. Study and Interpretation the Chemical of Natural of Characteristics Water, Third. ed. USGS, Alexandria.

Holloway, J.M., Dahlgren, R.A., 2002. Nitrogen in rock : Occurrences and biogeochemical implications. Global Biogeochem. Cycles 16. https://doi.org/10.1029/2002GB001862

Junk, G., Svec, H.J., 1958. The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources. Geochim. Cosmochim. Acta 14, 234–243. https://doi.org/10.1016/0016-7037(58)90082-6

Kaiser, H.F., 1960. The Application of Electronic Computers to Factor Analysis. Educ. Psychol. Meas. 20, 141–151. https://doi.org/10.1177/001316446002000116

Keller, M., Bohnsack, D., Koch, R., Hinderer, M., Hornung, J., Al-Ajmi, H., Abu Amarah, B., 2019. Outcrop Analog Studies of the Wasia-Biyadh and Aruma Aquifers in the Kingdom of Saudi Arabia. AAPG Mem. 317–382. https://doi.org/10.1306/13642171M1183514

Kendall, C., 1998. Tracing nitrogen sources and cycling in catchments, in: Isotope Tracers in Catchment Hydrology. Elsevier B.V., Amsterdam, pp. 519–576. https://doi.org/10.1016/b978-0-444-81546-0.50023-9

Kendall, C., Doctor, D.H., 2003. Stable Isotope Applications in Hydrologic Studies, in: Treatise on Geochemistry. pp. 319–364. https://doi.org/10.1016/B0-08-043751-6/05081-7

Kendall, C., Elliott, E.M., Wankel, S.D., 2007. Tracing anthropogenic inputs of nitrogen to ecosystems. Ecol. Environ. Sci. 375–449. https://doi.org/10.1002/9780470691854.ch12

Kohl, D.H., Shearer, G.B., Commoner, B., 1971. Fertilizer Nitrogen: Contribution to Nitrate in Surface Water in a Corn Belt Watershed. Science (80-.). 174, 1331–1334.

Le Nindre, Y.M., Vaslet, D., Maddah, S.S., Al-Husseini, M.I., 2008. Stratigraphy of the Valanginian? To early paleocene succession in central Saudi Arabia outcrops: Implications for regional Arabian sequence stratigraphy. GeoArabia 13, 51–86.

Macdonald, S.M., Partners, 1975. Riyadh Additional Water Resource Study. Riyadh.

Magaji, U.I., 1995. Assessment of hydrogeological parameters from thin-section study of middle cretaceous sandstones, Wasia formation, Saudi Arabia. King Fahd University of Petroleum and Minerals.

Mayer, B., Boyer, E.W., Goodale, C., Jaworski, N.A., Van Breemen, N., Howarth, R.W., Seitzinger, S., Billen, G., Lajtha, K., Nadelhoffer, K., 2002. Sources of nitrate in rivers draining sixteen watersheds in the northeastern US: Isotopic constraints. Biogeochemistry 57, 171–197.

Ministry of Agriculture and Water, 1984. Water Atlas Of Saudi Arabia. Riyadh.

Moshrif, M.. ., Kelling, G., 1984. Stratigraphy and Sedimentary history of Upper -

Lower and Middle Cretaceous rocks, Central Saudi Arabia. Miner. Resour. Bull. DMMR, Jiddah, Saudi Arab.

Paliwal, K. V, 1972. Irrigation with saline water.

Philip, J.M., Roger, J., Vaslet, D., Cecca, F., Gardin, S., Memesh, A.M.S., 2002. Sequence stratigraphy, biostratigraphy and paleontology of the (Maastrichtian-Paleocene) Aruma Formation in outcrop in Saudi Arabia. GeoArabia 7, 699–718.

Piper, A.M., 1944. A graphic procedure in the geochemical interpretation of water-analyses. Eos, Trans. Am. Geophys. Union 25, 914–928.

Powers, R.W., Ramirez, L.F., Redmond, C.D., Elberg, E.L.J., 1966. Geology of the Arabian Peninsula Sedimentary Geology of Saudi Arabia. U.S. Geol. Surv. Prof. Pap. 560–D, 154.

Richards, L.A., 1954. Diagnosis and improvement of saline and alkali soils. LWW.

Sharief, F.A., Magara, K., Abdulla, H.M., 1989. Depositional system and reservoir potential of the Middle Cretaceous Wasia Formation in central-eastern Arabia. Mar. Pet. Geol. 6, 303–315. https://doi.org/10.1016/0264-8172(89)90027-5

SOGREAH, 1968. Water and Agricultural Development Studies in Area V. Riyadh.

Stadler, S., 2006. Investigation of natural processes leading to nitrate enrichment in aquifers of semi-arid regions. University of Karlsruhe, Germany.

