Hydrogeological and Environmental Studies of Water Resources in Wadi El-Natrun, Western Desert, Egypt

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Hydrogeological and Environmental Studies of Water Resources in Wadi El-Natrun, Western Desert, Egypt

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Dedication

For all my family,

*For all their unforgettable kindness over so **many** years, whose support and encouragement **throughout my** life has undoubtedly allowed me to overcome obstacles and troubles. This journey would not have been possible without you. I am forever grateful for your support. Thank you for following me down this long and winding road. This work is also especially dedicated in loving memory of my **Mother, grandparents and Prof. Hosni Soliman.***

Noha

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ABSTRACT

Providing sustainable sources of water in arid area for a growing population is great challenge. This dissertation spots more insight on hydrogeology and environmental changes using geochemistry and isotope hydrology to address water resources and to identify the sources and processes that govern the storage and movement of water on the area of study using stable $^{18}O$and ^{2}H isotopic compositions and groundwater geochemistry of groundwater to trace the sources and processes that govern the storage and movement of water on the area of Wadi El- Natrun.

The objectives of the present work were to; (1) investigate, compare, review and evaluate the groundwater in the area of Wadi El-Natrun, (2) Field survey and laboratory experiments were used to determine the geochemistry and origin of groundwater with focus on the seasonal variations. Five field trips were done to gather information and collect groundwater samples of Wadi El-Natrun. Ground water samples were collected seasonally during a field expedition led in the time from December 2014 until March 2018. Laboratory experiments were undertaken to investigate the groundwater geochemistry and origin.

This thesis deals with the hydrogeology of Wadi El-Natrun. It is composed of five chapters which investigate (1) Chapter one introduces an overview, previous work and objectives of the research, (2) Chapter two describes the geomorphology, geologic setting and stratigraphy (3) Chapter three deals with the aquifer systems in Egypt, the climate changes in Africa and Egypt, (4) Chapter four deals with geochemistry in addition to, O and H isotopic data that characterize sources of groundwater in the aquifer and (5) Chapter five presents future aspects.

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LIST OF ABBREVIATIONS

micromhos per centimeter	µmhos/cm
milliequivalents per liter	meq/1
milligrams per liter	mg/1
change in ratio of hydrogen isotopes (^2H : ^1H), relative to a standard	δ^2H
change in ratio of oxygen isotopes (^{18}O :^{16}O), relative to a standard	$\delta^{18}O$
Billion Cubic Meter	BCM
National Oceanic and Atmospheric Administration	NOAA
National Climatic Data Center	NCDC
African Humid Period	AHP
International Atomic Energy Agency	IAEA
Global Meteoric Line	GMWL
Total dissolved solids	TDS
World Health Organization	WHO
Food and Agriculture Organization	FAO
International Desalination Association	IDA
North Western Sahara Aquifer System	NWSAS
Nubian Sandstone Aquifer System	NSAS
Center for Environment and Development for Arab Region and Europe	CEDARE
International Union for Conservation of Nature	IUCN
Ministry of Water Resources and Irrigation	MWRI
The General Company for Research and Groundwater	REGWA
Research Institute of Groundwater	RIGW
National Aeronautics and Space Administration's	NASA
Continental Oil and Transportation Company.	CONOCO
Intergovernmental Panel on Climate Change	IPCC
The Global Network of Isotopes in Precipitation	GNIP
Liquid Water Isotope Analyzer	LWIA
X-ray diffraction	XRD
X-ray fluorescence	XRF

CHAPTER 1
INTRODUCTION

1.1 Overview

Egypt is situated between latitudes 22° and 32°N and longitudes 24° and 36°E in the extreme North-Eastern corner of the African Continent; bordering the Mediterranean Sea, between Libya and the Gaza Strip, the Red Sea, north of Sudan and embraces the Asian Sinai Peninsula serving a land bridge between Asia and Africa (Figure 1.1). The majority of landscape is desert with narrow arable land. Egypt possesses a fast steadily growing population during the last few decades with a restricted distribution of population around the River Nile. Tremendous efforts are carried out by the government to face the demand of Egypt's population through economic reform and huge investment in communications and physical infrastructure (Cia. Gov., 2018).

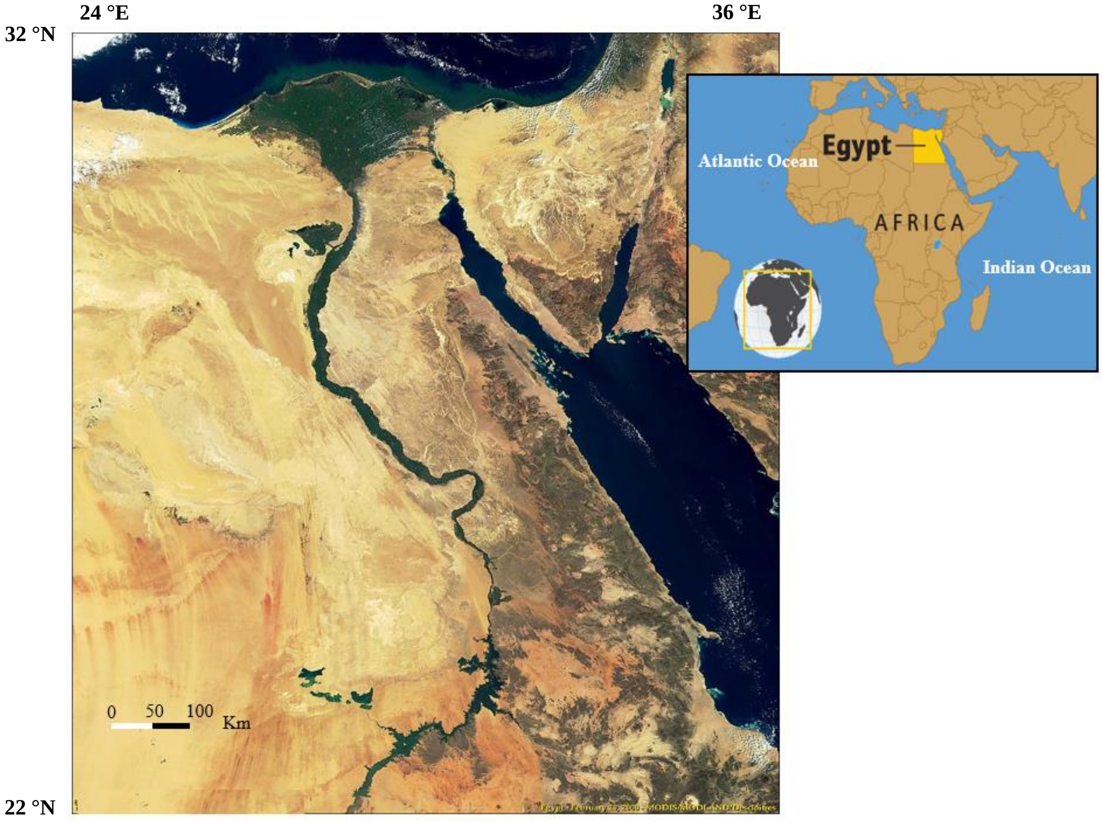

Figure 1.1: Location map of Egypt (NASA, 2000).

1. 2 Motivation

Water scarcity is a crucial crisis facing humankind especially in arid and semi-arid regions. Egypt suffers from water shortage (Figures 1.2 and 1.3). The scarcity of water will be even more critical in the future. Modernization and increasing of water needs for industrial, agricultural, and human daily usage representing extreme pressure on the available water resources. There are concerns towards food and water security and Egypt is extremely vulnerable. The threshold value of water scarcity is 1000 m^3/capita/year. Egypt has passed that threshold already in nineties and is expected to drop to only about 600 m^3/capita/year (MWRI, 2005). Therefore, groundwater is the main source for drinking water in Nile countries (Masiyandima and Giordno, 2007). The cultivated areas in Egypt have been increased over the past three decades. In the coming decades, the optimum challenge will be the task of increasing food production despite the limited water resources, especially in arid and semi-arid regions (FAO, 2003).

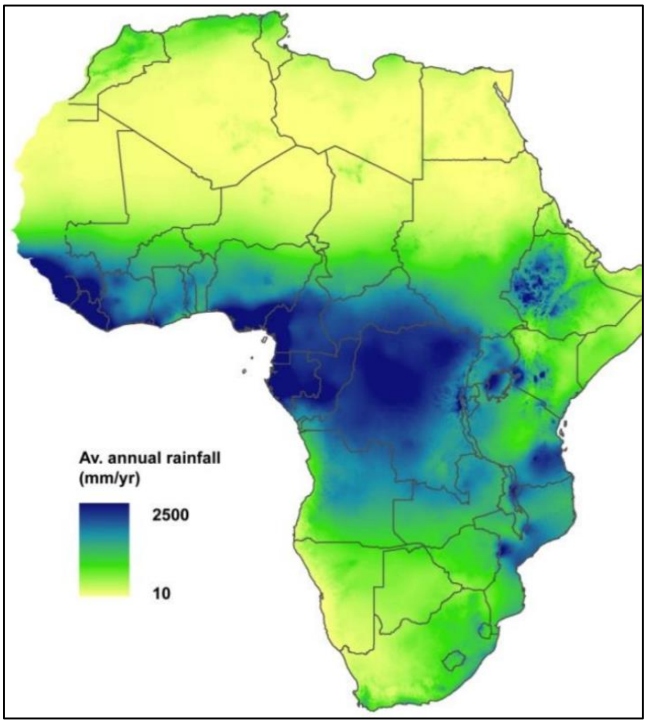

Figure 1.2: Annual rainfall across Africa (Macdonald, 2009) from using data from New *et al.* (1999).

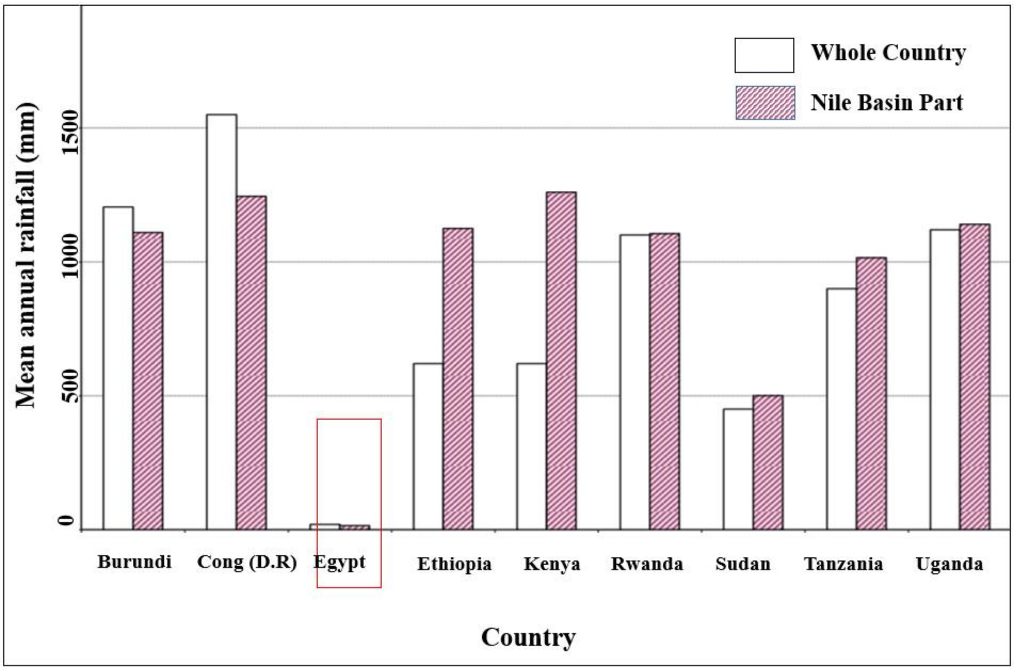

Figure 1.3: Average annual rainfall on the Nile countries (FAO, 1997).

The Nile River is the only reliable renewable water supply in Egypt providing more than 95% of freshwater as it consumes nearly its entire share from the Nile River water depending on it for drinking and irrigation therefore, different renewable water resources should accompany agricultural land expansion (Said, 1993; Hamza and Mason 2004; Antipolis, 2011). At the present time, water shortage lies ahead as a consequence of political disputes around Nile River treaties and the establishment of Renaissance Dam making it an important domestic and international political issue for Egypt recent international negotiations over allocations throughout the river Nile Basin.

The population overgrowth is one of the crucial national problems facing the Egyptian government. Egypt is ranked 14th in the list of countries by population with a population of approximately 98 million with about 1.8 million increase annually. Furthermore, the population is expected to reach 119 million by the year 2030 and 153 million by the year 2050 (Worldometers, 2017). Most of the population and economic activity are concentrated in the highly fertile Nile Valley and Nile Delta, which makes up around 5% of Egypt's total area.

Groundwater is used in association with surface water in the areas bordering the Nile Delta. On the other hand, in regions like the Western Desert where water is scarce, groundwater constitutes a principal portion of water supply and the pressure on it is increasing as the River Nile can't cover the increased demands. The government policy is to increase the reclaimed lands using groundwater for planting high standard crops for exportation to Europe and Middle East. National Water Resources Plan expanding the cultivated area by 3.4 million hectares. Reclamation projects were started by new agricultural communities to meet the needs of the increasing population away from the Nile Delta and Nile River valley and to get over the desertification phenomena in Egypt. The expansion in land reclamation is greatly assisted by private investors using groundwater for irrigation (ex. Toshka, El Salam Canal, Ain Dalla, Farafra, and the million and half feddans projects). Consequently, the cultivated areas in Egypt have been increased over the past three decades. Agriculture is the chief consumer of water in Egypt representing around 63 BCM of the total demand (Figure 1.4).

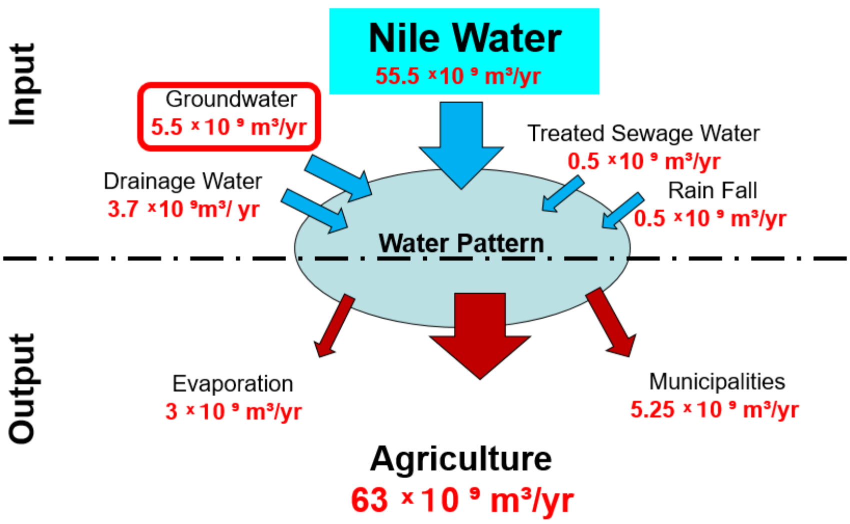

Figure 1.4: Main inputs and outputs of water budget in Egypt compiled after Allam (2001).

Land reclamation activities around the Nile Delta, Western Desert and Sinai have been largely extended leading to great pressure on groundwater and serious drawdown in water level (Figure 1.5). Depletion of groundwater resources and mismanagement resulted in a growing concern on the sustainability of available water resources.

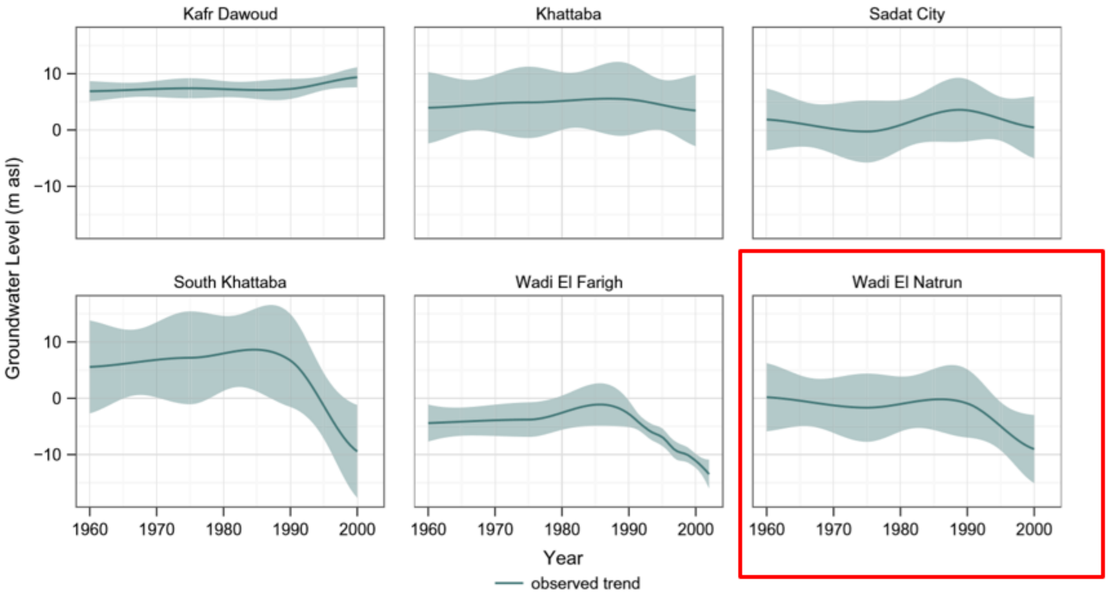

Figure 1.5: Changes in water table depth in Western Nile Delta from 1960 to 2000 (Baietti *et al.*, 2005; Ibrahim, 2005).

The groundwater table has fallen and salinity problems has arisen as a consequence of excessive extraction and a quick drop of productive land are expected over the period 2007-2025 (World Bank, 2007). The unfavorable environmental impacts on social and economic aspects constitute a massive pressure on the infrastructure. Wadi El-Natrun region has no other choice but to plan for an economically and environmentally sustainable development in accordance with hydrologic research as water resources management and assessment is important for acquiring better water including quality and quantity.

A successful management is needed to sustain the continuity of those projects. The acquisition of sufficient knowledge about the aquifer facilitate the way to an adequate management strategy to a rational use of the resources.

This thesis introduces an approach for the impacts of dry land environmental change on groundwater over time (four years). A particular focus is placed on isotopic analysis and geochemistry of groundwater used to assess the impact of seasonal variations on groundwater in Wadi El-Natrun.

1.3 Study Area

Wadi El-Natrun attracted the attention because it is a part of extreme arid province (Meig, 1953). It's a part of Saharian zone (Emberger, 1955). Wadi El-Natrun is a part of the Western Desert adjacent to the Nile Delta, a prominent endorheic elongated narrow depression (oval trough-like with gentle flanks) west of Cairo-Alexandria Desert Road and parallel to it approximately 90 km south of Alexandria and 110 km northwest of Cairo. It attains a length of about 50 km and a width ranging from 5 to 10 km, wide in the middle (8 km) and narrower at both ends (2.6 km in the north and 1.24 km in the south). It is bounded by longitudes 30° 10´ 19´´ and 30° 37´ 6.3´´ E and latitudes 30° 13´ 51´´ and 30° 36´ 13´´ N almost parallel to the Rosetta Branch of the Nile around 50 km from it (Figure 1.6). The bottom of Wadi El-Natrun is 23 m below sea level and 38 m below the water-level of the Rosetta Branch of the Nile.

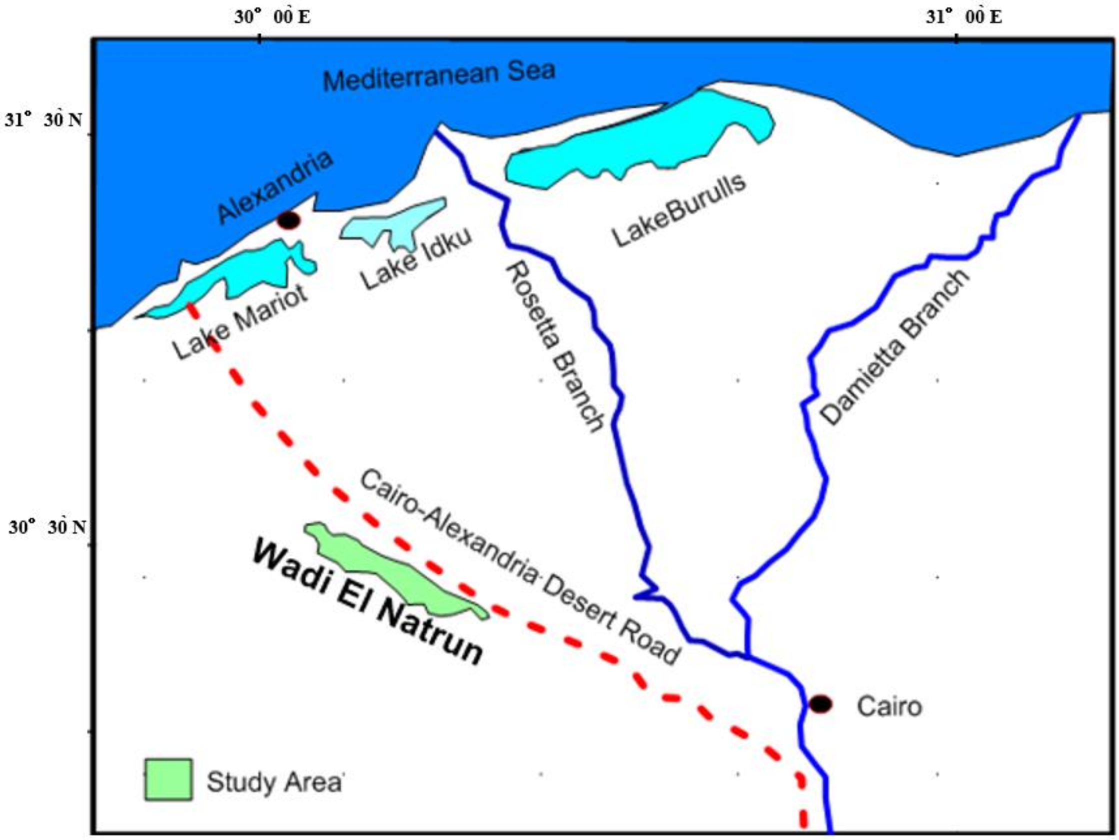

Figure 1.6: Location map of Wadi El-Natrun.

Wadi El-Natrun is one of the first selected areas as a new reclamation site since Late Fifties, tempting people who induced land development as it's a promising area for agricultural activities due to the existence of ground water, its low relief topography and good accessibility. The general lowland area of the depression is about 50 m below the level of its borders (Abd El Malek and Rizk, 1963).

Wadi El-Natrun covers an area of around 272 km², the lowest part of the depression, encircled by contour zero, inland saline lakes and salt encrustation occupy the area surrounded by contour zero (Abu Zeid, 1984). One of the conspicuous features in the Wadi El-Natrun depression are the natural water lakes, located at about 23 m below sea level. The area of Wadi El-Natrun has always been confined as a possible area for reclamation and utilization due to its location, accessibility, investment facilities provided by the government and the presence of groundwater in a good quality for irrigation. The area has been mapped several times for oil and groundwater perspectives.

The name Wadi El-Natrun was introduced by an Arab traveler named El-Maqurizi in the 16th Century. The word Natrun is derived from the Latin word "natrium" for the element sodium. The history of the area dates back to the Pharaohs, who used salts from the lakes for the process of mummification, they called it Ain Horus, which means the eye of the God Horus because it appears to be shaped like an eye The Romans extracted silica for glass as well. During the British occupation of Egypt, railroad system was built to move the salt from Wadi El-Natrun to Cairo. Wadi El-Natrun is known for the presence of evaporites that are used in various industries (Lucas and Harris, 1962). Wadi El-Natrun was famous as a source for building materials to the biggest two cities in Egypt, Cairo and Alexandria (Abu Zeid, 1984).

1.4 Climate

The main feature of the Egyptian climate is the almost uniform aridity. The climate of Wadi El-Natrun is dominated by arid to semi-arid climatic conditions (low and very variable rainfall, a long dry summer, a high rate of evaporation, and low humidity and a short temperate Winter).