Stadler, S., Osenbrück, K., Knöller, K., Suckow, A., Sültenfuß, J., Oster, H., Himmelsbach, T., Hötzl, H., 2008. Understanding the origin and fate of nitrate in groundwater of semi-arid environments. J. Arid Environ. 72, 1830–1842. https://doi.org/10.1016/j.jaridenv.2008.06.003

Steineke, M., Bramkamp, R.A., Sander, N.J., 1958. Stratigrafic Relations of Arabian Jurassic Oil.

Stöckl, L., 2010. Hydrological and hydrochemical controls on radioactivity in deep groundwater in Saudi Arabia.

Subyani, A., Sen, Z., 1991. Study of Recharge Outcrop Relation of the Wasia Aquifer in Central Saudi Arabia. J. King Abdulaziz Univ. Earth Sci. 4, 137–147.

Subyani, A., Sen, Z., 1989. Geostatistical Modelling of the W a S I a Aquifer in 110, 295–314.

Todd, D.K., Mays, L.W., 1980. Groundwater hydrogeology. John Willey sons Inc., New York.

Tokhais, A.S., 1982. A Quantitative Study of the Wasia Well Field (Saudi Arabia).

Tripathi, A.K., Mishra, U.K., Mishra, A., Tiwari, S., Dubey, P., 2012. Studies of Hydrogeochemical in Groundwater Quality around Chakghat 2, 4051–4059.

Van Buchem, F.S.P., Pittet, B., Hillgärtner, H., Français, I., Grötsch, J., Mansouri, A., Billing, I.M., Droste, H.H.J., Oterdoom, W.H., 2002. High-resolution Sequence Stratigraphic Architecture of Barremian / Aptian Carbonate Systems in Northern Oman and the United Arab Emirates (Kharaib and Shu ' aiba Formations). GeoArabia 7, 461–500.

Vaslet, D., Al-Muallem, M.S., Maddeh, S.S., Brosse, J.M., Fourniquet, J., Breton, J.P., Le Nindre, Y.M., 1991. Explanatory notes to the geologic map of the Ar Riyad Quadrangle, Sheet 24 I, Kingdom of Saudi Arabia. Saudi Arab. Deputy Minist. Miner. Resour. Jeddah, Geosci. Map, GM-121 54.

Wells, E.R., Krothe, N.C., 1989. Seasonal fluctuation in δ15N of groundwater nitrate in a mantled karst aquifer due to macropore transport of fertilizer-derived nitrate. J. Hydrol. 112, 191–201.

Wilcox, L.V., 1948. The quality of water for irrigation use. United States Department of Agriculture, Economic Research Service.

Xue, D., Botte, J., De Baets, B., Accoe, F., Nestler, A., Taylor, P., Van Cleemput, O., Berglund, M., Boeckx, P., 2009. Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater. Water Res. 43, 1159–1170. https://doi.org/10.1016/j.watres.2008.12.048

Zaidi, F.K., Mogren, S., Mukhopadhyay, M., Ibrahim, E., 2016. Evaluation of groundwater chemistry and its impact on drinking and irrigation water quality in the eastern part of the Central Arabian graben and trough system, Saudi Arabia. J. African Earth Sci. 120, 208–219. https://doi.org/10.1016/j.jafrearsci.2016.05.012

Vitae

Name :Abid Gasmalbari Ahmed Khogali

Nationality :Sudanese

Date of Birth :1/31/1992

Email :abid.gasm8@gmail.com

Address :Khartoum-Sudan

Academic Background :**Master of Science in Geology**
King Fahd University of Petroleum and Minerals, 2019
Dhahran, Saudi Arabia

Bachelor of Science in Geology
University of Khartoum, 2013
Khartoum, Sudan

Professional Experience :**Research Assistant**
King Fahd University of Petroleum and Minerals
Jan 2017- Present
Dhahran, Saudi Arabia

Teaching Assistant
University of Khartoum
Jan 2014- Jan 2017
Khartoum, Sudan

Publications

: Khogali, A. G., 2020, Evaluation of nitrate pollution sources using nitrogen and oxygen isotopes approach in the groundwater of Al-Kharj area in Central Saudi Arabia, 13th International geological conference, March 2020, Jeddah, Saudi Arabia (**Accepted**)

: Khogali, A. G., 2020, Assessment of groundwater quality and characterization of Wasia-Biyadh aquifer in the area east of Al-Kharj city, Central Saudi Arabia, the 2nd International Conference on Water Resources in Arid Areas (WRAA2020), March 2020, Oman (**Accepted**)

: Khogali, A. G., 2020, Geochemical assessment of potential sources for nitrate in the Wasia aquifer, Al-Kharj area, Central Saudi Arabia (**On Progress**)

: Khogali, A. G., 2020, Characterization, hydrochemical evolution and assessment of groundwater quality of Wasia aquifer in the area east of Al-Kharj city, Central Saudi Arabia, Groundwater for Sustainable Development Journal (**On Progress**)