Wadi El-Natrun is characterized by annual rainfall of 41.4 mm, evaporation rate 114.3 mm and average temperature is 21 C°, wind speed average is 3.4 m s^{-1} and the mean relative humidity is 48%. Hence, this province is found to be very arid (Egyptian Meteorological Authority, 2006) winds are usually from the north, northeast and northwest. The majority of rain falls during December, January, and February (Switzman, 2013). According to NOAA's National Climate Data Centre (NCDC) dataset of Wadi El-Natrun, the average daily precipitation is 31.5 mm as recorded from 1996 to 2012. The depression secures a relatively sheltered climate unlike the surrounding desert area. Mean annual rainfall reaches 55 mm (Zahran and Willis, 2009).

Table 1.1: Summary of meteorological data in the study area and near counterparts (Egyptian Meteorological Authority, 2006).

Station	**Temperature (°C)**		**Relative Humidity**	**Evapotranspiration**	**Rain fall**
	Max.	**Min**	**(%)**	**(mm/day)**	**(mm/yr)**
Giza	35	7.6	59.7	8.8	41.8
Shibin El-Kom	35.7	8	53.7	9.6	55.1
Wadi El-Natrun	34.4	6.6	57.5	8.6	48.2
El Tahrir	35	6	69.2	6.6	92.6
Damanhour	32.8	7.8	61.5	4.4	163.2
Alexandria	33	9.2	63.4	5	201.7

1.4.1 Evaporation and evapotranspiration

Evaporation is the transfer of liquid water into the atmosphere. The area is characterized by a high rate of evapotranspiration. The average actual evapotranspiration ranges from about 9 mm/day in the south to about 4.4 mm/day in the north and from Summer to Winter.

The average meteorological data in the study area and major surrounding cities were provided by the Egyptian Meteorological Authority from six metrological stations (Table 1.1) in Giza, Shibin El-Kom, El-Tahrir, Wadi El-Natrun, Damanhour and Alexandria. The total reference of evapotranspiration is 1515 mm/yr which equals 0.021 aridity index and classified as hyper-arid (United Nations Environment Programme, 1992). The daily evaporation of open water varies from approximately 1.5 mm to 7.5 mm in December and in July, respectively. about ~1600 mm/year (Geirnaert and Laeven, 1992).

1.5 Lakes

Egypt possesses few natural inland lakes. The inland saltmarshes are found as Sabkhas around springs, lakes, and wells of the Western Desert Oases and Depressions (Siwa, Dakhla, Kurkur, Dungul, Baharia, Farafra, El Fayoum, Qattara, Wadi El-Natrun, etc…) (Zahran, 1972). Saline lands constitute around 10% of the Earth’s land surface (O’leary and Glenn, 1994).

A chain of seven large alkaline, hypersaline lakes in addition to a number of ephemeral pools extends along Wadi El-Natrun, parallel to its axis (Figure 1.7).

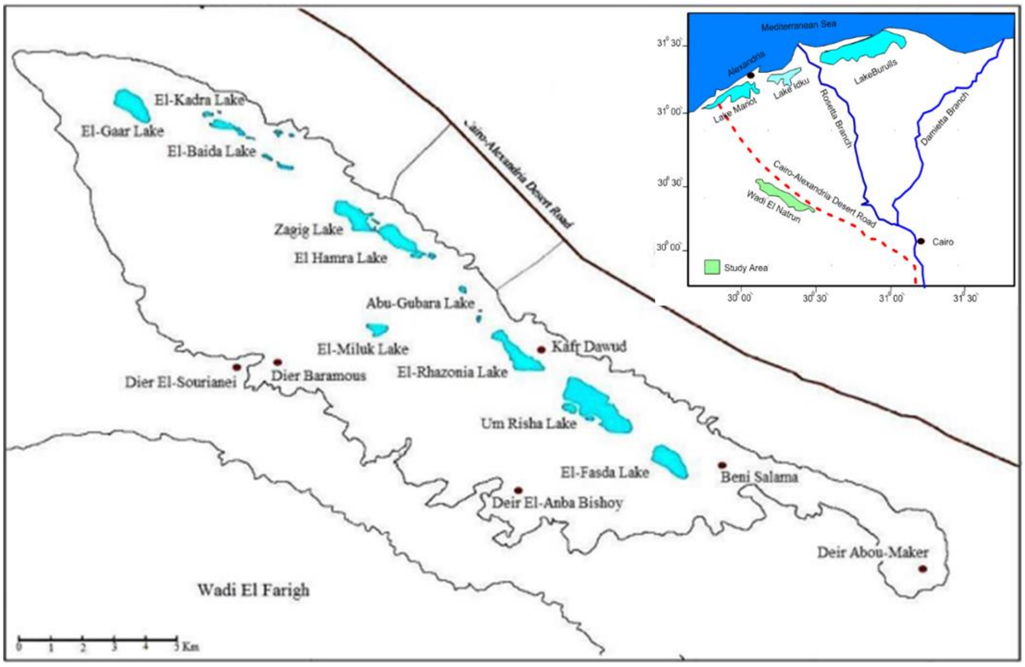

Figure 1.7: Location map of Wadi El-Natrun and its hypersaline lakes.

The lakes have attracted many workers due to their sensitivity to climatic changes. The saline water environment of Wadi El-Natrun bear similarity to that found in Playa-ephemeral lakes and perennial saline lake complexes shown elsewhere. Evaporation removes surface waters effectively and produce concentrated brine progressively (Eugester and Hardie, 1978; Lent and Lyons, 1995).

Wadi El-Natrun lakes were exploited as main source of natron in the ancient world. Natron was used in the process of mummification by the ancient Egyptians (James and Slaughter, 1974; Omara and Sanad, 1975). It occurs as solution in lake water, deposits on their bottom, and crust around edges of the lakes (Zahran and Willis, 2009). In addition, natron was used in glass production from archaeological evidences just beside the lakes of Wadi El-Natrun under the reign of Roman empires (Neena, 2003). Wadi El-Natrun is now no longer exploited for torona instead halite is exploited from a very small lake (Nakhla *et al.*, 1986).

Various environments and climatic changes are preserved in the lakes of Wadi El-Natrun. Wadi El-Natrun is considered as an alkaline environment of athalassohaline system which results from non-sea water sources and contains different ion ratios (Satyanarayana *et al.*, 2005). It lies 23 m below sea level and is characterized by a series of small disconnected lakes in the bottom of the Wadi. Some of these lakes are relatively larger in size and have permanent water reservoirs in all or some of their parts. Chemical and physical conditions in the lakes are affected by changes in evaporation and precipitation. Various plants are found at the edge of the lake area nearby water edge along marsh lands.

The lakes are named (El Fasda, Umm Risha, El Razonia, Abou Gebara, El Hamra, El Zugum, El Zaagig, El Beida, El Khadra, Gaar, El Sabkha and Afauna). They occur approximately along the longitudinal axis of Wadi El-Natrun (Gaar Lake, about 2.4 km^2; El Bida Lake, about 2.3 km^2; El Zugum Lake, about 1.6 km^2; El Hamra Lake, about 1.1 km^2; El Razonia Lake, about 0.87 km^2; Umm Risha Lake, about 2.45 km^2 and El Fasda Lake, about 0.72 km^2). All of the lakes are below sea level with the lowest in Gaar Lake (-23 m) and the highest in El Khadra Lake (-19 m). The water level changes around the year with relatively higher in Autumn and Winter and lower in Spring and Summer (El-Fayoumy, 1964). The largest lakes are Gaar Lake in the northwest side of the depression and Lake Umm Risha Lake in the southeast direction.

The evaporitic lakes vary in size depending on their position in the wadi and the climate. The level of the water in these lakes fluctuates seasonally, becoming higher in winter and lower in summer. In Summer, the smaller lakes dry up completely, and only few pools are left (Atia *et al.*, 1970). Other smaller, but almost permanent, lakes are El Hamra, El Fasda, El-Bida, El Khadra, El Zugum (Zaagig) and Abou Gebara.

The number of lakes is contradictory due to high rate of evaporation as Stocker (1927) recorded 16 lakes, El-Hinaawi and Atwa (1973) mentioned 10 lakes and Imhoff *et al*. (1979) noted the presence of only 6 lakes. Zahran and Willis (2009) recorded 8 principal lakes present along 30 km long axis of the depression lying from northeast to southwest as follows: El Gaar, El Khadra, El Bida, El Zugum, El Hamra, Abou Gebara, Al Razonia, Umm Risha, and El Fasda.

Halite is most common mineral in most of the lakes along most of the year. Trona (a sodium carbonate-dehydrate mineral) occurs in the lakes in exploitable quantities in some lakes. It is rarely found as pure, single-phase trona (Atia *et al*., 1970; Shortland, 2004).

The western part of the lakes is frequently occupied by aeolian sand. The largest lakes are Lake El Gaar in the northwest and Lake Umm Risha in the southeast direction. The depth of the lakes ranges from 0.5-2 m due to seasonal changes in evaporation and seepage influx (Mesbah *et al*., 2007).

The lakes of Wadi El-Natrun have pH values of 11 with salt contents more than 30% comprising sulphates, carbonates, chlorides, sodium, and minor amounts of potassium and traces of calcium and magnesium (Johaness *et al.*, 1979). Wadi El-Natrun is an outstanding aquatic ecosystem among saline lakes distinguished by hyper salinity and alkalinity poor in (NO_2^-, $NO_3^-SiO_2$ and Ca^{2+}, Mg^{2+}, K^+, and rich in Cl^-, SO_4^{2-}, Na^+, CO_3^{2-}, HCO_3^-, and PO_4^{2-}). The productivity and distribution of aquatic life is affected by water chemistry and lake depth (Taher, 1999; Sayed and Abdo, 2009). The geochemical and biological characteristics of evaporation need to be considered in the study of inland saline lakes. The maximum water level is observed between December and March and the lowest level is during Summer season. The lakes water shows a high alkaline nature (pH ranges from 9.12 to 9.85), with very poor oxygen.

1.6 Previous Work

Recently and during the past few decades Wadi El-Natrun and its alkaline saline lakes have been of great importance. The area of Wadi El-Natrun has been studied by numerous eminent authors dealing, in particular, with the geology and hydrogeology, microbiology and geochemistry of the lakes. Various environments and climatic changes are preserved in the lakes. Wadi El-Natrun is one of the oldest centers of monastic settlements in Egypt continuing from the period between the 4th and 6th Century and four monasteries are inhabited at present (Moussa *et al.*, 2009). The following is a brief history of studies that were conducted on Wadi El-Natrun in chronological order:

The study of Wadi El-Natrun was stared by Andrews (1902) who described the vertebrate fauna collected from Qaret El Muluk in the area of Wadi El-Natrun. Hume (1925) compiled geological logs for some water wells sunk in Wadi El-Natrun from the data from the "Salt and Soda Company".

Geoistrazivanja (1962) reported the results of test drilled wells and four production wells in the Western Desert and along the Cairo- Alexandria Desert Road, respectively. Shata *et al.* (1962) illustrated that the south eastern part of Wadi El-Natrun is hydraulically connected to the Nile behind the Barrage South of Cairo, hence are chemically similar. White *et al*. (1963) reported that the water of Wadi El-Natrun is less carbonated than Nile waters. The groundwater of Wadi El-Natrun are recycled water (meteoric waters). According to the salinity classification water is good potable. The seasonal changes in Wadi El-Natrun is indicated by increase in salinity from August to December and then decreases to a minimum in June.

El-Hinnawi and Atwa (1973) classified the groundwater of Wadi El-Natrun as good potable to fresh waters belonging to sodium bicarbonate and Ca-Mg bicarbonate classes.

Abdel Baki (1983) elucidated that the Lower Miocene aquifer is recharged from southern section of the Nile Delta basin whilst Wadi El-Natrun and Moghra depression in the northwest and west are recharged from the Lower Miocene aquifer.

Abu Zeid (1984) studied 25 vertical stratigraphic sections representing the outcrops of Wadi El-Natrun, in addition to collecting macro and microfossils from beds of the studied sections. Farid (1984) argued the various plans for the development of groundwater in the Nile Delta area. Geirnaert and Laeven (1992) discussed the composition and groundwater history of groundwater in area west of the Nile Delta. Ahmad (1993) pointed out that groundwater moves from east to west across Wadi-El Farigh and is managed by an old buried Nile channel which deflects the flow of groundwater towards Wadi El-Natrun Depression. Fekry (1993) predicted the lowering in groundwater heads south and east of Wadi EI-Natrun by 10 m and up to 15 m in the span of 50 years as a result of the massive expansion in reclamation projects.

Gomma (1995) classified the water types of the Pliocene aquifer $NaHCO_3$ and NaCl water types. Mohamed (2002) studied the change in land use in the western delta between 1987 and 1998 and its effect on groundwater. Dawoud *et al.* (2005) made a GIS based model for the aquifer system at a study area west of the Nile Delta, he showed that the enhancement of irrigation system could decrease the annual aquifer potentiality by approximately 91% as a result of minimizing the infiltration rates. Gaame (2005) associated the deterioration of groundwater in wells west of Nile Delta region especially, on the Wadi El-Natrun and Wadi El-Farigh areas to poor well design, and over-pumping.

1.7 Objectives of the Study

The objectives of the current study can be summarized as follows:

1. Assemble ground-water quality data along successive four years.
2. Hydrochemical characterizations of the groundwater, identifying major anions and cations.
3. Identify origin of the groundwater using ^{18}O and ^{2}H isotopes to determine recharging sources.
4. Mechanism controlling variation among wells.
5. Evaluation of the groundwater suitability for different purposes.

This thesis is composed of five chapters which investigate the hydrogeology of Wadi El-Natrun. (1) Chapter one introduces an overview, previous work and objectives of the research. (2) Chapter two describes the geomorphology, structure and stratigraphy. (3) Chapter three handles occurrence of the groundwater in Sahara and an overview of the Holocene climatic changes in Africa and Egypt. (4) Chapter four deals with the geochemistry of groundwater, suitability for domestic and agricultural purposes and isotopic data that characterize sources of groundwater in the aquifer. (4) Chapter five introduces the water crisis and current situation with proposed solutions.

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CHAPTER 2
STRATIGRAPHY

2.1 Geomorphology

The area of west Nile Delta is distinguished by its mild topography and low relief. Wadi El-Natrun possess a desert geomorphology, it has aeolian sand accumulation which reaches 10 m thickness (El Fayoumy, 1964). The area is composed of four major geomorphologic units; alluvial plains, structural plains, tablelands and shifting sand (Shata, 1962; Attia, 1975; Omara and Sanad, 1975; Abdel Baki 1983).

The origin of the Wadi El-Natrun depression and its lakes was attributed to erosional processes accompanied by lowering of water table (El Fayoumy, 1964). Wadi El-Natrun is separated from Wadi El Farigh from southwest by Gebel El Mikheimin an elongated irregular scarp. The floor of Wadi El-Natrun is occupied by several mesas and butts composed of sands, clays, and sandstones capped with hard calcareous horizon. The high land areas are barren while vegetation is restricted to low lands.

The lowest part of Wadi El-Natrun is encircled by contour zero where sabkha, white salt encrustation and saline lakes occur (Abu Zeid, 1984). Physiographically, Wadi El-Natrun is composed of three main parts which are northern nilotic ridge, northern foot-slope that reaches 35 m high, and the main depression with its salt alkaline lakes (El-Hinnawi and Atwa, 1973). Wadi El-Natrun is characterized by the presence of scattered isolated hills (El-Shahat *et. al.*, 1997) such as Qaret El-Muluk (7 m high) and Ras El-Solymania (51 m high) and Bani Salama (50 m high).

2.2 Geological Setting

The structural features of Wadi El-Natrun has been studied by many authors on varying scales. The area of Wadi El-Natrun lies within the unstable shelf of northern Egypt and is structurally affected by the Marmarican Homocline which is dipping gently northward and the taphro-geosynclinal trough of the Nile Delta (El Fayoumy, 1964; Shata and El Fayoumy, 1970). The advent of Miocene was marked by a conspicuous tectonic movement that lead to NE-SW fault system in Wadi El-Natrun (Said, 1990).

El-Fayoumy (1964) believed that, Wadi El-Natrun is possibly a graben structure oriented in the NW-SE direction. This graben structure has a length of about 30 km and with an average width of about 10 km. Wadi El-Natrun anticline, the main geological feature, extends for about 35 Km in a northwest direction from Ras El- Solymania in the north to Deir Macarious in the south. The axis passes through most of the lakes of Wadi El-Natrun. Shata (1953) mentioned that the initial formation of Wadi El-Natrun graben structure took place, approximately contemporaneous with other graben structure detected in the Gulf of Suez region.

The west Nile Delta area is separated from the Delta basin by one or more of step faults having an eastern downthrown. Such faults enable the highly permeable Pleistocene deposits of the Nile Delta to meet up with the older sediments due west. Consequently, a westward flow of the Nile water to the western old sediments. The fault system in Wadi El-Natrun area is trending NW-SE parallel to Rosetta branch and the axis of the depression and tangential to the lakes this lineament separates the Miocene and Pliocene well exposed rocks at its southwestern side from the Pliocene and Pleistocene units at its northeastern side (El-Shazly *et al.*, 1975).

General Petroleum Company “GPC” (1977) showed that Wadi El-Natrun area is dominantly affected by seven faults; Wadi El-Natrun faults zone F1, F2 and F3 have downthrown to the east and bounded Wadi El-Natrun unit from the west and El Tahrir Pleistocene unit from the east, fault 4 (F4) has a NW and its downthrown side to the south, fault 5 (F5) trends in NW direction with downthrown to the south. It bounds Wadi El-Natrun unit from the north and Wadi El-Farigh unit from the south, El Khatatba fault (F6) has a general direction in NE and downthrown side to the north. It bounds Tahrir Pleistocene unit from the north and Wadi El-Farigh unit from the south and fault 7 (F7) extends in downthrown side to the south.

2. 3 Stratigraphy

Wadi El-Natrun rocks are not well exposed and relatively show lack in fossils. Various lithostratigraphic units forms the surface of Wadi El-Natrun and its aquifer systems. The bottom of Wadi El-Natrun is occupied by eleven saline lakes, representing a discharge area. The flow of groundwater is observed from both the east (Nile Delta) and the west (Western Desert) towards the depression (Attia *et al.*, 2007 and RIGW, 1992). Localized flow fields has been developed due to the excessive pumping of groundwater used for irrigation (El-Sheikh, 2000 and Masoud and Atwia, 2010). Wadi El-Natrun is covered by lake deposits and old alluvial deposits of sand and gravel deposited during sea encroachment and the Nile intersect it (Philip *et al.*, 1975). They belong to Quaternary Period. Wadi El-Natrun area is dominated by a sedimentary section which is represented by the oldest Triassic Age to the youngest Pliocene Age with thickness greater than 4 km.

The area west of Nile Delta is distinguished by its mild topography and low relief. It is represented by the Quaternary and Neogene deposits. Quaternary deposits belong to Pleistocene and Recent whereas Neogene deposits are Miocene (subsurface) in age (Said, 1961; Said, 1993). Wadi El-Natrun is is basically composed of shallow marine, brackish water deposits, and clayey facies at the base and fluviomarine and shallow marine deposits at the top. Pliocene deposits reach up to 150 m. In general, Wadi El-Natrun is covered by sedimentary succession of Oligocene, Miocene, Pliocene and Pleistocene epoch. Oligocene rocks outcrop in area of southwest corner of Nile Delta. Miocene and Pliocene are generally distributed in west and south of Wadi El-Natrun whereas Quaternary sediments dominate towards north.

The surface of Wadi El-Natrun is mainly covered by Pleistocene sands and gravels in addition to, sabkhas and salty crusts along the scattered lakes along its axis. The surface is underlain by Pliocene epoch which is represented by sands, clays, sandy clays, and limestone intercalations and is unconformably underlain by 150 m thick early Miocene rocks (El Hinnawi and Atwa, 1973).

Blanckenhorn (1921) assigned a Late Pliocene age to the beds exposed in Wadi El- Natrun depression. Ball (1939) described the Pliocene rocks of Wadi El-Natrun as of a fluviatile or estuarine origin. These rocks consist of sand and gypseous clay, containing remains of elephants, giraffs and other land animals together with crocodiles and fish. Sandford and Arkell (1939) assigned Plio-Pleistocene to Early Pleistocene times to the gravel terraces of the west Nile Delta. Shata (1955) has recognized two series belong to the Pliocene in Wadi El−Natrun area. The upper series is composed of porcellaneous limestone with flint, while the lower series is composed of thick shale beds alternating with argillaceous sandstone. The exposed Pliocene rocks at Wadi El-Natrun are divided into the Mikheimin formation (Lower Pliocene) and the Muluk formation (Upper Pliocene) (Abu Zeid, 1984).

The subsurface thickness of sedimentary marine and continental rocks overlying the basement reaches up to (4000 m) (Figure 2.1) according to oil drilling test well No.1 (Phillips, 1970).

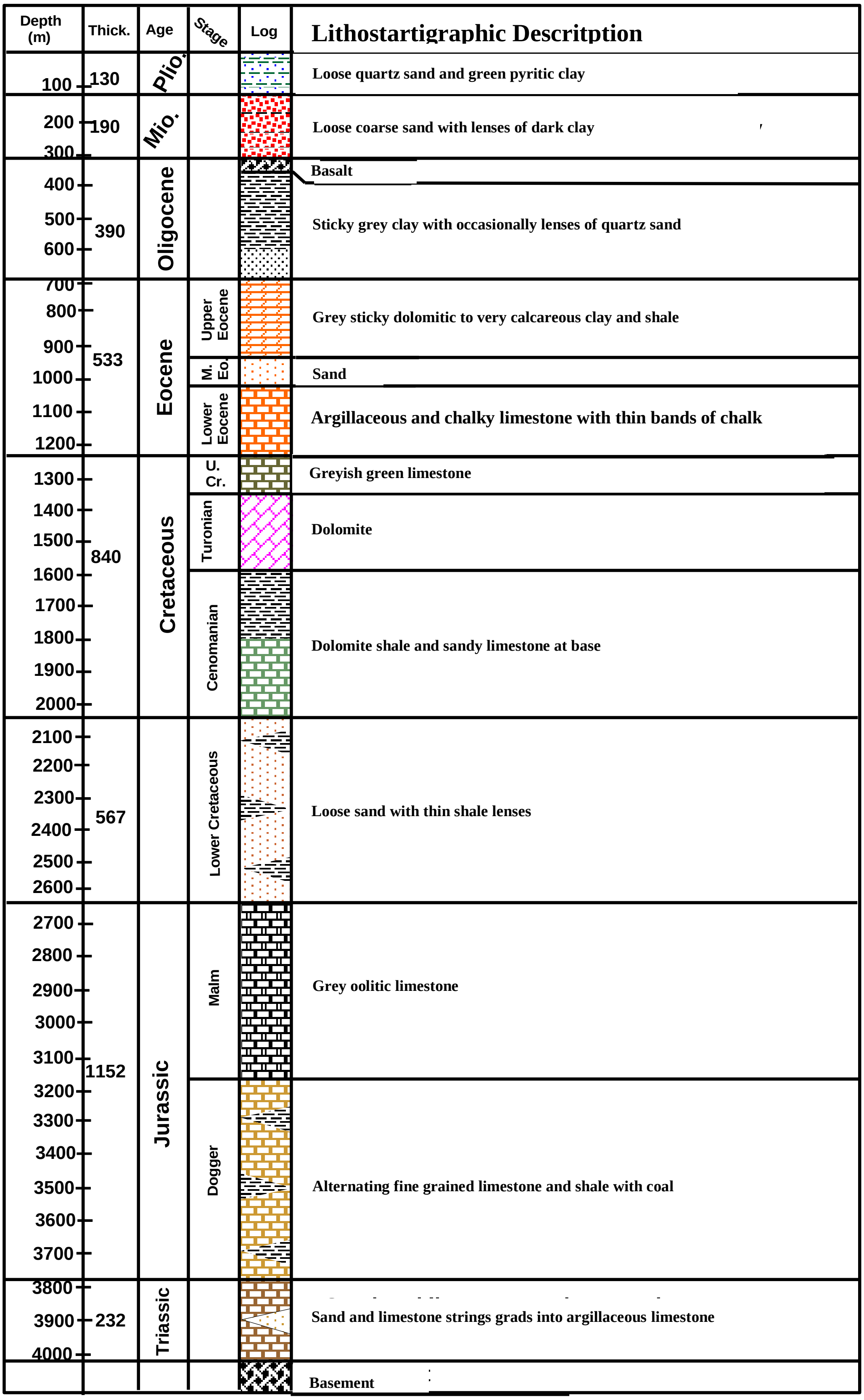

Figure 2.1: Lithostratigraphic section of Wadi El-Natrun (Philips, 1970).

The oldest exposed rocks in Wadi El-Natrun area is Miocene rocks, occupying most of the area to south of the wadi (depression) whereas within Wadi El-Natrun depression the surface exposures are dominated by Pliocene shallow marine and continental formations and post Pliocene fluvio-marine deposits. The study of Wadi El-Natrun exposed rocks in addition to drilled wells (surface and subsurface) Shata (1962) divided rocks into three units from exploratory core base 200 m of Miocene shallow marine lacustrine deposits composed of coarse and fine-grained sand followed by Pliocene strata measuring around (200 m) and are divided into two units. Upper calcareous grit and impervious clay whereas the lower unit is dominated by green clays. These two rock units are topped by widely distributed Quaternary and Recent strata. The Quaternary rocks are differentiated into Pleistocene and Recent. Recent rocks are represented from top to base by windblown sands and downwash deposits and silt deposits of the Nile Delta (25 m).

Tertiary rocks are represented by (Oligocene, Miocene and Pliocene) rocks (Abu Zeid, 1984). The Triassic succession is made up of shale and limestone intercalations whereas the Jurassic strata are mainly composed of limestone and shale with sandstone lenses. The Cretaceous rocks unconformably underlie the Eocene deposits. Cretaceous rocks are divided into lower and upper Cretaceous rocks. The Upper Cretaceous strata are mainly represented by carbonate rocks with shaly facies whereas the Lower Cretaceous strata are dominated by sandy rocks intercalated with clay and cemented by calcite. The Eocene rocks are made up of limestone at the base and topped by clay and shale (El Shazly *et al.*, 1975). Pliocene rocks are differentiated into Wadi El-Natrun Formation (70 m) of brackish water deposits and Lower El Mekhimien Formation (100 m) marine deposits.

The Miocene El Raml Formation (200 m) is represented by poorly fossiliferous deltaic sand and sandstone (Abou-Khadrah, 1973). Said (1962) assigned fluvio-marine environments for Lower Miocene Moghra formation. Sanad (1973) and Omara and Sanad (1975) classified the area lying between Wadi El-Natrun and El Moghra depression into: Early Miocene (El Moghra Formation), Early Pliocene Formation (Wadi El-Natrun Formation), Late Pliocene (El Hagif Formation), Early Pleistocene include old gravel and Late Pleistocene-Recent represented by young gravel, loam deposits, sand dune chains and sand dunes (Omara and Sanad, 1975).

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CHAPTER 3

HYDROGEOLOGICAL SETTING

3.1 Introduction

Water is an indispensable and vital element of ecosystem. Thus, providing sustainable sources of fresh water for the global population of more than 7 billion people is a prominent challenge of the 21st Century. Groundwater is a crucial component of water resource systems. However, it has been broadly ignored as a basic water resource. Groundwater is a significant water supply source extracted by pumping, as water scarcity is an outstanding crisis facing humankind particularly in arid and semiarid regions characterized by absence of regular rainfall such as the extending area across Africa coast and southern Europe accompanied with the rapid growth of population and increase of water demand to sustain industrial, agricultural, and human daily usage representing an extreme pressure on the available water resources. Groundwater represents about 30% of globe's total fresh water about 1/4 of all water used for domestic, agricultural and industrial uses (Figure 3.1) and (Tables 3.1 and 3.2). Moreover, it is the source of base flow that recharges water in rivers and lakes.

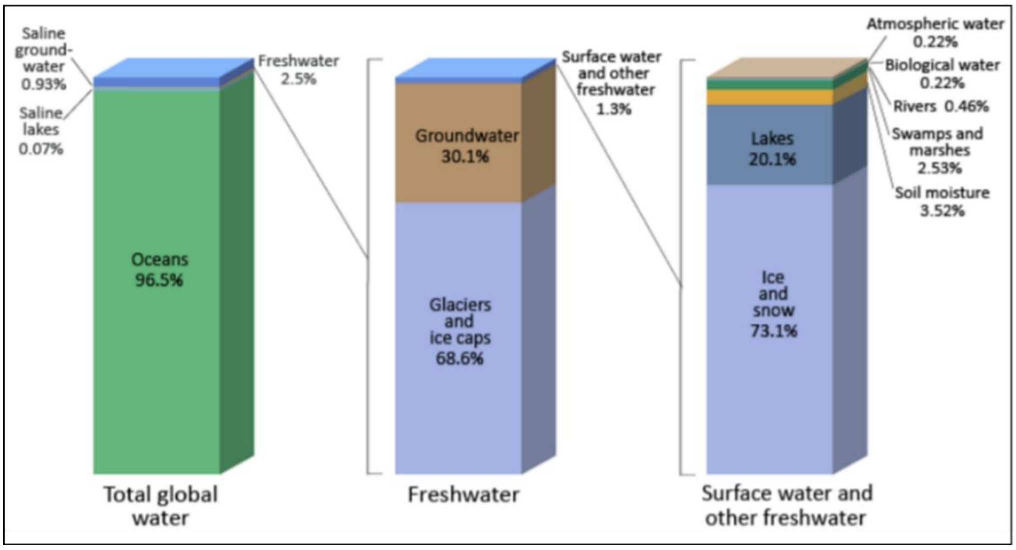

Figure 3.1: Distribution of Earth's water (Shiklomanov, 1993).

Table 3.1: Distribution of water resources (Chin, 2000).

		% Total Water	% Fresh Water
Oceans		96.5	
Groundwater	**Fresh**	0.76	30.1
	Saline	0.93	
Soil Moisture		0.0012	0.05
Polar Ice		1.7	68.6
Lakes	**Fresh**	0.007	0.26
	Saline	0.006	
Rivers		0.0002	0.006

Groundwater systems had evolved under almost stable conditions before human intervention reflecting hydrodynamic conditions that had prevailed probably several thousands of years under recent climatic regimes (Edmunds, 2001). Until the 1980s, groundwater was not important factor in the hydrological system and the governments assumed that they control its use and extraction (Falkenmark, 1981). Groundwater supplies drinking water for two billion people and sustains about 40% of global agricultural uses (Aeschbach-Hertig and Gleeson, 2012). The deterioration in groundwater quality is a serious problem in arid and semi-arid parts of the world (Liu *et al.*, 2015).

Table 3.2: Distribution of water resources (Mook, 2001).

	Volume in 10^3 km^3	% of total fresh water	Flux 10^3 km^3/year	Turn-over time year
Salt water				
Oceans	1,350,000		425	3000[1]
Fresh water				
Ice	27,800	69.3	2.4	12,000[2]
Groundwater	8000	29.9	15	500[3]
Lakes	220	0.55		
Soil moisture	70	0.18	90	0.8[4]
Atmosphere	15.5	0.038	496	0.03[5]
Reservoirs	5	0.013		
Rivers	2	0.005	40	0.05[6]
Biomass	2	0.005		
Total	40,114	100		

Egypt lies mainly within the hyper arid desert environment. The majority of landscape is barren desert and sparsely populated or unpopulated (Davis and Bernstam, 1991). The resources of water supply are shown on (Table 3.3) rainfall is basically along the northern coast. The River Nile is the only reliable renewable water supply in Egypt. More than 95% of Egypt's water comes from the Nile. Egypt consumes almost all of its share from the Nile River and water resources are critically important therefore, different water resources should be operated accompanied to agricultural land expansion to satisfy the demand of all Egyptians particularly in the future to face the population overgrowth.

Table 3.3: Water resources availability and usage in Egypt modified after (Nashed *et al.*, 2014).

Water Resource	**Reserve (bcm)/yr**	**Used (bcm)/yr**	**Author**
Nile Water	55.5*	55.5	*Swain(1997).
Nile water evaporation	-2*:-3**	-2:-3	*Abu Zeid (1992) **Allam(2007).
Nile water needed for navigation	-0.3*	-0.3*, -0.4**	*Abu Zeid (1992) **FAOAQUASTAT(2005)
Rainfall	1.8*	>0.165**	*FAOAQUASTAT(2005) **Hefny and Shata (2004); Abdallah (2006)
Reused Nile water (groundwater extraction)	7.5*	7**	*Abdel-Shafy and Aly (2007); Mostafa *et al*. (2004). **MWRI(2010) P.C
Reused Nile Water flow	0.7*:1.3**	0.7-1.3	* Khalifa (2011) **Egypt State Information Service (n.d.).
Desalinated seawater	0.275	0.275	International Desalination Association (2013)
Fossil groundwater	2.7*:4.16**	>1.6**	* Allam (2007) ** Nour and Khattab (1998) and Hefny and Shata (2004)
Total	78.7:>81.7	71.2:>76.5	

Egypt consumes up to 79.5 BCM/yr (MWRI, 2014). The extracted groundwater quantity reaches up to 4.6 BCM/yr (El Arabi, 2012). In 2010, the estimated groundwater extraction was ~ 8 BCM comprising 6.2 BCM from the Nile Basin seepage waters, 1.7 BCM from the eastern and western deserts coast (ICARDA and AusAID, 2011).

Nowadays, Egypt has carried on developing projects based on groundwater. Currently, there are political disputes around the Nile River treaties. By 2025, the deficiency in water supply is expected to jump up from 13.5 BCM/yr to 26 BCM/yr if the current rate of usage goes on the same rate (Omar and Moussa, 2016).

Reclamation projects in Egypt are vital. The projects established west of Nile Delta depend on groundwater as the only available resource. Great numbers of wells have been drilled. A rapid extension of the reclaimed area (Figure 3.2) has occurred since the 1990s which is obvious from satellite data (King and Salem, 2012).

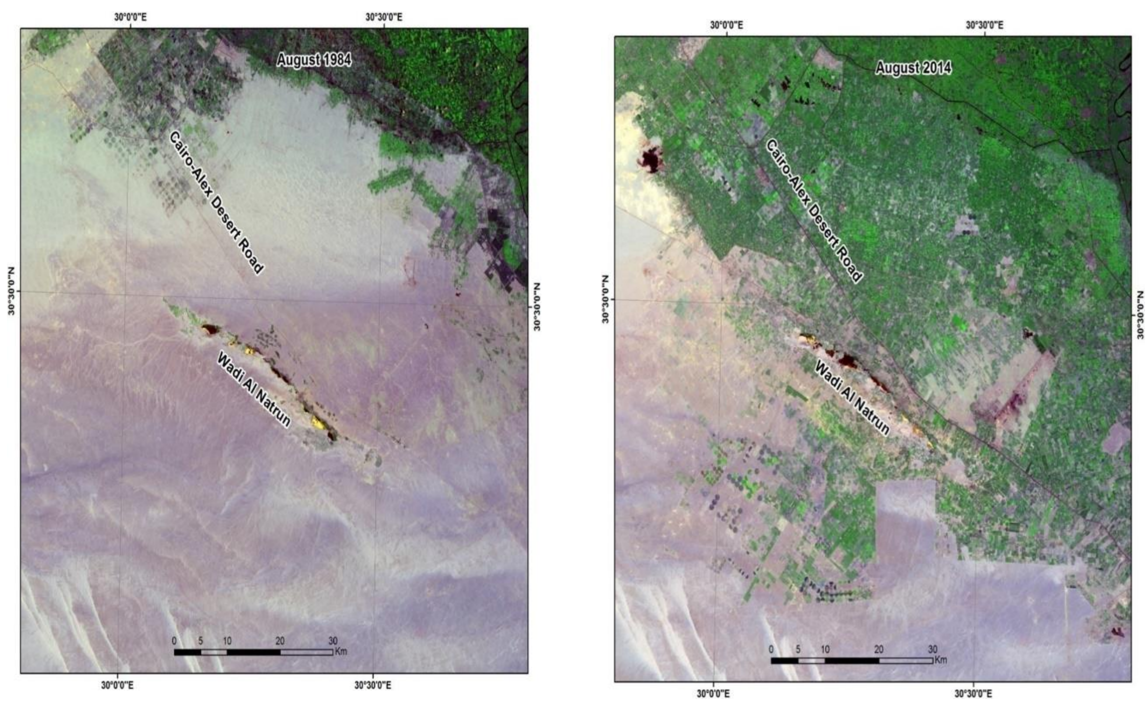

Figure 3.2. Satellite image of Wadi El-Natrun (Remote Sensing Authorization, 2015).

3.2 Regional Hydrogeology

Groundwater exists in Western Desert and Sinai in aquifers where most of it is deep and non-renewable. The total estimated volume of groundwater is about 40,000 BCM. The growing concern on the sustainability of available water resources lead to intensive studies to monitor water resources.

The following is a brief review of different aquifers that represents the hydrogeological framework of Egypt:

According to RIGW (2004), the hydrogeological framework of Egypt is represented by six main aquifer systems (Figure 3.3): The Nile aquifer, the Moghra aquifer, the Nubian aquifer, the carbonate aquifer, the coastal aquifer and the fissured hard rock aquifer. Each aquifer differs from the other by its unique properties.

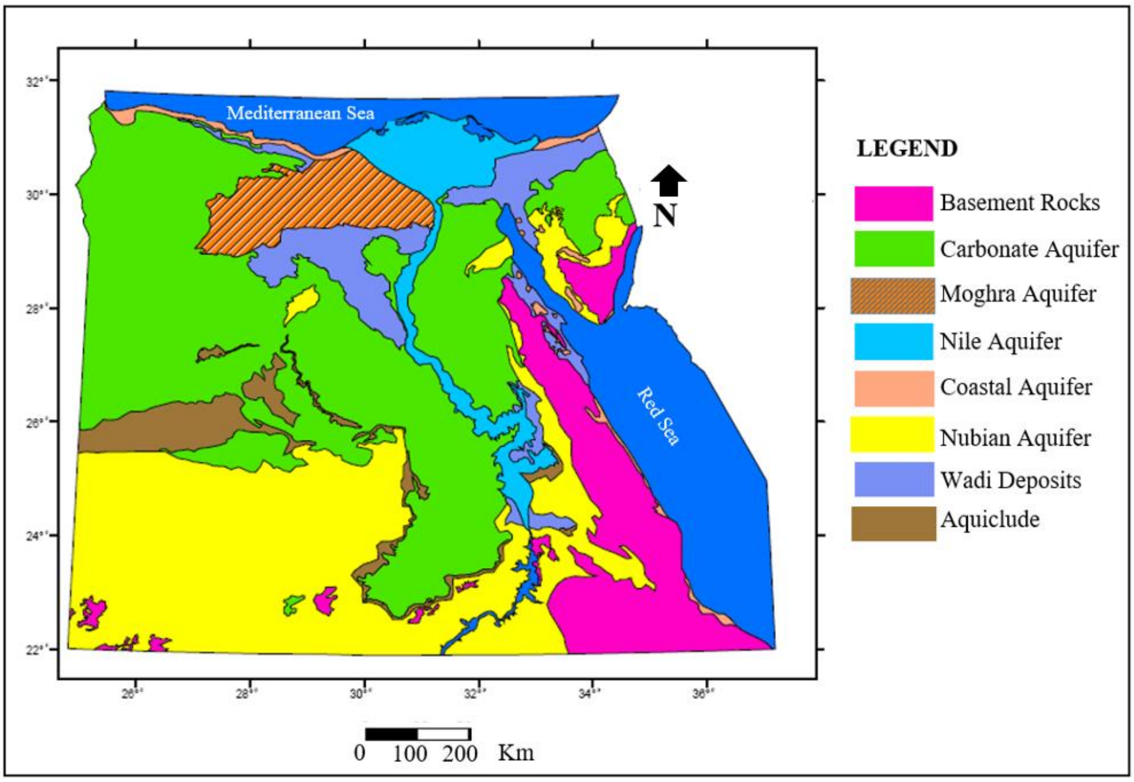

Figure 3.3. Aquifer system in Egypt modified after RIGW (2004).

3.2.1 The Nile Delta Aquifer System

The Nile Delta aquifer extends along 22,000 km² along the western fringe of the Nile Delta. It is designated to Neogene and Quaternary sediments occupying the Nile flood plain and desert fringes on both sides. The Nile Delta aquifer is dominated by graded sand and gravel topped by a clay to silty clay layer. The aquifer attains a thickness of 300 m south of Egypt and thins out to the north where it reaches a few meters in Cairo. However, it increases gradually to the north along the Mediterranean coast line reaching a thickness of more than 1000 m. The water seepage from drainage and irrigation canals from the Nile comprise continuous recharge sources to the aquifer (Attia, 1985). The Quaternary strata of the Nile Delta are hydrologically important as it comprises the immensity of the main Nile Delta aquifer (Shata and Hefny, 1995). The Nile aquifer is connected to the Mediterranean Sea and is affected by saline water intrusion (Kashef 1983).

3.2.2 The Nubian Sandstone Aquifer System

The Nubian sandstone aquifer system is designated to the Paleozoic-Mesozoic rocks (Klitzsch and Wycisk 1999). Its widely distributed along the Western Desert, Sinai and parts of the Eastern Desert. The groundwater can be reached at shallow depth in places like Siwa Oasis (north of Western Desert) or deep depth reaching more than 1 Km deep as in east Uweinat and Kharga (south of the of Western Desert). The Nubian Sandstone Aquifer was recharged during the humid periods (5,000 to 10,000 years and > 25,000 years) and considered as non-renewable water resource (Sefelnasr, 2007).

3.2.3 The Moghra Aquifer System

The Moghra aquifer is designated to the Lower Miocene sediments occurs chiefly in the western edge of the Delta extending till Qattara Depression. The aquifer varies in thickness from about 60 m to about 900 m. Groundwater quality varies from good to high saline. Diab *et al*. (1995) attributed the recharge of aquifer to the deep percolation from the Nile alluvium in the east.

3.2.4 The Coastal Aquifer System

The coastal aquifer system is designated to the Quaternary and Neogene sediments in the area along Mediterranean and the Red Sea coasts. The water-bearing formation along the west coast of Mediterranean Sea is mainly oolitic limestone and calcareous sandstone. It attains thickness of about 40 m. Allam *et al*. (2002) evaluated the groundwater as brackish in general and basically recharged by rainfall.

3.2.5 The karstified Carbonate Aquifer System

The karstified carbonate aquifer is designated to the northern and middle potions of the Western Desert. It consists of Upper Cretaceous to Eocene rocks.

3.2.6 The Fissured and Weathered Hard Rock Aquifer System

The fissured carbonate aquifer is designated to the Upper Cretaceous to the Eocene rocks occur in the north and middle parts of the Western Desert. It is made up of limestone, dolomite, chalk and marl. It attains a thickness of 200 m up to 900 m. The salinity of groundwater ranges from 1000 to 8000 ppm (Attia 1998). The upward flow of groundwater through sandstone from the adjacent formations and from the surface water infiltration recharge the aquifer.

3.3 Local Hydrogeology

The west of Nile Delta region possesses high population due to water supply and soil potentialities. The surface water is represented by artificial canals and drains bisecting the area, linking River Nile by and western Nile Delta. These canals are basically dug in Quaternary deposits. The surface canals are in a direct connection with the Pleistocene aquifer (Soliman *et al.,* 2014). A large groundwater basin underlies the Delta of the Nile with an area of approximately 12000 km². It is bounded by the Mediterranean Sea in the North and by the Suez Canal in the East. The study of groundwater west of Nile Delta was initiated by the Desert Institute (1966) followed by REGW (1968). The area is affected by a notable decline in groundwater level, deterioration in water quality and decrease in well yields. The aquifer is present along alluvial plain of Nile Delta. It consists of graded sand and gravel, changing to fine and clayey facies in the north belonging to Pleistocene Age. The aquifer is topped by a clay cap which is considered to be a semi-confining layer. The thickness of aquifer ranges from 10 m at south to 30 m at north, it disappears at the eastern and western desert fringes. The Nile Delta aquifer is mainly made up unconsolidated coarse sands and gravels intercalated with clay lenses of deltaic deposits Pleistocene age ranging in thickness from 200 to 300 m and rests on a thick clay belonging to Pliocene Age (Sherif, 1999).

3.3.1 The Surface Water System

The surface water system in the area east and north of the study area is marked by a network of drainage and irrigation canals (Figure 3.4).

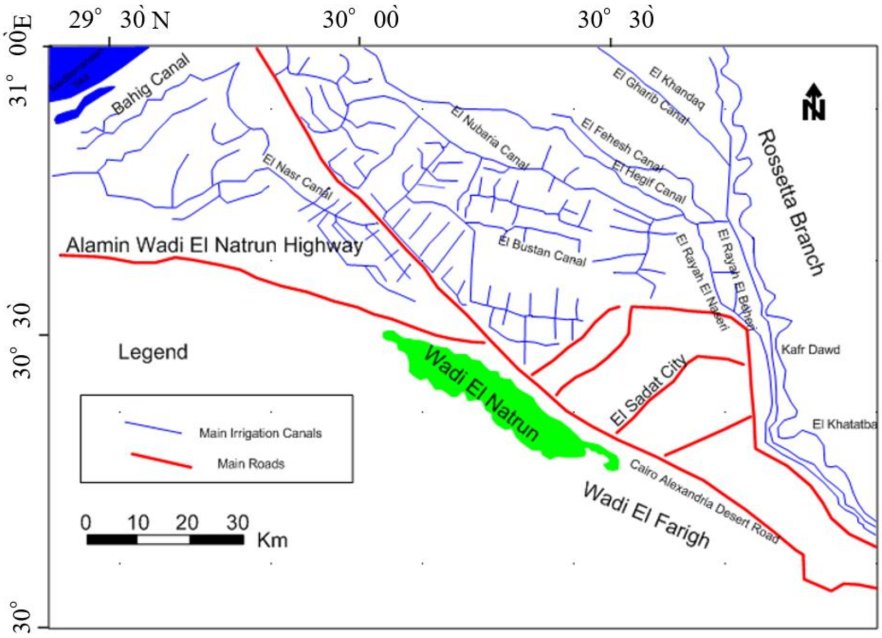

Figure 3.4: Surface water systems in the north and east of the study area after (Embaby, 2003).

Major canals that are distributed along the area west of Rosetta branch are El-Nubariya Canal (~50.3 km); El-Entlaaq Canal (~23.5 km); El Nasr Canal (~22.6 km); and El- Rayah El-Naseri (~ 21.8 km).

3.3.2 Wadi El-Natrun Aquifer System

The water bearing formations in the study area and its vicinities are divided according to geologic formations into different five aquifers named: The Recent, Pleistocene, Pliocene, Miocene and Oligocene aquifers. These sandy to clayey aquifers are hydraulically connected and considered as one hydrological unit (Figure 3.5). The Recent and Pleistocene (Quaternary aquifer) Pliocene, Miocene, and Oligocene aquifers. In this work, samples were collected from the Pliocene Aquifer. Wadi El-Natrun is characterized exclusively by the Pliocene and Recent aquifers. The increase in the number of groundwater wells and over-exploitation caused by increase of water demand associated with population growth led to groundwater depletion (Acra and Ayoub 2001).

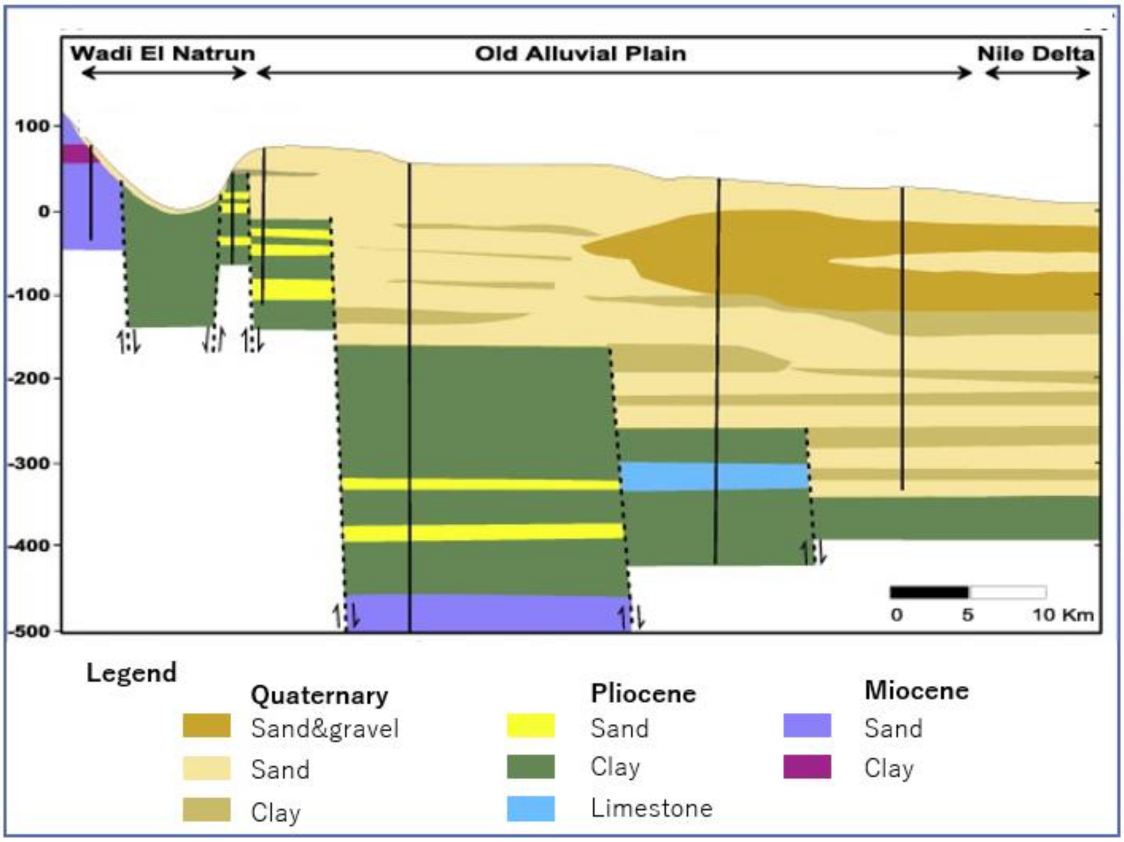

Figure 3.5. Geological/hydrogeological cross-section of the shallow aquifers between Rosetta branch and Wadi El-Natrun modified after (Dawoud *et al.*, 2005).

The thickness of the fresh water bearing formation in the Wadi El-Natrun aquifer ranges from 15 to 25 m (REGWA, 1993). Wadi El-Natrun is located just south west of Tahrir province. The water level generally decreases from east to west. The Recent aquifer occurs only in Wadi El-Natrun. It attains a thickness of 8 m up to 10 m. The Pliocene aquifer is exclusively restricted to Wadi El-Natrun (El Fayoumy, 1964). It is overlain by the Pleistocene aquifer and is differentiated into two water bearing formations (horizons) (Upper El Solymanya Member, semi confined) (Lower El Muluk Member, confined) (El Fayoumy, 1964 and Omara and Sanad, 1975). The upper horizon is around 15 m and is presented to the east of Wadi El-Natrun. The lower horizon is around 10 m and is (dominated) in the depression. The Pliocene aquifer is composed of clay facies interbedding with water bearing sandy layers (semiconfined), it is believed that Pliocene and Pleistocene aquifers are connected hydraulically. The Pliocene aquifer possess a lower storage capacity and transmissivity than other aquifers (RIGW, 1990). The lithology is represented by sand and clay facies. It ranges in thickness from 150 to 300 m (Masoud and Atwia, 2010; Ibrahim, 2005). The thickness of the aquifer deposits reaches 140 m with 90 m saturated thickness. The total estimated recharge of this aquifer reaches 60 million m^3/day. The thickness of this aquifer decreases from east to west and from south to north. The Pliocene aquifer discharges artificially to the productive wells and naturally to lakes and Recent aquifer. As a result of that several problems have appeared due to the inappropriate management of water resources leading to notable decline of the groundwater level with salinization and water pollution (Liu *et al.*, 2001; Dassi *et al.*, 2005; Fehdi *et al.*, 2009). The Pliocene aquifer is the main aquifer system in Wadi El-Natrun area. It consists of three water bearing zones. The upper zone is mainly made up of sand and sandstone with 15 m thick (El-Fayoumy, 1964). The upper zone is separated from the middle zone by clay beds and less sandy measuring 10 m thick (Upper-Middle Pliocene). The lower zone (Lower Pliocene) is separated from the overlying layer by 10 m thick clay and/or sandy clay from 10-15 m thick and is made up of sand and carbonaceous clays in its base (El-Hinaawi and Atwa, 1973). The lower and middle parts of the aquifer act like one hydraulic unit. The upper aquifer is phreatic and the lower aquifer is under confined conditions (El- Awdy, *et al.*, 1997). Average transmissivity is 943 m^2/d and storativity (S) 7.5 x 10^{-4} m^2/d with average 35 m thick of saturated zone (General Petroleum Company, 1978) (Table 3.4). The annual rate of groundwater withdrawal from Delta aquifers and the Nile Valley attain number of 6.13 BCM (Abdel-Galil *et al.*, 2004).

Table 3.4: Hydraulic parameters in Wadi El-Natrun.

Author	Saturated Thickness (m)	Storativity (S)	Transmissivity T (m²/day)	Hydraulic conductivity
Pavlov (1962)	-	-	-	15.38
Saad (1962)	3950	3.95×10^{-3}	1292	52.98
El Shazly *et al* (1975)	-	-	-	77.76
GPC (1978)	-	-	1240	-
Abdel-Baki (1983)		6.92×10^{-3} to 4.33×10^{-2}	4130 to 5927	-
Warner *et al.* (1984)	-	4.9×10^{-3}	-	-
RIGW (1990)		1.7×10^{-2}	230 327-500	
Ibrahim (2000)	-	-	3034	-
Molla *et al.* (2005)	-	-	-	30 to 100

The Miocene aquifer is mainly distributed west and south of Wadi El-Natrun. It’s also named Moghra Formation. It’s composed of sand and sandstones interbedded with clay. Unconfined aquifer whereas in Wadi El-Natrun is semi-confined it lies below the Pliocene aquifer. water table slopes westward and northward. Both northwest of Wadi El-Natrun and Moghra Depression act as discharging area. The discharge of groundwater takes place naturally either through the outflow into the drainage system, evapotranspiration and inter-aquifer flow of groundwater or artificially through the direct extraction by wells, which is the main discharge component from the aquifer. The average rate of evapotranspiration in the study area is about 1900 mm/yr. RIGW and MWRI estimated the annual extraction in 1985 was about 0.353 BCM from the Pleistocene aquifer 0.001

BCM from the Pliocene aquifer and 0.106 BCM from the Miocene aquifer. The sum extraction of three aquifers was about 0.460 BCM from around 1650 wells. However, by 2006, the annual extraction of groundwater witnessed a profound increase reaching about 1.040 BCM from the Pleistocene aquifer, 0.154 BCM from the Pliocene aquifer and 0.6 BCM from the Miocene aquifer. The extension in reclamation area to in the west of Nile Delta is the direct reason for such dramatic increase. Wadi El-Natrun possess high, moderate, low and very low sensitive parts for desertification. The western south parts of the depression are high and moderate sensitive whereas the northern part of the depression is marked by a very low and low sensitive for desertification (Ali and El Baroudy, 2008).

3.3.3 Origin of Groundwater in Wadi El-Natrun

The origin of the groundwater in the Wadi El-Natrun has been reviewed by numerous authors. Wadi El-Natrun acts as an endorheic basin that collect water, the groundwater flow toward Wadi El-Natrun depression comes from all directions as a radial flow from the seepage of the Rosetta branch and surface water canals (Pavlov, 1962; Shata and El Fayoumy, 1967; Atia *et al*., 1970; El- Maghraby, 1990; Geirnaert and Laeven, 1992). The Lower Miocene aquifer is recharged from southern section of the Nile Delta basin whilst Wadi El-Natrun and Moghra depression in the northwest and west are recharged from the Lower Miocene aquifer (Abdel Baki, 1983). The movement of groundwater from east to west across Wadi El Farigh is managed by an old buried Nile channel which deflects the flow of groundwater towards Wadi El-Natrun Depression (Shata *et al*., 1962 and Ahmad, 1993). Rain has no effect in recharge of aquifer as annual rainfall is 39.3mm (El-Hinnawi and Atwa, 1973). Geriesh *et al.* (2015) postulated that current groundwater flow could be affected by the climatic changes during Holocene Period (5500-8000 yr B.P) where the eustatic sea level has been fluctuated between humid and dry periods leading to the draining and refilling of the Pleistocene aquifer in Nile Delta for several times.

3.4 Climate Changes in Egypt and Other Saharan Areas

3.4.1 Arid Areas

Arid and semi-arid zones comprise more than one third of Earth surface where evapotranspiration exceeds rainfall with varying degrees of aridity (McKnight and Hess, 2000). These areas are basically situated between 18° and 40°latitudes of both N and S of the equator (Figure 3.7) including large parts of northern and southern Africa, the Middle East, Western USA and the southern areas of South America, most of Australia and large areas of central Asia and even parts of Europe (NOAA, 2010). Water availability is vulnerable to changes in climate which in turn will exceed the present pressure of water pollution that has influence on ecosystems, human health, and water system reliability in vast areas of the world (Stocker *et al.,* 2013). Desertification results from group of actions which are motivated in arid and semi-arid environments as water is the main limiting element of vegetation growth (Batterbury and Warren, 2001).

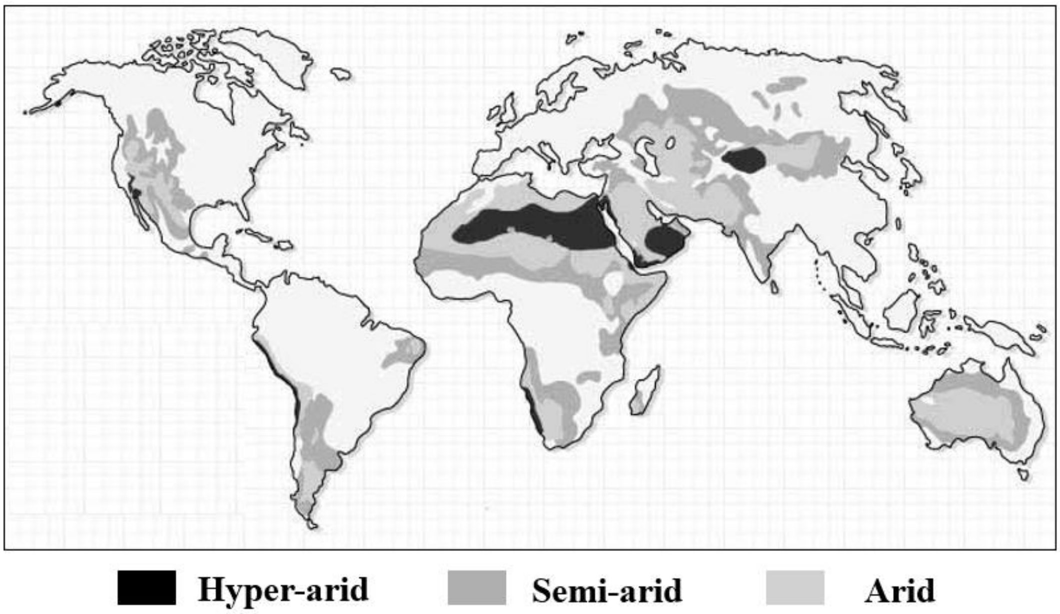

Figure 3.6: Distribution of hyper-arid, arid and semi-arid regions along the globe (IUCN, 2004).

3.4.2 Sahara (The Great Desert)

Sahara is the 3rd largest desert in globe following Antarctica and the Arctic. It occupies an area of 9,200,000 km² covering a major part of north Africa (Figure 3.7) stretching from the Red Sea in the east, the Atlantic Ocean in the West, and the Mediterranean Sea in the north. It has only 3.5 million inhabitants.

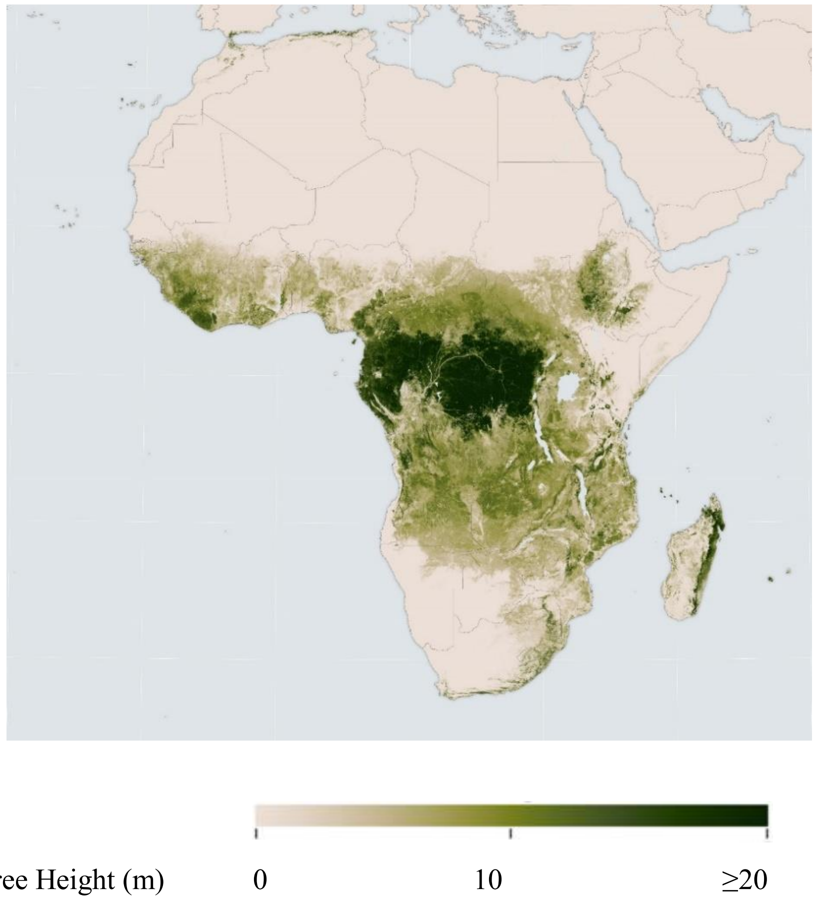

Figure 3.7: NASA Earth Observatory (2017).

In Africa, only 5% of arable regions is irrigated and more likely reliable to climate change (Siebert *et al.*, 2010). Consequently, food production per capita is endangered (Funk and Brown, 2009). Groundwater is used as a primary water resource for drinking in rural areas where a few reasonable substitutes are available (MacDonald and Calow, 2009). The water supply expansion in domestic water helps profoundly in moving people out of poverty (Hunter *et al.*, 2010). People utilize1000–1700 m^3 of the globe's surface as well as groundwater resources annually; which ranges between 22% and 150% of the annual global supply of fresh water (Hoekstra and Wiedmann, 2014). This proportion is supposed to increase in the next 30 years. Providing a clean groundwater based on proper method in accordance with water abundance will allow sustainable management (Calow *et al*., 2010). Although groundwater is a renewable resource, suitable time is necessary to allow replenishment of underlying groundwater aquifers. Groundwater supplied drinking water for two billion people and sustains about 40% of global cropland irrigation (Aeschbach-Hertig and Gleeson, 2012). The growing population associated with the rise of water demand (Figure 3.8) led to acceleration in the number of wells influenced by groundwater depletion and over-exploitation (Hwang *et al.,* 2004).

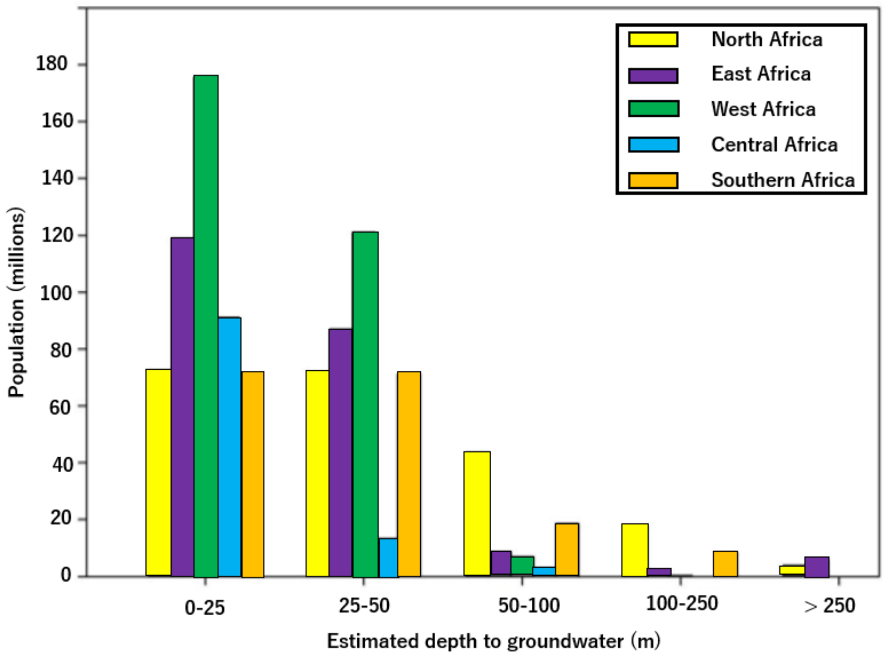

Figure 3.8: Distribution of regional population over different depths to groundwater (Bonsor and MacDonald, 2011).

3.4.3 Groundwater in Saharan Areas

Groundwater represents one third of modern-day human water uses. It is the main source for domestic, industrial, and agricultural uses in arid and semi-arid regions. There is a steady decline in water tables from 0.5 to 2 m/yr where abstraction exceeds recharge affecting development, human requirements and ecosystem (Matete and Hassan, 2005). Arid and semi-arid environments low rain fall result in low surface water runoff and exclusively rely on groundwater in arid and semi-arid zones may become drier (Bates *et al.*, 2008). Groundwater is the sole reliable of water for increasing number of land-users with the vulnerability aridity and climatic changes (WWAP, 2009). Consequently, the development of water resources in arid and semi-arid areas is crucial. The groundwater aquifers in Sahara are depleted in heavy isotopes compared with the average δD and $\delta^{18}O$ values recorded in precipitation (Conrad and Fontes, 1970).

The sedimentary aquifers in Africa (Figure 3.9 to 3.12) contain around 0.66 million km^3 in storage and 0. 44 million km^3 of this water present in eight Sahara countries (MacDonald *et al.*, 2012). Arid areas in Africa depends on groundwater reserves to sustain life and to face the effects of climate change. The sedimentary aquifers in the North African countries Libya, Algeria, Egypt and Sudan possesses the largest groundwater volumes. The Nubian Sandstone aquifer system which underlies (Egypt, Libya, Sudan, and Chad) and is represented by more than 2.5 km thick. Researchers from the British Geological Survey and University College London made the first attempt to map the groundwater aquifers across Africa. The largest groundwater volumes across Africa present in the North African countries Libya, Algeria, Egypt and Sudan large sedimentary aquifers, representing 0.66 million km^3.

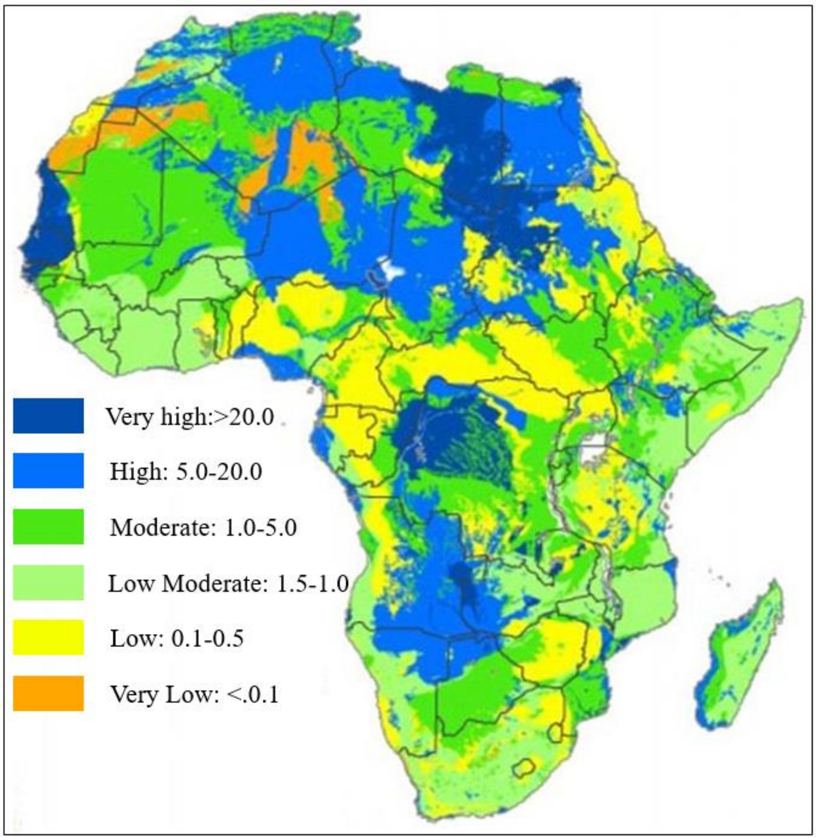

Figure 3.9: Aquifer productivity (Liters per second) (MacDonald *et al*. 2011).

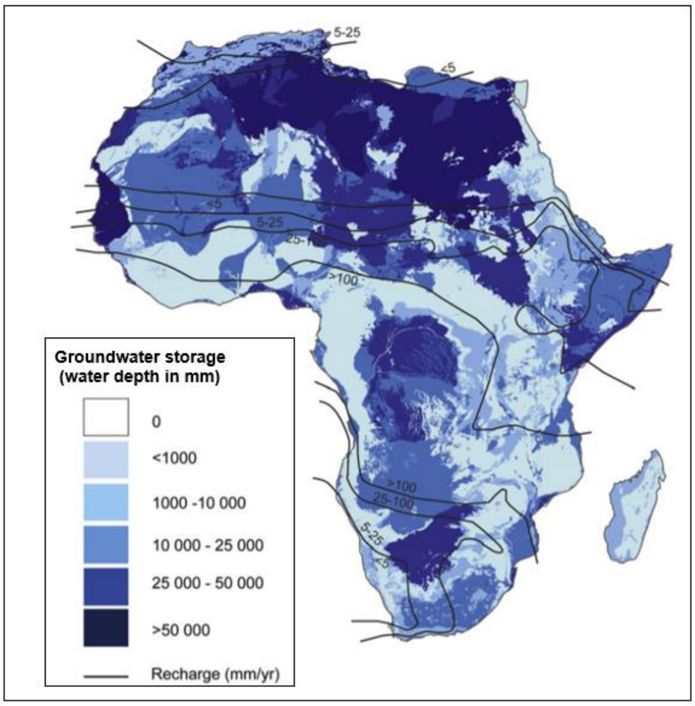

Figure 3.10: Storage of groundwater for Africa on basis of effective porosity and saturated aquifer thickness (Döll and Fiedler, 2008).

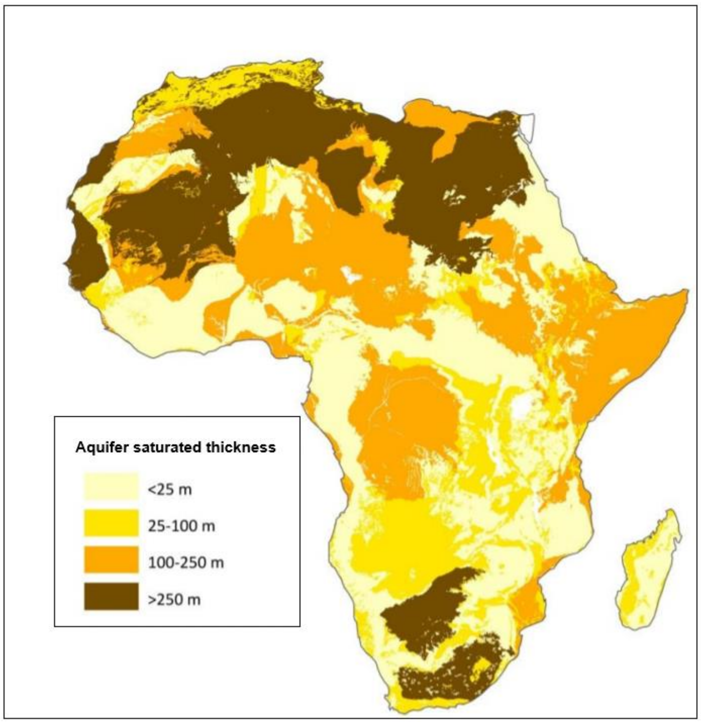

Figure 3.11: Thickness of saturated aquifer across Africa (MacDonald *et al.,* 2011).

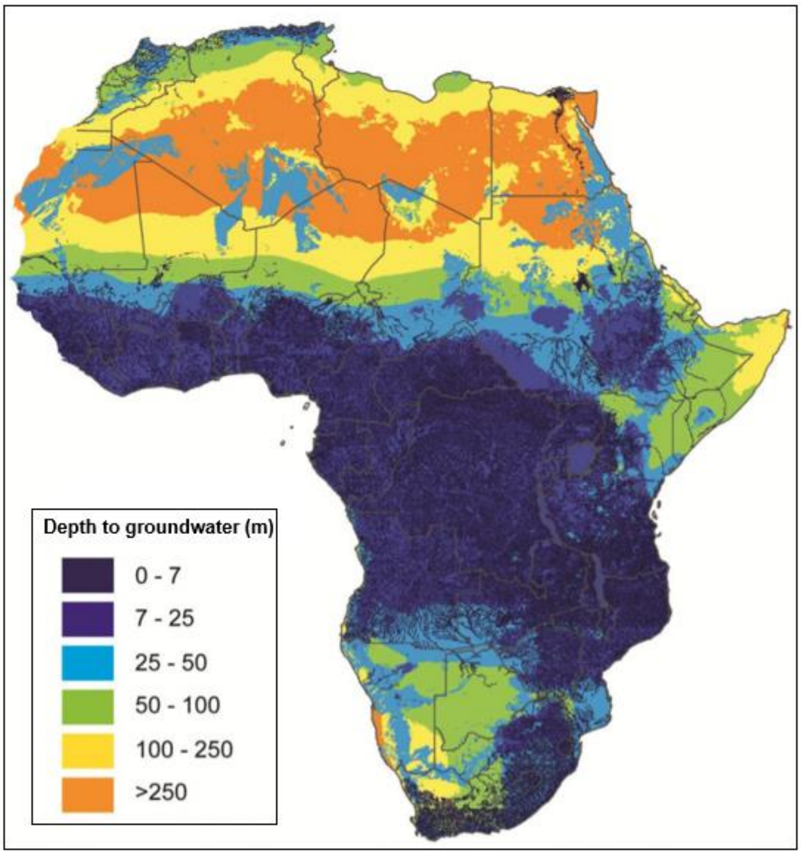

Figure 3.12: Estimation to depth to water in Africa (Bonsor and MacDonald, 2011).

3.4.4 Management Challenges

Mismanagement of groundwater has led to contamination and depletion particularly in early drilled shallow wells. Monitoring of groundwater especially in arid areas by large and small consumers is a great challenge as the community is based on groundwater. Monitoring of land degradation and Sustainable Land Management (SLM) is related to the awareness of functions and changing conditions of the socio-ecological systems within the area and its adjacent (Safriel *et al.*, 2005). Agriculture consumes up to 66% of water usage (Scanlon *et al.,* 2007) and hence, is a crucial factor in global environmental change. The groundwater exploitation in Africa were used as a source for cultivation water supply along several millennia (King *et al.*, 2010). The number of wells has been increasing over the last three decades. The North African aquifer system receives minimal recharge compared to extraction and paleowater reserve in deep aquifers hence, is considered as non-renewable (CEDARE, 2001 and OSS, 2003).

An expansion in Normalized Difference Vegetation Index (NDVI) was recorded by comparing Landsat images (from 1987 and 2003) of the studied areas, covering an area of 10,942 and 6,970 hectares in the Nefazaoua NSAS and North Western Desert, respectively. The latter has increased by 150% whereas the Nefazaoua has recorded 44% expansion. The expansion can be ascribed to groundwater irrigation expansion mostly unauthorized (Siegfried, 2004). Sustainable management of groundwater is a perquisite in arid areas where a large volume of the available groundwater resources is being utilized as it is the main source for providing fresh water.

In the arid regions of many developing desert areas, the advent of technologies in pumping methods led to a revolution in Groundwater coupled with private sector engagement in agricultural activities have increased the challenge of groundwater management on both social and ecological aspects (Giordano and Villholth, 2007 and Shah, 2009). Groundwater exploitation is mostly operated by farmers representing around 70% of groundwater extraction per year as a consequence the groundwater reserve is depleted in a way that threatens the future generations and influences the climate change (WWAP, 2009).

3.4.5 East African Monsoons and Paleoclimatology

The last 6000 Yr BP have attracted the attention of scientific research due to gradual change in climate conditions unlike glacial-interglacial changes (Wanner *et al.*, 2008). The current hyper-arid Saharan desert during Early Holocene epoch ~ 5:11 (Ka) ago was marked by presence of large and small lakes (Figure 3.13) (Jolly *et al.*, 1998; Wanner *et al.* 2011). Holocene climatic changes were cyclic (Burroughs, 2003). Egypt's climate is controlled by various climatic regimes, drived by the dry continental air that flows from Sahara and Arabian Peninsula in addition to tropical air from the Atlantic and Indian oceans (Buckle, 1996).

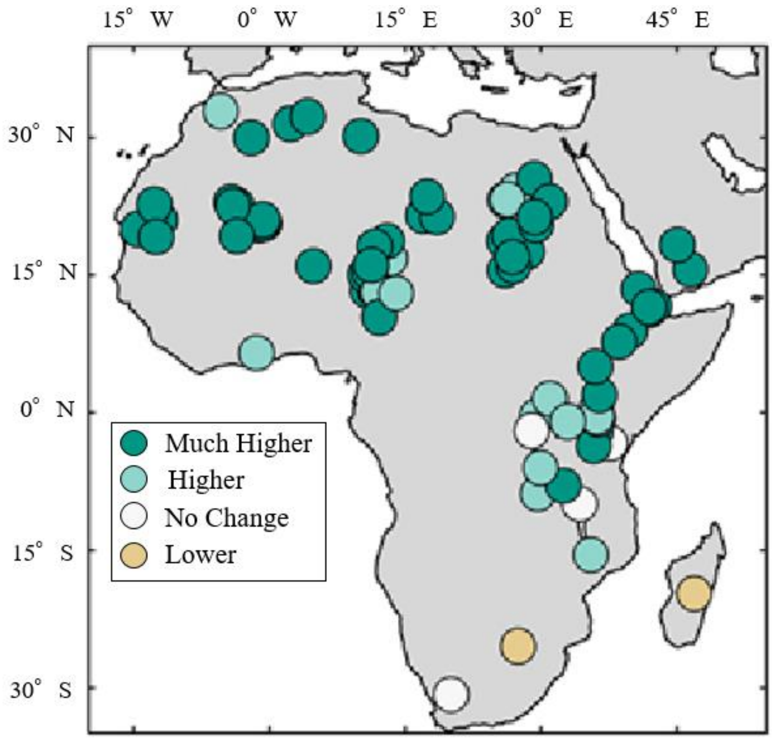

Figure 3.13: Lake levels distribution across Africa 9000 yrs. BP. (COHMAP members, 1988; Street-Perrott *et al.*, 1989; Tierney *et al.*, 2011; deMenocal and Tierney, 2012).

The paleohydrological and paleoecological records from eastern Sahara reflected that the dry conditions emerged in Egypt prior to Sudan. The African monsoon circulation was impaired as a result of the decrease in the north Atlantic temperature (Tjallingii *et al*., 2008). The seasonal precipitation in Egypt is controlled by the African monsoon. wind blows inland from the cooler oceans toward the warm continents, and to the opposite directions in winter (Oliver, 2005). Therefore, the summer monsoons are wet whereas winter monsoons are dry; the most important impact of the monsoon circulation is the seasonal rainfall however, not as profound like Asian monsoon (Buckle, 1996).

Holocene is the youngest geologic epoch, it began when the Earth's climate and environment approach their modern form (Oliver, 2005). The Holocene started by the termination of the last glaciations 8500 BC. The Holocene climate were marked by fast climatic changes (Oliver, 2005; Williams and Nottage, 2006). There transitions between humid and arid phases was dramatic, the rain was heavy Lake Victoria where White Nile originates in addition to other equatorial lakes. Another source of water to the White Nile is water of the River Sobat from the Ethiopian mountains (Whittington and Guariso, 1983). The equatorial countries (Kenya, Uganda, Rwanda, Burundi, Central African Republic and the Democratic Republic of Congo) represent a catchment area (Hassan, 2007).

A drop in the flooding levels of Nile and decrease in humidity occurred between 6100 and 5100 BC (Lario *et al.*, 1997; Nicoll, 2004). There was a severe famine in Egypt from the year 4000 to 3000 BC. (Hassan, 2008). The decrease in the flood levels started for short time after 3700 BC, followed by a long time of high floods until 3000 BC (Sterling, 1999).

The Sahara had alternating periods of aridity and increased rainfall that could be attributed to former variations in the monsoon system and extent of the intertropical convergence zone (ITCZ). Many parts of the Egyptian desert received numerous humid phases along the past

300,000 years. Surface water encroached channels and formed drainage patterns, some of which are now exposed, and others are covered by eolian sand. These drainage patterns are important to evaluate the potential of groundwater (Bonnefille *et al.* 1995; Haynes *et al.* 1989). The development of current landforms is inherited from the complex interaction of the dominating geomorphologic processes and past hydro-climatic fluctuations and (Williams 2009). The early Holocene was marked by one or more wet periods in North Africa (Gasse *et al.*, 1990). These wet periods have initiated a substantial recharge to groundwater that is noted particularly in the phreatic aquifers of arid regions (Fontes *et al.*, 1993).

In many arid and semi-arid regions, the currently utilized groundwater was recharged during previous humid episodes of the Pleistocene and Holocene whereas recent recharge is small and changeable (Edmunds, 2001). Minor climatic perturbations at the century to decadal scale like the little ice age or prolonged drought of the past millennium (800-1000 BP). Various aquifers possess evidence of paleowaters that were recharged during the early Holocene or Pleistocene when the global climates and recharge patterns were crucially non-identical. Groundwater movement specifically in coastal parts was enriched by the lowering of sea level by up to 130m during late Pleistocene glaciation. Some severe wet periods took place by around 7000 BP of the ice age end and the rise of modern sea levels as in Africa consequently, distinctive groundwater recharge occurred unlike the modern era (about 4000 years) characterized by extreme aridity forming arid and semi-arid areas.

3.4.6 Climate Change

The tropics have played an essential role in the global climate changes as it likely decoupled from high latitude climate. Precessional variations in insolation may directly affected the intensity of African precipitation, irrelevant to high-laitude climate variability (Denison *et al.*, 2005). Precipitation is the crucial interannual variable in African climate. Seasonal variations in the position of the Intertropical Convergence Zone (ITCZ) apply a remarkable control on the seasonal pattern of precipitation maxima over much of Africa (Nicholson, 2000). North, West, Central, East, and Southern Africa are affected by a discrete atmospheric circulation system, separated in large part by the ITCZ. They encounter characteristic patterns of interannual, teleconnections, variability, and surface features (Semazzi *et al.*, 1988).

3.4.6.1 The Holocene climate and African Humid Period (AHP)

The current hyper-arid Sahara (Figure 3.14) possessed green landscape and nearly covered by grasses and bushes (The timing and inclination of this period are controversial). The African Humid Period was triggered by the dramatic increase in summer precipitation as a response to orbital forcing of African monsoonal climate and strengthened by terrestrial and oceanic circuit. The termination of African Humid Period has been controversial; this transition was not simultaneous or instantaneous along Africa (Kuper and Kröpelin, 2006). The Sahara encountered severe climatic changes during Holocene Epoch. The African Humid Period (AHP) reached its maximum in north Africa between 6000 and 9000 yr BP (deMenocal and Tierney, 2012). The Sahara is considered to be a natural gallery displaying depiction and decorations in rocky caves or surfaces. The Sahara used to be dwelled by various of animals and hunters (giraffes, hippos, aurochs, antelopes, and elephants). The population of the Sahara was fluctuated during Holocene. A great increment in human population was recognized from 11,000 yr BP. Followed by drop in number between 7600 and 6700 yr BP. ended by substantial diminish in population between 6300 and 5200 yr BP. accompanied to the offset of AHP (Manning and Timpson, 2014).

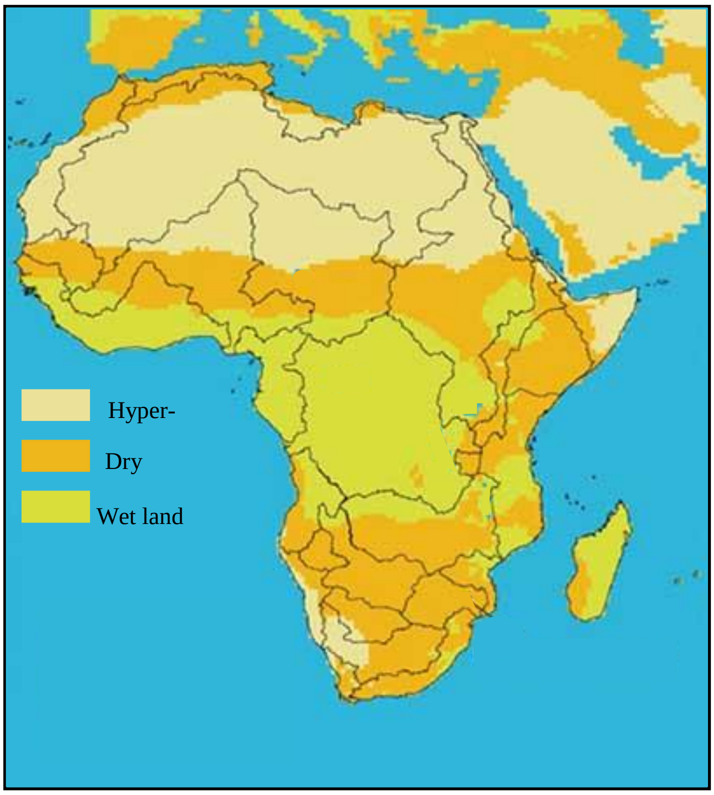

Figure 3.14: Map of Africa and land distribution.

The African Humid Period is the latest of hundreds earlier humid events spanning since Miocene (9 Ma) and maybe earlier driven by the African monsoonal climate that responds to periodic variation in Earth's orbit around the Sun repeatedly each 20,000 yrs. North Africa has undergone outstanding climate changes from Early and Middle Holocene till present. A dramatic change has affected the landscape from vegetation marked by small and large lakes into hyper-arid desert (deMenocal and Tierney, 2012). The start of the aridity has a reflection (impact) on density change of population and concentration on hunting and fishing in addition to domesting animals (Caneva 1991; McCorriston and Martin 2009). Broad area of Africa was variable wet during the early Holocene, the remarkable climate change during Holocene was the African Humid Period (Liu *et al*., 2017). Using fluvial sediments, (Kropelin and Soulie-Marsche, 1991) assumed that the early to mid-Holocene was more humid than nowadays.

3.4.7 Egyptian Culture History and Climate Change

Egypt is vulnerably subjected to Global Warming consequences (World Bank, 2009). During the 20th Century temperature increased 0.7°C and is vulnerable to a further 1 to 4°C increase during the 21st Century (IPCC, 2007). A global increase in temperature in the average of 0.15 degrees Celsius per decade is observed from mid-1970's (Brohan *et al*., 2006).

In North Africa, the African Humid Period lasted from 15 to 5 ka (DeMenocal *et al*., 2000) whereas South Africa indicated overall warm conditions from 10 to 6 ka (Holmgren *et al.*, 2003). During the Early Holocene, East Africa and the Arabian Peninsula witnessed a humid condition (Figure 3.15) (Street-Perrott *et al.* 1989; Tierney *et al.* 2011). Numerous water bodies continually occupied Sahara (Brooks, 2006).

Figure 3.15: Map of Africa 5000 BP.

The African Humid Period (AHP) was an outstanding hydrological system and has been hub for the study of African paleoclimate and its implications (Brovkin, *et al*. and Claussen *et al.* 1999). It had an impact on the rise of pharaonic civilization along the Nile (Hoelzmann, *et al.* 2001). The borderline of monsoon rainfall started to be directed southwards from 6000 to 4000 BC and as a consequence the vegetation began to shrink throughout the Sahara and southern Arabia (Nicoll, 2001 and Kindemann *et al.*, 2006).

Between the year 5000 to 2000 BC Egypt was green Sahara however, it changed slowly to dry and ended up by hyperarid conditions in 1500 BC. The trend of paleoclimate records during the last 3000 is arid. The paleoclimate studies assist in forecasting future behaviors, sociological, economic and political consequences. The closure of African Humid Period in the eastern Sahara is considered to be gradually associated with rainfall decrease during the mid-Holocene (Weldeab *et al.*, 2007 and Francus *et al*., 2013). Hence, the Egyptians were affected by these changes. It still supported an abundant humid-climate flora and fauna and significant human populations. The rainfall was supposed to reach 500 mm/year at least, where the surface waters allured people and wildlife (Nicoll, 2004). People who inhabited the plains of the Egyptian Eastern Sahara, moved to the oasis depressions (Dakhla and Farafra, to the Nile, or to Gilf Kebir) in response to intensification of aridity during the millennia of 5000 and 4000 BC (Linstädter and Kröpelin, 2004).

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CHAPTER 4
HYDROGEOCHEMISTRY

4.1 Introduction

Hydrogeochemistry or chemical hydrogeology is a subdivision of hydrogeology. The increase in pressure on both quality and quantity of groundwater by overexploitation has an effect on the vulnerability of water system. Recently, one of the tremendous environmental challenges is water shortage. A dramatic decline in groundwater levels and decrease in freshwater force government to take action for preventing the increasing pressure on groundwater which leads to vulnerability of water resources (both quality and quantity) and the aquatic environment. Enhancement of an integrated sustainable water management policies using scientific data is mandatory for a better reconnaissance about water quality, quantity, management and assessment.

Dincer *et al.* (1974) demonstrated that the semi-arid areas overlain by sands and sandy soils are tremendously favored as recharge zones. Sand dune-covered areas may sustain remarkable direct recharge from heavy storms. The soil type and soil thickness are key variables in controlling recharge. Deterioration of the groundwater quality is crucial problem in arid and semi-arid regions (Liu *et al.*, 2015). The factors affecting groundwater resources acquire great interest as a part of Nile Basin water resource (Kebede *et al.,* 2017).

The attention is diverted from groundwater development to sustainable groundwater management of suitable quantity and good quality to assure the long-term availability (Limaye, 2003). To overcome the growing demands and pressures on hydrologic systems. Analytical tools and information on management evaluations of water resources are of utmost important to help decision makers in facing the encountered challenges. Providing sustainable sources of water in arid area for a growing population is a great challenge, the hydrochemical study is essential for assessing and classifying of water quality. The chemical composition of groundwater is primarily based on the geology in addition to, major geochemical processes and reactions occur within the groundwater system controlling water quality. Graphical presentation of chemical analyses simplifies understanding of groundwater and aquatic system.

The sources of groundwater in Wadi El-Natrun have been debatable and the behavior of isotopic composition as well as salinity have not been closely and/or fully discussed along span of time (four years in the current study). The tendency of groundwater to salinization is a basic problem for groundwater in Egypt; especially the precipitation is not significant.

The following chapter introduces insights into the geochemistry and sources of groundwater by methods of isotopic and chemical studies.

4.2 Isotopes in Hydrology

Isotopic techniques and geochemical analyses allocate the best way to assess present recharge and to track recharge history particularly in semi-arid and arid regions, for identification of the source and the age of water. Isotopes are atoms, which possess identical atomic number, however, they have a varied mass number and as the atomic number (number of protons) defines an element, thus, isotopes are the same element with a different neutrons number (van Grieken and de Bruin, 1994). They are used broadly for studying water resources including both surface and groundwater. Urey (1947) established the foundations of stable isotopes geochemistry. The term “Isotope Hydrology” has been used since the 1950s and started to become an interdisciplinary science. It could be defined as the application of environmental isotopes and tracers to study parts of the hydrological cycle (Aeschbach-Hertig, 2006). The isotopic content is managed by paleoclimate, latitude, altitude, temperature, evaporation and condensation cycle (Clark and Fritz, 1997) and consequently is of utmost interest in determination of hydrogeology, hydrology and paleoclimatology (Paternoster *et al.*, 2008).

The stable isotopic content represents a powerful tool for investigating groundwater mixing and aquifer recharge (Maloszewski *et al.*, 1990 and Blavoux and Letolle, 1995). The combination of geochemical data and stable isotopes give basic information about processes related to water cycling and rock–water interaction that may change water quality in surface water and groundwater systems.

The ratio of $\delta^{18}O$ is controlled by precipitation and evaporation changes (Figure 4.1) because of temperature fluctuations, presenting a very good record of the climate. ^{16}O evaporates first as it is lighter than ^{18}O, so in warm, tropical areas, the ocean is high in ^{18}O. Furthermore, as water vapor condenses to form rain, water droplets rich in ^{18}O precipitate first as it is heavier than ^{16}O that's why the cold and polar regions are depleted in ^{18}O as it all precipitates out in the lower latitudes, but they are high in ^{16}O. Moreover, the tropics possess a large amount of ^{18}O but have little ^{16}O. Changes in the climate can greatly affect the ratio of ^{18}O and ^{16}O and can alter their distribution throughout the globe (Table 4.1). In addition to the effects of evaporation and precipitation, the amount of ice near the poles affects $\delta\ ^{18}O$ ratio. When temperatures are cold in the polar regions, ^{16}O becomes locked in glaciers after it precipitates in the high latitudes. Therefore, in warmer climates when glaciers melt, they release the ^{16}O that is trapped in them, and the oceans become enriched in ^{16}O. As a result, the amount of ice in the high-latitudes take part in regulating $\delta\ ^{18}O$ value.

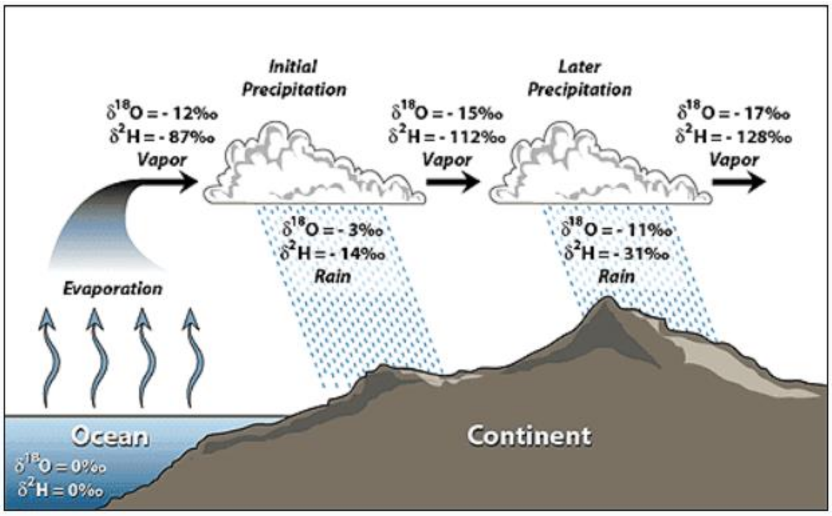


Figure 4.1: Diagram of δ^2H and $\delta^{18}O$ fractionation (Coplen *et al.*, 2000).

Table 4.1: The isotopic ratios of water in natural reservoirs after Mook (2001)

Natural reservoir	**δ ^{18}O (‰)**	**δ D (‰)**
Ocean water	-6 ~ +3	-28 ~ +10
Arctic sea ice	-3 ~ +3	0 ~ +25
Marine moisture	-15. ~ -11	-100 ~ -75
Lake Chad	+8 ~ +16	15 ~ +50
Alpine glaciers	-19 ~ -3	-130 ~-90
Greenland	-39 ~ -25	<-150 ~-100
Antarctica	-60 ~ -25	<-150 ~ -100
(Sub)Tropical precipitation	-8 ~ -2	-50 ~ -20
Mid-latitude rain∗	-10 ~ -3	-80 ~ -20
Mid-latitude snow∗	-20 ~ -10	-160 ~ -80

∗ from the summer/winter precipitation at the IAEA station Vienna.

Environmental stable isotopes (^{18}O, D) are applicable and beneficial tracers for hydrologic characterization in groundwater systems flow regimes and origin of groundwater recharge (Leontiadias *et al.*, 1988). Unless diluted or mixed with waters of various isotopic composition, groundwater often preserves its stable isotopic signatures (Fontes 1980 and Gat 1981). Therefore, natural stable isotopes are prosperously used in identifying origin and quality of groundwater as it commonly possesses an identifiable isotopic contents along ten thousand years unless exposed to temperature above 60-80°C (Gat and Gonfiantini, 1981). Isotopes are used to demonstrate various hydrogeological processes as well as indicators of past and present climate changes and of palaeowaters.

Subsurface waters are classified according to its origin into meteoric and paleowater. The following is a brief summary:

Meteoric Waters

Meteoric waters are directly originated from precipitation or fresh surface water, recharged through unsaturated soil zone. Clayton *et al*. (1966) delineated that waters from numerous sedimentary basins were basically from meteoric origin.

The empirical equation known as the Global Meteoric Water Line (GMWL) $^2H = 8\ \delta^{18}O + 10$ was founded by Craig (1961). A linear correlation between δ^2H and $\delta^{18}O$ (Gat and Carmi, 1970; Rozanski *et al.*, 1993) in samples of precipitation, snow water, and river water from all over the world collected from a worldwide network of stations has been established (Figure 4.2), water samples from rainfall stations were collected globally by the IAEA (International Atomic Energy Agency), Dansgaard (1964) and Gat (1980) confirmed the same results: $\delta^2H = (8.17 \pm 0.08)\ \delta^{18}O + (10.56 \pm 0.64)$ by comparing the results with local and global meteoric water lines. The correlation coefficient $r^2 > 0.95$ which in turns shows a close association between oxygen and hydrogen so their ratios and fractionations can be discussed altogether. Normally, the isotopic composition decrease from low to high latitudes (Figure 4.2).

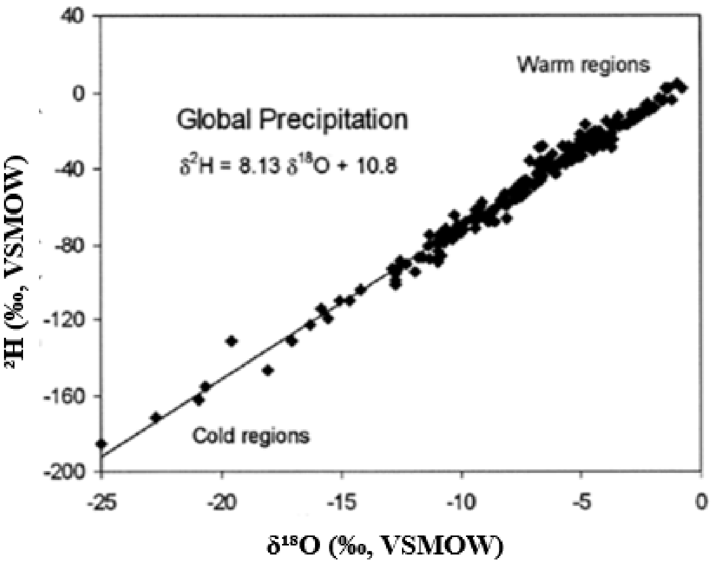


Figure 4.2: Linear relationship between δ^2H and $\delta^{18}O$ in global precipitation (from Clark and Fritz 1997) after Craig (1961) and Rozanski *et al*. (1993).

Local Meteoric Water Line (LMWL) is defined as the line derived from rainwater collected from local sites whether one or set of sites in certain area. The slope of local lines possesses a value around (8 ± 0.5).

There are five crucial factors affecting the isotopic composition of precipitation: latitude, altitude, continental, amount, and seasonality (Dansgaard, 1964). Meteoric waters (i.e. atmospheric moisture, precipitation and its derivatives: ground and surface waters, glacial and surface ice) are mostly depleted in the heavy isotopes compared to oceanic waters (Mook, 1982). Temperature and $\delta^{18}O$ possess a strong correlation in the hydrological cycle, as isotopic fractionation is strongly dependent on temperature under equilibrium conditions (e.g. condensation). The decline in temperatures urge condensation and isotopic fractionation, precipitation becomes more depleted in ^{2}H and ^{18}O resulting in more negative $\delta^{2}H$ and $\delta^{18}O$ values (Clark and Fritz, 1997). In humid areas, the isotopic composition matches local precipitation whereas in arid areas, groundwater is enriched in heavy isotopes. The deviation of isotopic values away from GMWL is due to evaporation of water or mixing up with evaporated water which causes increase in the oxygen and hydrogen isotope ratios of the residual fraction and this residual water no longer follows the trace of meteoric water line (MWL) (Kendall *et al.*, 1998). In that case the plot is below (MWL) commonly with slope range (2:5)

Paleowaters

Paleowaters are groundwater that was formed during geologic past. In some arid regions like North Africa, that has encountered extreme climatic changes. A different climatic conditions across the past several hundred thousand years as humid intervals are called pluvial times. Gat and Issar (1974) differentiate the isotopic composition of paleowaters from recent water as lately recharged groundwaters are affected by evaporation (Figure 4.3). The deviation of groundwaters that have undergone evaporation before, during, or after recharge is easily recognized by their isotopic composition. Their heavy isotope content is higher than that of nonevaporated waters in the region and these waters do not obey the relationship $\delta D = 8\ \delta^{18}O + 10$ (Craig, 1961).

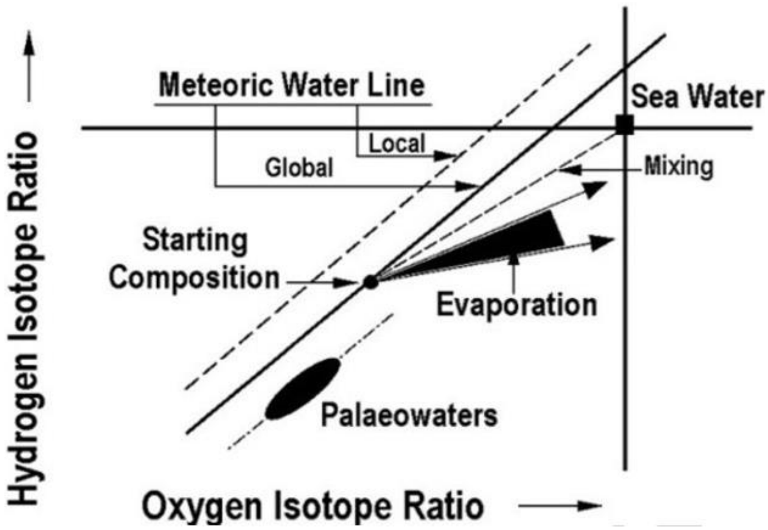


Figure 4.3: Diagram of δ^2H and $\delta^{18}O$ in natural waters (Gat *et al.*, 2001; Aggarwal *et al.*, 2007).

In an evaporative environment, isotopic composition of water is ultimately enriched in heavy isotopes $\delta^{18}O$ and δ^2H (Gat, 1984). The process of evaporation is divided into the following stages (Craig and Gordon, 1965):

A. Presence of saturated sublayer of water vapor at water-atmosphere interface (depleted in heavy isotopes).

B. Excessive depletion in vapor results from migration of vapor from the boundary layer and different diffusion rates.

C. The vapor reaches turbulent region and mixes up with vapors from other sources.

D. Condensing of vapor (turbulent region) and back reacting with water surface.

Under very arid conditions and only in small water bodies the enrichments in heavy isotopes is tremendous. Gonfiantini (1986) demonstrated the isotopic composition of small, shallow lake in the Western Sahara where δ^2H and $\delta^{18}O$ value are (+129‰ and +31.3), respectively. Crombie *et al*. (1997) noted that $\delta^{18}O$ values of ancient Western Desert ground water ~ -11%.

4.2.1 Isotopic Fractionation in Water

Isotopic fractionation was depicted by Urey (1947) as an exchange of isotopes (e.g. ^{18}O and ^{16}O) between any two molecular species or phases that are participating in a reaction. These reactions may be changes of state,

$H_2O_{Water} \leftrightarrow H_2O_{Vapour}$

Fractionation can be defined as the process of isotopes partitioning during changes in state. The fractionation occurs naturally as a result of mass differences between species with identical chemical characteristics. The fractionation process result in unequal concentration of an isotope over another. It is expressed as fractionation factor (α) or fractionation coefficient (ε) (Clark and Fritz, 1997). Isotopic fractionation can originate from equilibrium and/or kinetic equilibrium.

$\alpha = R_{reactant}/R_{product}$

4.2.2 Mechanism of Fractionation

4.2.2.1 Equilibrium Fractionation

The term equilibrium fractionation is used to describe the isotopic exchange reactions that take place between two different phases of a compound at a rate that maintains equilibrium, as with the transformation of water vapor to liquid precipitation. The fractionation associated with the equilibrium exchange reaction between two substances A and B (i.e., the fractionation of A relative to B) can be expressed by use of the isotope fractionation factor α (alpha) (Mook, 2006):

$H_2O_{Water} \leftrightarrow H_2O_{Vapour}$

$\alpha_{A-B} = R_A/R_B$ R= $^{18}O/^{16}O$ or $^{1}H/^{2}H$ where R = the ratio of the heavy isotope to the lighter isotope (D/H, $^{18}O/^{16}O$)

The relationship between fractionation factors α and δ-values can be expressed as followed (Clark and Fritz, 1997):

$\alpha_{A-B} = (\delta_A + 1000) / (\delta_B + 1000)$

The isotopic difference in these tow compounds can be expressed by the enrichment factor ε in ‰-notation

$\varepsilon_{A-B} = (\alpha_{A-B} - 1) * 1000$

Broadly speaking the α value shift by just a few percent from the equal-energy value of 1.00 (Friedman and O'Neil, 1977). The equilibrium fractionation factors (α) for the water liquid-vapor phase transition for δ^2H at 20°C equals (1.084) and at lower temperature of 0°C equals (1.111) (Majoube, 1971). At equilibrium, ^{16}O is enriched in the vapor phase, while ^{18}O is enriched in the liquid phase (Clark and Fritz, 1997). The rate of evaporation in water depends on hydrogen bond strength, while the rate of condensation depends on the concentration of water in the gas phase (Clark and Fritz, 1997).

Rainout, or condensation in clouds, is controlled by equilibrium fractionation (humidity=100%), and to produce rain, cooling of a vapor mass must occur first. The cooling causes equilibrium fractionation between the vapor and the condensing phases, which preferentially partitions ^{18}O and ^2H into rain (or snow) (Clark and Fritz, 1997). As a result, rain becomes isotopically enriched (+$\delta^{18}O$ and +δ^2H), whereas the residual vapor becomes isotopically depleted (Clark and Fritz, 1997). The Resultant rainouts are now depleted, with respect to earlier rainfall events, according to a Rayleigh-type distillation ($\delta^{18}O$ and δ^2H) (Clark and Fritz, 1997). The predictable fractionation of ^{18}O and ^2H associated with meteorological processes help in tracing the origin of water across the hydrological cycle.

4.2.2.2 Kinetic Equilibrium

The term kinetic (non-equilibrium) fractionation is used to describe the fractionation that is unidirectional, where equilibrium is not attained. In kinetic processes the lighter, i.e. lower atomic mass, of two isotopes of an element will form the weaker and more easily broken bond (Gat *et* *al.*, 2007). The lighter isotope is more reactive; therefore, it is concentrated in reaction products, enriching reactants in the heavier isotope. Kinetic fractionation is affected by surface temperature, wind speed, salinity and humidity (Clark and Fritz, 1997). Changing temperatures also drive changes in equilibrium isotopic fractionation. In addition, any sudden changes in temperature that move a system past thermodynamic equilibrium can lead to kinetic isotopic fractionation (Clark and Fritz, 1997). Kinetic fractionation is affected by several factors such as the temperature, wind speed, salinity, and the humidity, which considered as the most important factor (Kendal *et al.*, 1998). At lower humidity, water-vapor exchange is decreased, and evaporation becomes an increasingly non-equilibrium process (Clark and Fritz 1997).

4.2.2.3 Other Fractionation Effects

In salt solutions, isotopic fractionations took place between water in the hydration sphere and free water (Truesdell, 1974). The ratio of D/H on water vapour in isotope equilibrium with a solution increases with addition of salt, the hydrogen fractionation expands in the following order $CaCl_2$> $MgCl_2$>$MgSO_4$>KCl~NaCl>$NaSO_4$ (Horita *et al.*, 1993).

4.2.3 Rayleigh Equation

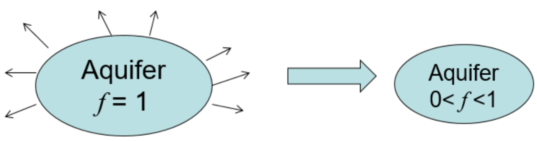
The Rayleigh equation describes the oxygen and hydrogen stable isotopes fractionation of a homogenous reservoir during water condensation/precipitation. The equation was derived by Lord Rayleigh fractional distillation of mixed liquid. (Rayleigh, 1896). i.e. the removal of water and the isotope fractionation during a physicochemical reaction. The usage of "Rayleigh fractionation" is restrained to chemically open systems where the isotopic species removed at every instant were in thermodynamic and isotopic equilibrium with those remaining in the system at the moment of removal. Ideal Rayleigh distillation occurs where the reactant reservoir is finite and well mixed, and does not re-react with the product (Clark and Fritz, 1997; Kendall and Mcdonnell, 1998).

Where R = ratio of the isotopes (e.g., $^{2}H/H^{1}$) in the reactant, R^{o} = initial ratio, X_1 = the concentration or amount of the more abundant (lighter) isotope (e.g., ^{16}O), and X_1^{o} = initial concentration.

Hence, if $f = X_1/X_1^{o}$ = fraction of material remaining, then:

$R = R^{o} f (\alpha\text{-}1)$

The Rayleigh equations can be used to describe an isotope fractionation process if: (1) material is continuously removed from a mixed system containing molecules of two or more isotopic species (e.g., water with ^{18}O and ^{16}O), (2) the fractionation accompanying the removal process at any instance (Figure 4.4) is described by the fractionation factor α, and (3) α does not change during the process (Kendall and Mcdonnell, 1998). Under these conditions, the evolution of the isotopic composition in the residual (reactant) material is described as (Kendall and Mcdonnell, 1998) $(R / R^{o}) = (X_1 / X_1^{o})\ \alpha\text{-}1$



$$\alpha = \frac{R_{\text{aquifer}}}{R_{\text{removed}}}$$

$$R_{\text{aquifer}} = R^{0}_{\text{aquifer}} f^{(\frac{1}{\alpha}-1)}$$

Figure 4.4: Schematic graph of mechanism of water loss from aquifer.

4.3 Previous Work

Isotopic values of D and ^{18}O of water resources in Egypt have been studied by several authors (Tables 4.2 and 4.3) and (Figure 4.5). The stable isotopes of Wadi El-Natrun area and its surroundings were studied by (Gomaa, 1995; Awad *et al.*, 1997; Dahab *et al.*, 1999; El Gamal, 2005 and Abotalib *et al.*, 2016).

Table 4.2: Stable isotopes values of various water resources in Egypt.

Water Resource	**Author**	**D (‰)**	**^{18}O (‰)**
Present Nile Water	Aly *et al*. (1989)	31.6	3.6
Old Nile Water	Awad *et al*. (1994)	4.3	-0.6
Paleowater	Sultan *et al*. (1997)	-72:-81	-10.6:-11.5
Rain Water	Geirnaert and Laeven (1992)	-8.8	-2.65

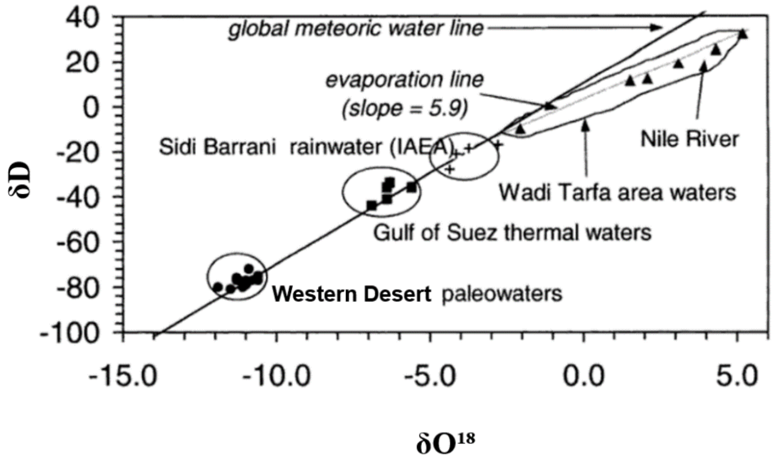


Figure 4.5: Relationship between δ^2H and δ^{18}O of different water resources in Egypt (Sultan *et al*., 2002) after different authors (Table 4.2).

Table 4.3: Different authors who studied water resources in Egypt.

Author	**Location**
Sultan *et al*. (1997).	Nubian aquifer paleowaters
Sturchio *et al*. (1996).	Gulf of Suez
IAEA/WMO (1998).	Sidi Barrani
Craig (1961)	Global meteoric water line

Gomaa (1995) attributed increase in salinity of Wadi El-Natrun to overpumping and influence of Wadi El-Natrun's salt lakes. He the identified two chemical water types (sodium chloride and sodium sulfate). El Gamal (2005) showed that the increase in TDS of groundwater resulted from various factors as follows:

1- The occurrence of clay beds of great thickness of lagoonal and marine origin with high content of salts inherited in the deposits of the aquifer, in addition to the salt lakes and marches.

2- The high rate of evaporation

3- The low groundwater recharge from the irrigation canals in the east and north.

4- The mismanagement of the farms and over-pumping due to excessive irrigation.

El Gamal (2005) identified four water types exist in the Pliocene aquifer: The first type $NaHCO_3$ represents 50 % of the samples and occupies the southern part of Wadi El-Natrun, the second type Na_2SO_4 represent（33 %） of the samples; the third and fourth types ($MgCl_2$ and $CaCl_2$) water types represent (17 %) and are restricted to high salinity samples. The delta values in the groundwater wells near the surface water are enriched in heavy isotopes, whereas the farthest wells are depleted in the heavy isotopes. Intermediate values are observed between these two extremes, this may be explained by mixing between old water that is present in the aquifers and the young water that infiltrates from the surface water. This interpretation is supported by linear mixing trends observed for the stable isotopes.

Dahab *et al.* (1999) studied the isotopic composition (δD and $\delta^{18}O$) in Wadi El Farigh and Wadi El-Natrun, they identified two mixing lines, one line (AB) between paleowater with δD = -84 ‰ and $\delta^{18}O$= -10 ‰ and Nile water before the completion of the Aswan High Dam with δD

= 4.3 ‰ and $\delta^{18}O$ = -0.60 ‰, the second line (AC) between paleowater and the Nile water after the completion of the Aswan High Dam with δD = 28.7 ‰ and $\delta^{18}O$ = 3.5 ‰.

El Gamal (2005) indicated that most of the water in Wadi El-Natrun area was infiltrated before the completion of the dam in 1969. He also excluded the recharge from precipitation and supported the recharge from the Nile.

4.4 Aim of Study

The current study aims to identify the recharge sources of groundwater in Wadi El-Natrun area, mechanism of isotopic fractionation and salinization and water quality assessment towards better understanding of groundwater characterization and recharge which in turn leads to good monitoring and sustainability of groundwater in response to the fact that there is a profound deterioration in groundwater quality and quantity.

4.5 Methods

Field and laboratory experiments were conducted to achieve the objectives of the study. The field work was conducted to gather information about the status and changes on groundwater geochemistry along four years. The study of same wells from 2014 until 2018 allowed tracking behavior of the wells and mechanism of fractionation and salinity. Laboratory observations were conducted on samples collected from five surveys from December 2014 until March 2018. The first survey aimed to explore the investigation area and collect water samples. The first survey was followed by another four trips aimed at successive collection of water samples from the same studied wells in the 1st expedition.

4.5.1 Field Procedures

The field work was conducted to gather information about the status and further changes on groundwater geochemistry with time. Groundwater samples were taken from 10 drilled wells (Figure 4.6); samples' collection extended from December 2014 to March 2018 (December 2014, February 2015, July 2016, November 2016 and March 2018). Wells are mostly located in the plains around the lakes and the extracted groundwater is used for irrigation and domestic uses. Total of 45 water samples were collected from wells with depths varying from 50 m to 85 m (Table 4.4) during five different times where a short term monitoring along four years by taking samples during different times.

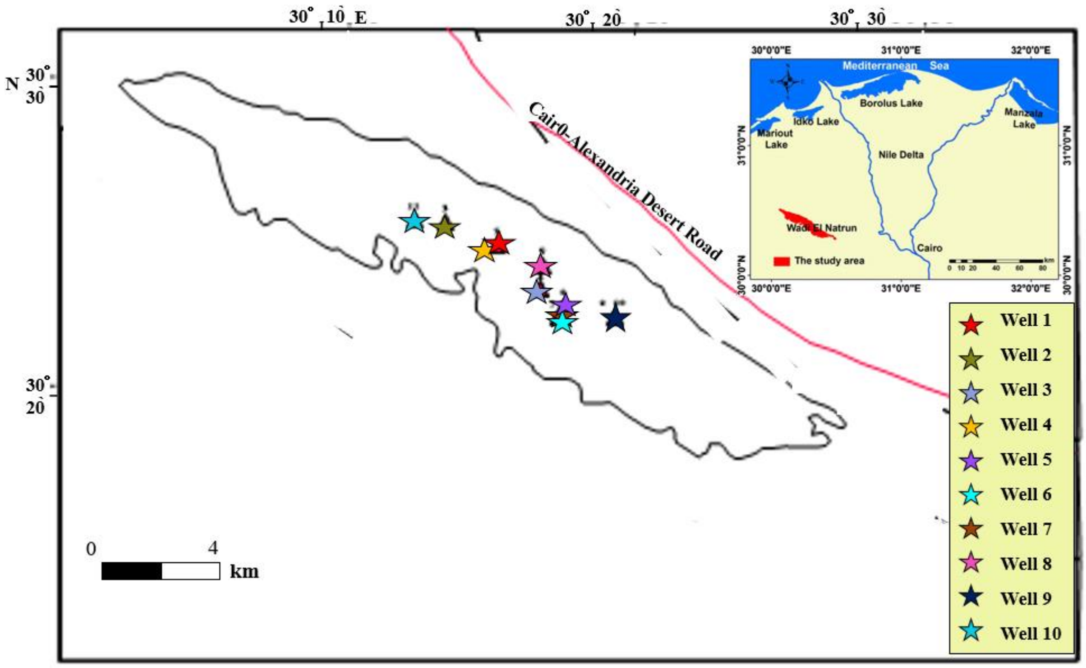


Figure 4.6: Location of the studied wells.

Table 4.4: Field measurements of the studied wells during March 2018.

Location	Well No.	Elevation (m) a.s.l	Location	Well No.	Elevation (m) a.s.l
Lat. 30°25′ N Long. 30° 17′ E	1	6	Lat. 30° 23′13"N Long. 30° 19′36"E	6	-7
Lat. 30°26′ 41"N Long. 30° 15′ 31"E	2	1	Lat. 30° 25′ N Long. 30° 19′ E	7	-12
Lat. 30°24′ 12"N Long. 30° 20′ 9"E	3	2	Lat. 30° 25′ N Long. 30° 19′ E	8	21
Lat. 30°25'51"N Long.30°17'24"E	4	12	Lat. 30° 16′38"N Long. 30°21′35"E	9	17
Lat. 30° 23′38" N Long. 30°19′48" E	5	-17	Lat. 30° 26′44" N Long. 30° 14′23" E	10	-9

Geographically, wells can be divided into deep and shallow wells (Figures 4.7 and 4.8). shallower wells have depths ranging from whereas deep wells attain depth ranging from 32 to 90 m. Samples from the following wells (1, 3, 8 and 10) possess high elevation and mostly low depths compared to wells (2, 4, 5, 6 and 7).

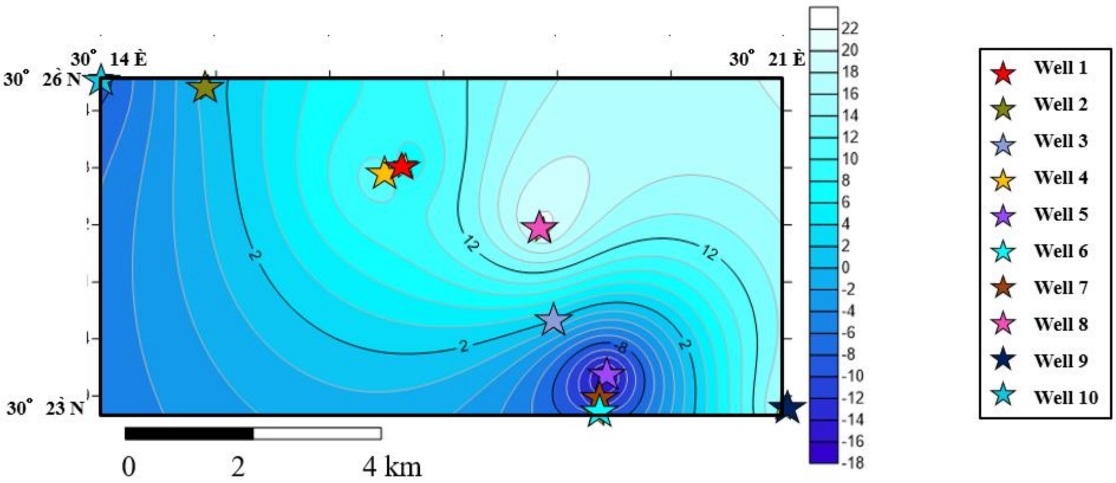


Figure 4.7: Contour map of surface elevation of the study area.

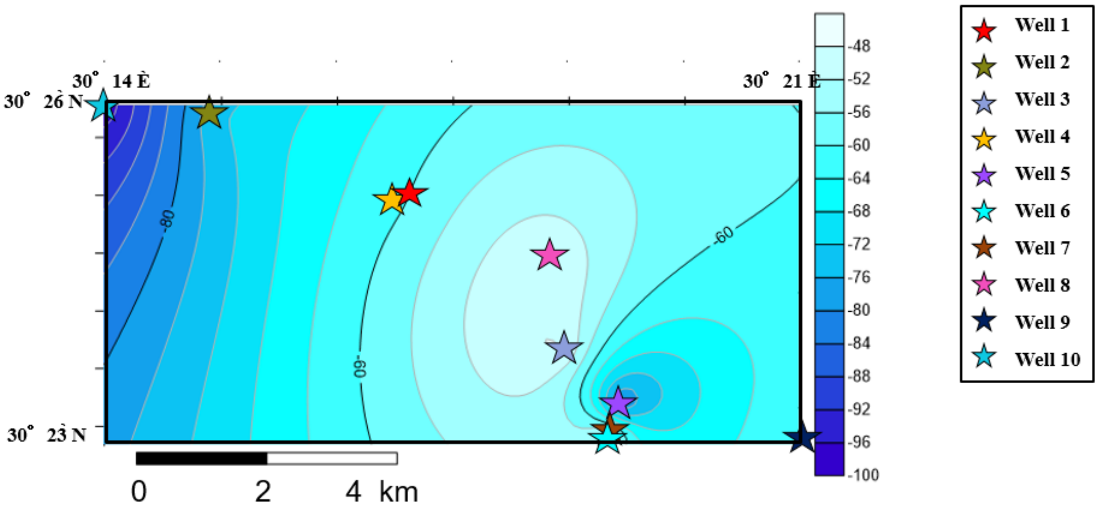


Figure 4.8: Contour map of wells depth in the area of study

Sampling was performed following to USGS manual for groundwater sampling: (1) wear appropriate disposable, powderless glove and change gloves before each new step during sample collection. Before sampling, wells were pumped sufficiently to flush the boreholes several times. (2) Soon after pumping began, pour and rinse water three times, use a syringe and a disposable cartridge for filtration (using a 0.45 µm cellulose acetate filter). Each well sample was collected in duplicated (50 and 500) mL polyethylene bottles to obtain reliable data for each well for major-ion and isotopic analyses. (3) temperature, pH, total dissolved solid (TDS) and specific electrical conductivity (EC) measurements were measured in the field immediately after sampling. (4) Labels were put on each sample. Samples were kept in temperature around 10°C and transported to Labs in Japan for isotopic composition and major ions analyses.

4.5.2 Analytical Procedures

4.5.2.1 Chemistry

The geochemical investigation provides an insight about the quality of groundwater and factors causing the deterioration. The studied samples were chemically analyzed to determine major cations and anions. The chemical analyses were carried out in Kyushu University. A total of 45 ground water samples and 5 Nile water samples were analyzed for major ions and isotopic composition. The concentrations of major cations (sodium, potassium, calcium and magnesium) were measured using Agilent 5100 ICP-OES model. Samples were acidified and diluted. Solution of sample was injected to ICP-OES and the solution is lead to Ar plasma. Ions are excited and back to ground state, then the energy difference between ground state and excited state is emitted as light. Prism distinguish this light by wave length and measure its intensity. The uncertainty value for ICP-OES method ~3% for (Na^+, Ca^{+2} and Mg^{+2}) and ~ 5% for K^+. Gran titration was used for bicarbonate measurement by estimating end point in strong acid (0.1N HCl). The uncertainty value for titration methods ~ 10%. The concentration of major anion (chloride, and sulphate) were measured by ion chromatograph using as KOH as eluent and H_2SO_4 as regenerating solution. The uncertainty values for anions (Cl^-, SO_4^{-2}, HCO_3^-) ion chromatography ~ 10%. The low values of uncertainty demonstrate that the accuracy of the analysis is within the acceptable range (Table 4.5). The results are displayed in graphical forms of trilinear Piper and Schoeller diagrams to make a visual comparison of the studied groundwater wells using Aquachem 4.0 software.

Table 4.5: Uncertainty of different measured elements.

Element	**Method**	**Uncertainty**
Na^+	ICP-OES	~3%
Ca^{+2}	ICP-OES	~3%
Mg^{+2}	ICP-OES	~3%
K^+	ICP-OES	~5%
Cl^-	Ion Chromatography	~10%
SO_4^{-2}	Ion Chromatography	~10%
HCO_3^-	Titration	~10%

4.5.2.2 Isotopic Composition

Environmental isotope measurement of the stable isotope ratio ($\delta^{18}O$ and $\delta^{2}H$) were conducted for groundwater of Wadi El-Natrun area to obtain additional insight into groundwater variations and to differentiate between different possible resources for aquifer recharge. Five water-sampling field expeditions were carried out along four years during (December 2014, February 2015, July 2016, November 2016 and March 2018). A total of 45 water samples from Wadi El-Natrun were analyzed for stable isotopic ratio of $\delta^{2}H$ and $\delta^{18}O$ using Liquid Water Isotope Analyzer (LWIA) equipped at Earth and Planetary Sciences Department, Faculty of Science, Kyushu University. We followed the Liquid Water Isotope Analyzer (LWIA) user manual (model 912-0008) (LGR, 2014) using 1 to 2 μL vial of filtered sample and same volume of standard solution.

The results are shown in terms of the conventional delta (δ) notation, in units of permil (‰) deviation relative to Vienna standard mean ocean water (V-SMOW; Coplen, 1996). Where

$$\delta = 1000 * \frac{(R_{sample} - R_{standard})}{R_{standard}} \qquad R = {}^{18}O/{}^{16}O \text{ or } {}^{1}H/{}^{2}H$$

R is defined as the ratio between the rare (often heavy) and common (often light).

For oxygen, the most abundant isotope is ^{16}O representing 99.76% of all oxygen on earth, while ^{18}O, the next most abundant isotope, represents 0.20%. For hydrogen, the most abundant isotope is ^{1}H representing 99.985% of all hydrogen on earth, while ^{2}H, the next most abundant isotope, represents 0. 015% (Table 4.6).

Table 4. 6: The natural abundances of oxygen and hydrogen isotopes after Mook (2001).

Oxygen		Hydrogen	
Isotope	Abundance (%)	Isotope	Abundance (%)
^{16}O	99.76	^{1}H	99.985
^{17}O	0.038	^{2}H	0.015
^{18}O	0.200	^{3}H	$< 10^{-15}$

As δ values for natural samples are typically very small, they are represented in parts per thousand (permil, ‰). The isotopic composition of oxygen ($\delta^{18}O$) in a sample, is calculated from the formula:

$$\delta^{18}O = 1000 * \frac{(^{18}O/^{16}O)sample - (^{18}O/^{16}O)VSMOW}{(^{18}O/^{16}O)VSMOW}$$

The isotopic composition of oxygen ($\delta^{2}H$) in a sample, is calculated from the formula:

$$\delta^{2}H = 1000 * \frac{(^{2}H/^{1}H)sample - (^{2}H/^{1}H)VSMOW}{(^{2}H/^{1}H)VSMOW}$$

The variation of $\delta^{18}O$ and $\delta^{2}H$ concentrations are controlled by fractionation during evaporation and condensation at equilibrium or non-equilibrium conditions. A positive $\delta^{18}O$ and/or $\delta^{2}H$ value signifies that the sample has more ^{18}O and/or ^{2}H than the reference, meaning that it is isotopically enriched, or "heavier". A negative $\delta^{18}O$ and/or $\delta^{2}H$ value, in contrast, means that the sample has less ^{18}O and/or ^{2}H than the reference, making it isotopically depleted, or "lighter".

The accuracy of analyses is calculated from standard deviation (1σ) of δ values for $\delta^{2}H$: ±1.80‰ and for $\delta^{18}O$: ±0.37‰.

4.6 Results

4.6.1 Description of Chemistry Classification

Field measurements show that the groundwater of the Wadi El-Natrun is slightly alkaline to alkaline, where the pH values range from 8.3 to 13(Table 4.7). Some wells show variation in the geochemistry along the time of study from 2014 until present. Sampling periods (February 2016) and (November 2016) show the highest TDS values. Generally, July 2016 show the lowest TDS values among the different sampling periods.

Table 4.7: Field measurements readings of some of studied wells in March 2018.

Location	**Well No.**	**Temperature (C°)**	**EC (dS/m)**	**pH**	**TDS**
Lat. 30°25′ N Long. 30° 17′ E	1	27.9	2.69	13	1500
Lat. 30°26′41"N Long. 30° 15′31"E	2	28.9	2.52	12.8	1400
Lat. 30°24′12"N Long. 30° 20′9" E	3	27.9	4.98	10.4	2300
Lat. 30° 23′38"N Long. 30° 19′48"E	5	24.6	2.43	8.3	1500
Lat. 30° 23′13" N Long. 30° 19′36" E	6	21.8	1.57	9.7	1100
Lat. 30° 25′ N Long. 30° 19′ E	8	27.6	1.59	13.2	600
Lat. 30° 26′44"N Long. 30° 14′23"E	10	28.8	1.88	12.7	1877

The summary of the groundwater chemical analysis results of different elements measurements and the calculated charge balance error are presented in (Tables 4.8:4.12).

Table 4.8: Measured elements of the collected samples in December 2014.

Well No.	CATIONS				ANIONS			Total Elements (mg/L)	Cations/ Anions Ratio
	Na^+ (mg/L) meq/L	Ca^{2+} (mg/L) meq/L	K^+ (mg/L) meq/L	Mg^{2+} (mg/L) meq/L	Cl^- (mg/L) meq/L	SO_4^{2-} (mg/L) meq/L	HCO_3^- (mg/L) meq/L		
2	405	83	8	39	515	350	224	1624	-0.01
	18	4	0.20	3	15	7	4		
3	592	104	7	39	599	690	186	2217	-0.00
	26	5	0.19	3	17	15	3		
4	151	20	4	7	117	49	233	581	0.01
	7	1	0.11	1	3	1	4		
5	385	96	6	45	490	396	245	1664	-0.01
	17	5	0.16	4	14	8	4		
6	213	19	4	9	199	51	251	746	-0.01
	9	1	0.10	1	6	1	4		
7	335	14	8	8	324	71	318	1078	-0.01
	15	1	0.22	1	9	1	5		
8	212	46	4	19	163	204	216	864	0.03
	9	2	0.11	2	5	4	4		
9	960	274	15	98	1060	1272	165	3844	0.04
	42	14	0.38	8	30	27	3		
10	538	148	11	69	783	542	217	2309	0.00
	23	7	0.28	6	22	11	4		

Table 4.9: Measured elements of the samples collected in February 2016.

Well No.	CATIONS				ANIONS			Total Elements (mg/L)	Cations /Anions Ratio
	Na^+ (mg/L) meq/L	Ca^{2+} (mg/L) meq/L	K^+ (mg/L) meq/L	Mg^{2+} (mg/L) meq/L	Cl^- (mg/L) meq/L	SO_4^{2-} (mg/L) meq/L	HCO_3^- (mg/L) meq/L		
1	748	166	15	65	732	1035	183	2945	0.01
	33	8	0.38	5	21	22	3		
2	366	66	7	21	414	251	265	1389	-0.00
	15.90	3	0.17	2	11.67	5	4		
3	386	99	7	38	462	446	150	1589	0.00
	17	5	0.18	3	13	9	2		
4	165	24	3	8	118	62	238	619	0.04
	7	1	0.08	1	3	1	4		
5	365	93	7	44	454	344	241	1549	0.01
	16	5	0.18	4	13	7	4		
6	212	30	5	14	231	78	260	831	-0.02
	9	2	0.13	1	7	1	4		
7	188	9	2	10	131	41	265	646	0.03
	8	0.43	0.06	1	4	1	4		
8	211	44	5	17	187	197	209	870	0.00
	9	2	0.13	1	5	4	3		
9	1015	310	15	115	1284	1364	177	4281	0.01
	44	16	0.38	9	36	29	3		
10	331	58	8	28	384	203	263	1274	0.01
	14	3	0.21	2	11	4	4		

Table 4.10: Measured elements of the collected samples in July 2016.

Well No.	CATIONS				ANIONS			Total Elements (mg/L)	Cations /Anions Ratio
	Na^+ (mg/L) meq/L	Ca^{2+} (mg/L) meq/L	K^+ (mg/L) meq/L	Mg^{2+} (mg/L) meq/L	Cl^- (mg/L) meq/L	SO_4^{2-} (mg/L) meq/L	HCO_3^- (mg/L) meq/L		
1	276 12	56 3	6 0.14	22 2	272 8	287 6	209 3	1128	-0.01
2	298 13	59 3	6 0.14	27 2	380 11	205 4	233 4	1208	-0.02
3	434 19	110 5	8 0.20	43 4	445 13	555 12	184 3	1779	0.02
4	157 7	24 1	3 0.07	9 1	137 4	68 1	231 4	629	-0.01
5	439 19	121 6	8 0.22	55 5	534 15	497 10	225 4	1879	0.01
6	196 9	34 2	4 0.11	16 1	232 7	67 1	245 4	794	-0.01
7	19 1	30 1	4 0.11	9 1	25 1	45 1	126 2	258	-0.10
8	225 10	49 2	5 0.13	19 2	201 6	217 5	209 3	925	0.01
10	742 32	179 9	13 0.33	77 6	876 25	830 17	244 4	2961	0.02

Table 4.11: Measured elements of the collected samples in November 2016.

Well No.	CATIONS				ANIONS			Total Elements (mg/L)	Cations /Anions Ratio
	Na^+ (mg/L) meq/L	Ca^{2+} (mg/L) meq/L	K^+ (mg/L) meq/L	Mg^{2+} (mg/L) meq/L	Cl^- (mg/L) meq/L	SO_4^{2-} (mg/L) meq/L	HCO_3^- (mg/L) meq/L		
1	447 18	104 4	9 0.20	39 3	483 15	622 7	163 4	1867	-0.01
2	310 26	60 5	7 0.19	25 3	431 17	192 15	231 3	1256	-0.00
4	175 17	26 5	2 0.16	41 4	149 14	96 8	231 4	720	-0.01
5	365 9	94 1	4 0.10	41 1	512 6	325 1	227 4	1568	-.01
6	201 15	30 1	3 0.22	12 1	265 9	54 1	243 5	808	-.01
7	203 9	31 2	6 0.11	12 2	273 5	39 4	249 4	813	0.03
8	390 42	85 14	9 0.38	38 8	484 30	382 27	196 3	1584	0.04
10	561 23	119 7	6 0.28	49 6	712 22	493 11	223 4	2163	0.00

Table 4.12: Measured elements of the collected samples in March 2018.

Well No.	CATIONS				ANIONS			Total Elements (mg/L)	Cations /Anions Ratio
	Na^+ (mg/L) meq/L	Ca^{2+} (mg/L) meq/L	K^+ (mg/L) meql/L	Mg^{2+} (mg/L) meq/L	Cl^- (mg/L) meq/L	SO_4^{2-} (mg/L) meq/L	HCO_3^- (mg/L) meq/L		
1	468	107	7	37	464	634	164	1881	-0.00
	20	5	0.18	3	13	13	3		
2	406	97	9	40	525	375	223	1674	-0.00
	18	5	0.23	3	15	8	4		
3	894	198	14	72	916	967	176	3237	-0.05
	39	10	0.36	6	26	20	3		
5	405	107	7	45	488	490	210	1752	-0.01
	18	5	0.18	4	14	10	3		
6	266	49	7	20	360	121	252	1076	-0.03
	12	2	0.18	2	10	3	4		
7	265	49	5	20	360	120	249	1069	-0.03
	12	2	0.13	2	10	3	4		
8	272	62	4	19	282	310	282	1231	-0.07
	12	3	0.10	2	8	7	5		
10	325	51	8	19	390	213	254	1261	-0.03
	14	3	0.21	2	11	4	4		

Major Cations

Sodium is the most abundant alkali metal in natural waters. Sodium and potassium occurrence in water expands the solubility of calcium carbonate (Garg, 1978). In the studied groundwater samples, sodium varies in concentration from (19 to 1015) ppm. Calcium is the principal cation in most of natural fresh water and is one of alkaline earth metals (Hem, 1970). Calcium is a common element almost encountered in all rocks, soils and waters (Buckmann and Brady, 1960). Concentration of calcium in the studied ground water samples of Wadi El-Natrun ranges from (9 to 310) ppm**.** Magnesium is abundant in carbonate rocks. It is around ten times soluble than calcium and magnesium has potential to stay dissolved than calcium (Davis and DeWiest, 1966 and Garg, 1978). Magnesium concentration ranges from (7 to 115) ppm. The concentration of potassium ranges from (2 to 15) ppm.

Major Anions

Chloride ion is founded in all natural waters and is basically derived from sedimentary rocks such as sandstones, shales, and carbonate rocks (Turekian and Wedepohl, 1961). The chloride in the studied samples ranges from (25 to 1284) ppm. Sulfate ion in natural waters mainly results from gypsum and anhydrite. In the present study, sulphate ion reaches up to 1364 ppm and possess a minimum value of 39 ppm. Carbonate and bicarbonate mainly exist in natural waters as a result of Ca and/or Mg carbonates dissolution and weathering of silicate minerals. The bicarbonate ranges from (126 to 318) ppm. The geochemistry of groundwater is controlled by many factors as lithology, residence time, water flow path and water composition (Tóth, 1999).

The excess concentration of three anions (Cl^-, $SO_4^{2-}$and HCO_3^-) has been balanced by excess sodium, calcium and magnesium (Na^+ Ca^{2+} and Mg^{2+}). These cations are most likely supplied by the dissolution of various minerals such as dolomite, gypsum, calcite, anhydrite or weathering of silicate minerals such as plagioclase, pyroxene, amphibolites and montmorillonite (Freeze and Cherry, 1979; Boghici and Van Broekhoven, 2001).

4.6.2 The Piper Diagram

The data of different ions were plotted on Piper diagram (Figure 4.9) sodium with a value ranges from 7 to 42 meq/l dominates the cationic components of the groundwater followed by calcium and magnesium. Chloride is the dominant anion found in the groundwater in the study area with the concentration ranging from 5 to 36 meq/l. Large percentages of the samples fall within the Na-Cl-SO_4 ~ (31%) type followed by Na-Cl-HCO_3 ~ (20%). Sodium, chloride, sulphate and bicarbonates are the main ions affecting the change. The remnant (49%) is represented by (Na-Cl-SO_4- HCO_3, Na-HCO_3-SO_4, Na-Ca-Cl-SO_4, Na-HCO_3-Cl and Ca-Na-Mg-HCO_3-SO_4-Cl) water type.

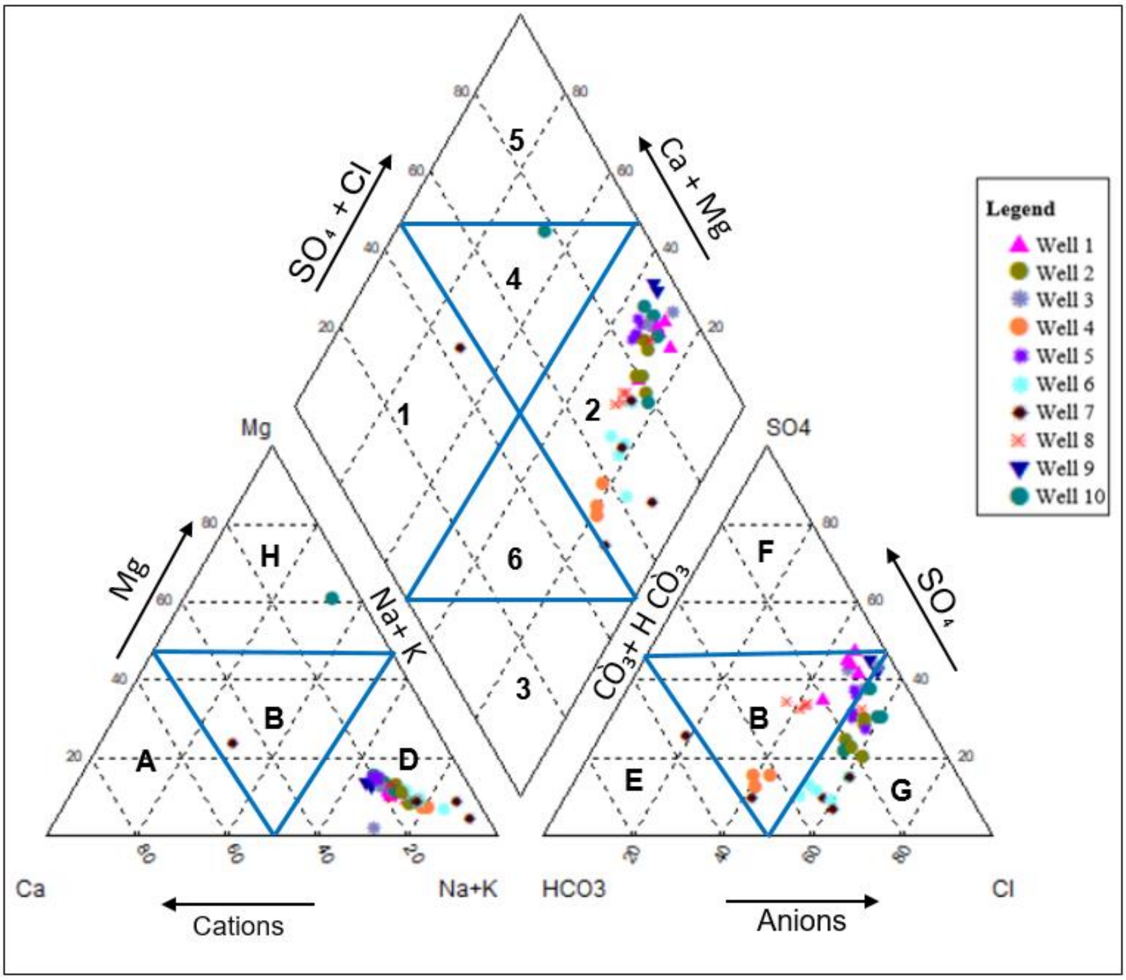


Figure 4.9: Piper diagram of the chemical composition of the studied samples.

Legend

A. Calcium type
B. No Dominant type
D. Sodium and potassium type
E. Bicarbonate type
F. Sulphate type
G. Chloride type
H. Magnesium type

1. Magnesium bicarbonate type
2. Sodium Chloride type
3. Sodium bicarbonate type
4. Mixed type
5. Calcium chloride type
6. Mixed type

The high concentration of Cl^- may be due to leaching of saline soil residues into the groundwater system, a typical characteristic of arid and semi-arid regions (Dahab, 2003 and Zaheeruddin and Khurshid, 2004). The $NaHCO_3$ water type reflects fresh water of meteoric origin. The Na_2SO_4 water type reflects the effect of the dissolution and leaching processes of evaporite deposits in salt marches around the salt lakes rich in sulfate by the meteoric water percolation.

4.6.3 The Schoeller Diagram

The plot of data on semilogarithmic graph (Figure 4.10) (Schoeller, 1962) revealed that sodium is the dominant cation followed by calcium and magnesium ($Na^+ > Ca^{2+} > Mg^{2+}$).

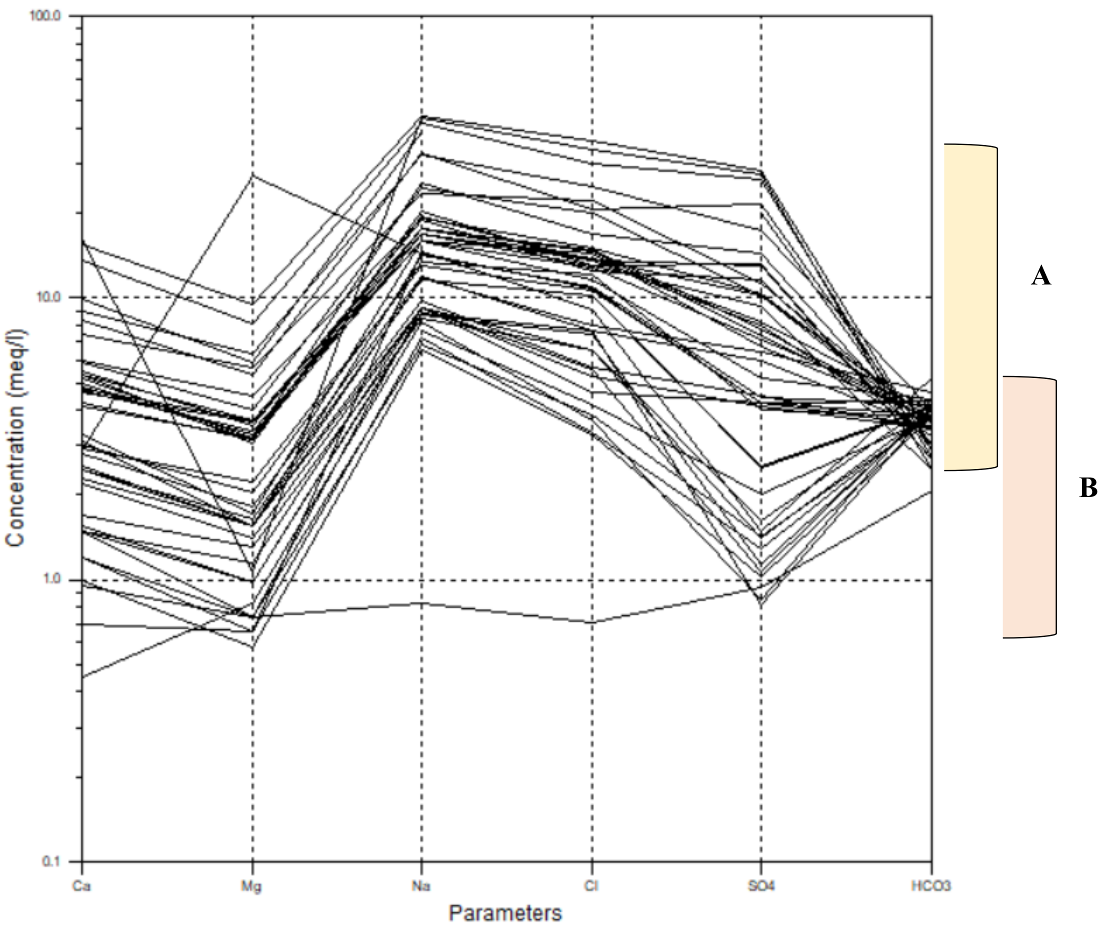


Figure 4.10: Schoeller diagram of the chemical compositions of the studied samples.

Some groundwater samples show increase of magnesium over calcium ($Na^+ > Mg^{2+} > Ca^{2+}$). Chloride and sulfate are the dominant anions in the studied samples followed by bicarbonate ($Cl^- > SO_4^{2-} > HCO_3^-$).

From the above Schoeller diagram two significant parts (A and B) can be observed, part (A) shows lower concentration levels of (HCO_3^-) value and exhibits higher concentration of (Cl^-, SO_4^{2-}, Na^+, Ca^{2+} and Mg^{2+}) ions. On the other hand, part (B) shows higher concentration levels of (HCO_3^-) value with lower concentration levels of (Cl^-, SO_4^{2-}, Na^+, Ca^{2+} and Mg^{2+}) ions.

4.6.4 Isotopic signature

The isotopic composition of the studied wells is shown on (Table 4.13) values of δD range from (-16.30‰ to 0.39‰) whereas the values of $\delta^{18}O$ range from (-2.46‰ to -0.76‰).

Table 4.13: Distribution of D (‰) and ^{18}O (‰) in the studied wells along five sampling times.

Well No.	**December 2014**		**February 2016**		**July 2016**		**November 2016**		**March 2018**	
	$\delta^{18}O$	**$\delta^{2}H$**	**$\delta^{18}O$**	**$\delta^{2}H$**	**$\delta^{18}O$**	**$\delta^{2}H$**	**$\delta^{18}O$**	**$\delta^{2}H$**	**$\delta^{18}O$**	**$\delta^{2}H$**
1			-1.28	-7.45	-1.80	-10.91	-0.60	-7.30	-1.62	-3.56
2	-2.41	-11.65	-4.76	-6.44	-2.20	-12.60	-1.90	-13.2	-2.37	-8.31
3	-1.40	-2.41	-2.68	-8.59	-1.60	-5.60	-1.40	-1.7	-1.33	0.39
4	-1.99	-8.54	-2.06	-9.38	-1.40	-6.90	-1.76	-7.3		
5	-2.15	-8.98	-2.03	10.30	-1.80	-6.20	-2.40	-11.10	-1.81	-3.84
6	-2.13	-10.39	-2.22	-10.50	-2.10	-12.10	-2.10	-12.10	-2.13	-5.45
7	-2.46	-12.87			3.60	29.30	-2.40	-14.00	-2.16	-8.15
8	-1.61	-5.63	-1.55	-6.88	-1.10	-3.40	-0.60	-1.20	-1.67	-3.34
9	-1.02	-2.99	-0.76	-3.21						
10	-2.48	-13.51	-2.69	-16.30	-3.50	-12.70	-2.30	-13.20	-2.59	-11.48

The data of the studied wells was plotted on the conventional Oxygen-18 and Deuterium diagram (Figure 4.11).

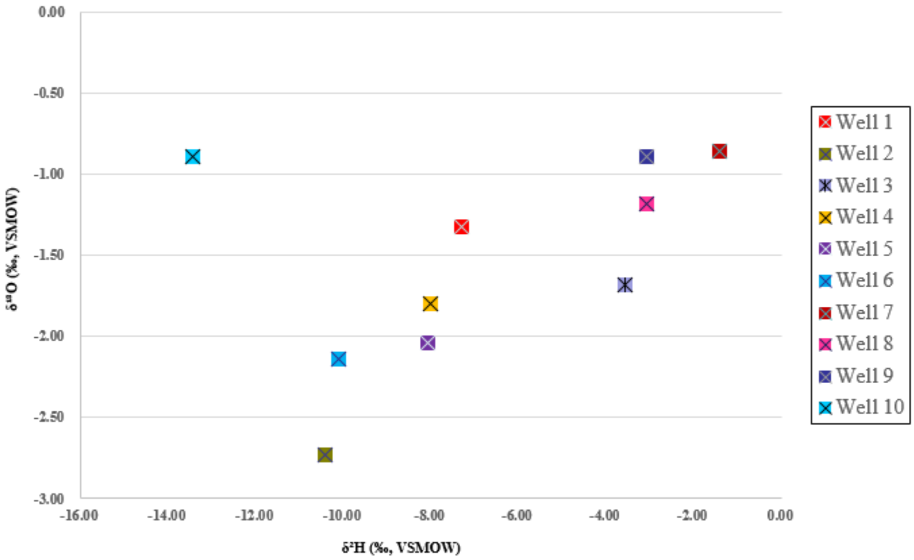


Figure 4.11: Average stable isotopic composition of the studied wells.

The temporal variation of isotopic contents during the different times (Figure 4.12) is not potentially high except for wells (2 and 7). There is depletion in isotopic content on peripheries of the depression compared to samples of the center area.

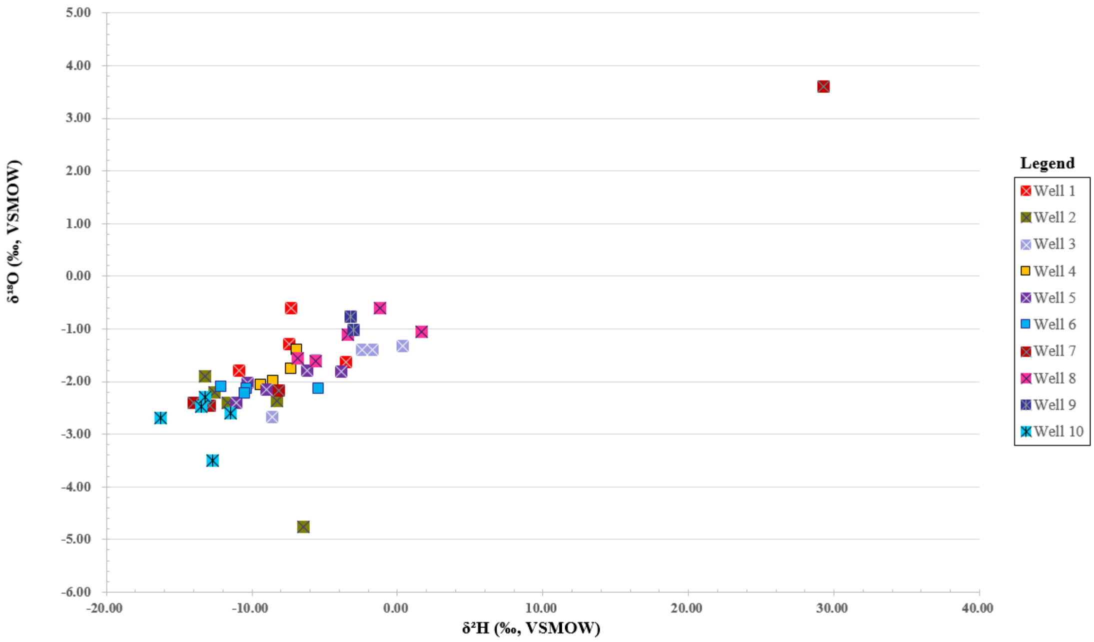


Figure 4.12: Stable isotopic composition of the studied wells along different sampling times.

The studied samples were plotted in relation to isotopic position with local precipitation, global meteoric water line, paleowater and Nile water (Figure 4.13) that were previously mentioned in (Tables 4.2 and 4.3) and (Figure 4.5).

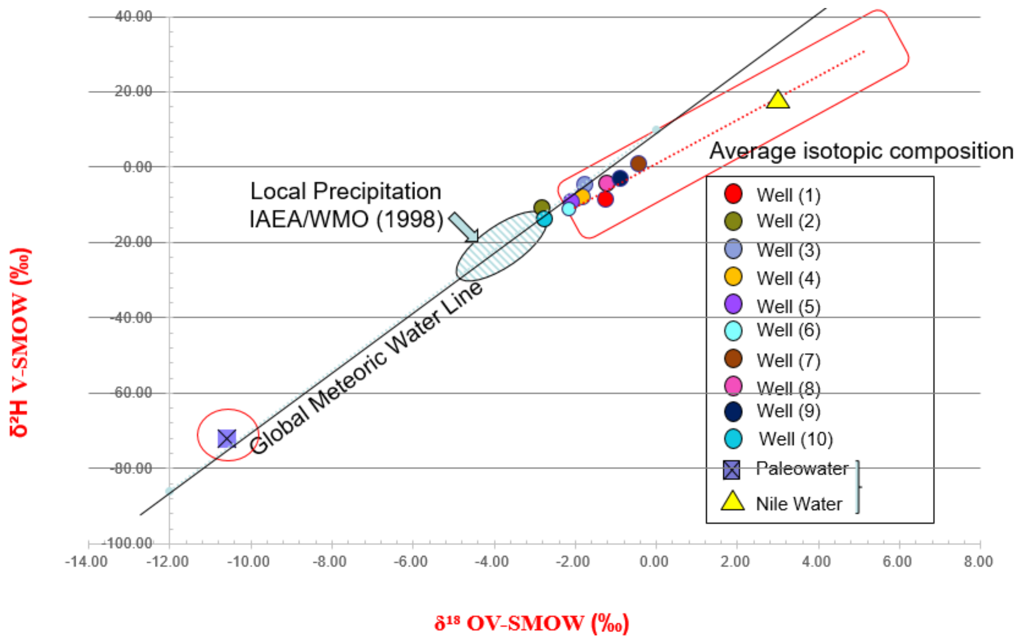


Figure 4.13: Stable isotopic composition of the studied wells and major recharging sources in Egypt.

4.7 Discussion

4.7.1 Classification and Geographical position

The classification of water type depends on major ions concentrations (Schmassmann *et al.*, 1984). The two major water types in the studied wells are the $Na\text{-}Cl\text{-}SO_4$ ~ (31%) and $Na\text{-}Cl\text{-}HCO_3$ ~ (20%) water types. The salinity of groundwater in Wadi El-Natrun ranges from 258 to 4280 ppm (Figure 4.14). Shallow water wells tend to display $Na\text{-}Cl\text{-}SO_4$ water type whereas deep-water wells tend to display $Na\text{-}Cl\text{-}HCO_3$ water type (Figure 4.8).

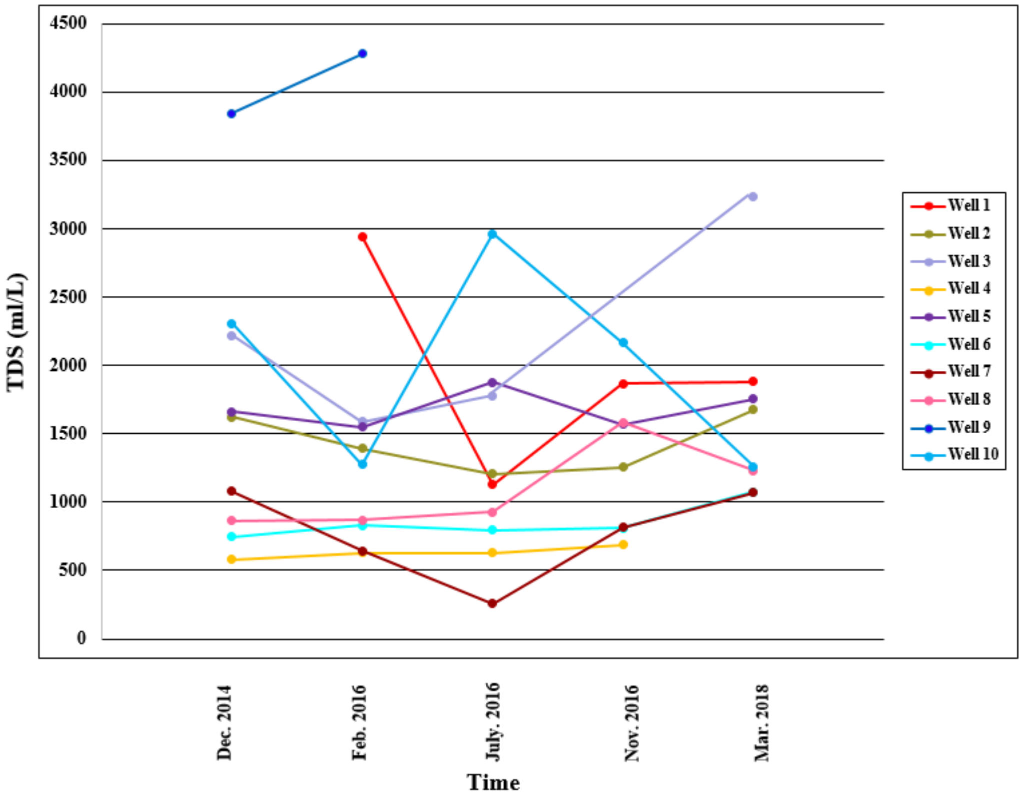


Figure 4.14: Total dissolved solids in the studied wells.

Generally, the salinity decreases from NE to SW. Groundwater salinity shows two apparent zones: (1) a low level of salinity (total dissolved solids (TDS) < 1500 ppm) SE and in the center (2) a TDS of more than 1500 ppm (Figure 4.15).

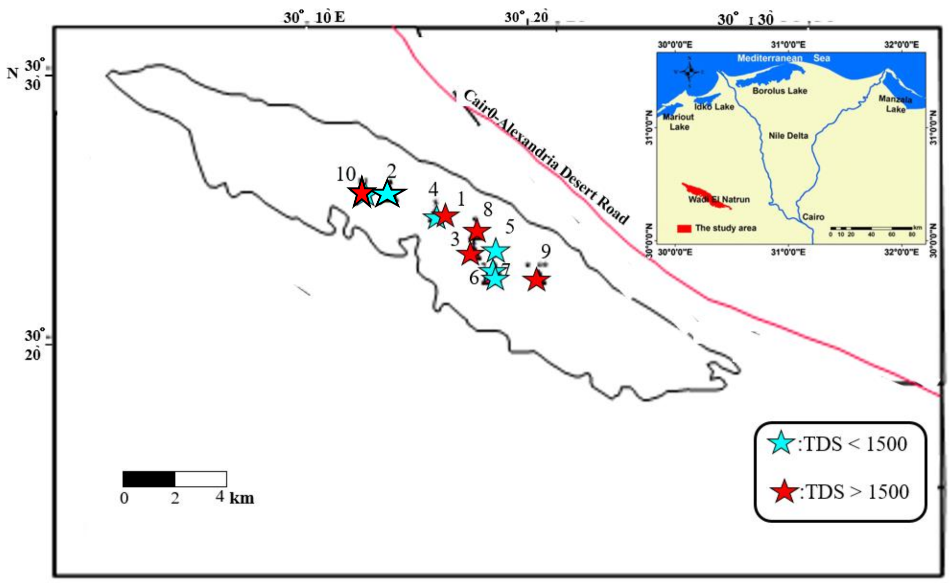


Figure 4.15: Distribution of the studied wells on basis of salinity.

The studied wells can be distinguished on basis of geochemical composition into: wells 4, 6 and 7 possess same chemical water type Na-Cl-HCO_3 whereas the other wells have basically Na-Cl-SO_4 and Na-Ca-Cl-SO_4. The wells in area of study are also classified into deeper and shallower wells. The deeper wells are generally belonging to Na-Cl-HCO_3 water type whereas the shallower wells are generally belonging to Na-Cl-SO_4 and Na-Ca-Cl-SO_4 water types.

The Schoeller diagram (Fig. 4.10) shows an interesting variation, where the concentration of major ions is low, and the concentration of bicarbonate become relatively higher. This is understood that the most of ions are from evaporites whose main constituents are (Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-}). When the influence from evaporites become small, another constituent or carbonate become conspicuous. It is interesting to note that the concentration of bicarbonate ion is more or less the same. A closer look at the figure discloses that the concentration of bicarbonate ion is negatively correlated with the concentration of sulfate ion. This may be interpreted as the order of evaporites end-member. The typical order of evaporites is (Ca+Mg) SO_4 > NaCl > HCO_3^- whereas the reverse direction is towards less typical evaporites.

As a matter of fact, bicarbonate ion is the product of weathering of carbonate and feldspar. The main anions in evaporites are (Cl^- and SO_4^{2-}) and the cations counterparts are (Ca^{2+}, Mg^{2+} and Na^+). We introduce a new index to discern water influenced by evaporites dissolution from water influenced by weathering. Using the molar concentration of sodium, magnesium and calcium (cations) and the molar concentration of chloride and sulfate (anions). The weathering-evaporation (W-E) index is defined by the equation:

$$\text{W-E. index} = (Na^{+}+Mg^{2+}+Ca^{2+})/(Cl^{-}+SO_4^{2-})$$

The value is higher than 1 in case of weathering process as chloride and sulfate are not weathering products unlike cations (sodium, magnesium and calcium). The ratio is around one in case the effect of weathering is not profound. Generally, the W-E index of the Na-Cl-HCO_3 water type is larger than one (>1) whereas the W-E index of the Na-Cl-SO_4 water type is around one (~1). As seen in the Schoeller diagram, TDS and W-E index is negatively correlated average value of correlation coefficient (r =-0.77, p >0.005).

The distribution of weathering-evaporation index of the studied wells is shown on (Figure 4.16). The studied samples show two groups one consists of wells (1,3,5 and 9) with value around one where as wells (4,6 and 7) show higher value around (1.4). Wells in the center (higher elevation) are generally subjected to evaporation rather than weathering (W-E index ~1) and tend to show greater variation in the TDS whereas peripheral wells (W-E index >1) are subjected to weathering rather than dissolution of evaporites process. This may be interpreted that water, which has a low TDS and a high W-E index, may be recharged from the peripheral area.

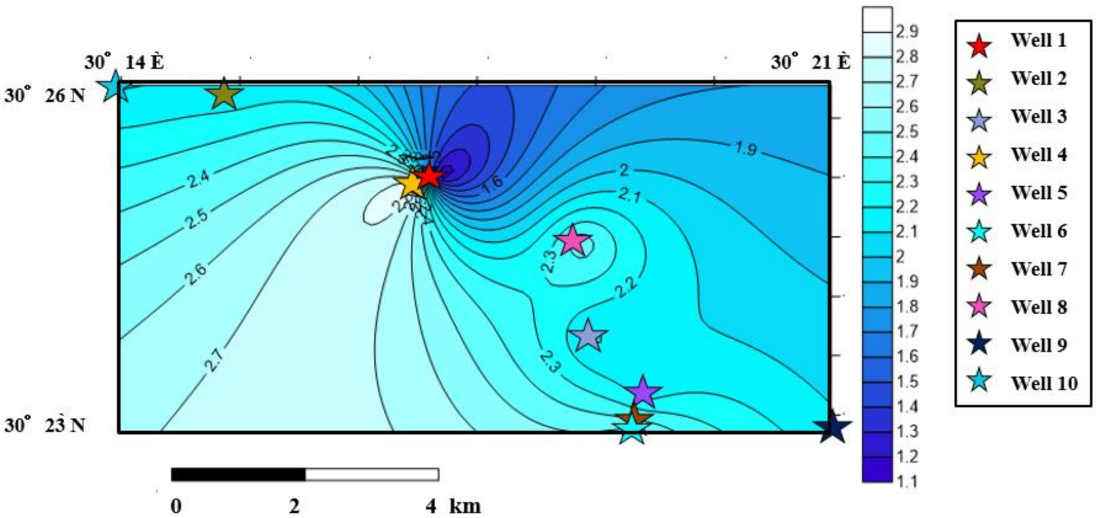


Figure 4.16: Contour map of W-E index ratio in the studied wells.

4.7.2 Assessment of Groundwater for Domestic and Agricultural Purposes

Assessment of the seasonal variation of groundwater recharge is needed for effective management of groundwater resources. We should not only concern about the water quantity but we should consider the quality as well. Analysis of major ions in groundwater were carried out to evaluate drinking water quality and suitability for irrigation.

4.7.2.1 Suitability for Drinking

The deterioration of groundwater quality may result in serious restrictions on its usages especially when it is used for domestic purposes. Water should be colorless, odorless, clear and free from excessive dissolved solids as well as harmful organisms to be suitable for drinking and domestic purposes. To assess the groundwater for drinking as well as irrigation purpose, physicochemical parameters of the collected water samples are compared with the guideline recommended by WHO (2004) and WHO（2012) standard limits of drinking water were adapted to assess the suitability of water for drinking and domestic uses (Table 4.14).

Table. 4.14: Comparison of studied water samples and (WHO, 2004 and WHO, 2012).

	Minimum (mg/l)	Maximum (mg/l)	WHO (2004) (mg/l)	WHO (2012) (mg/l)
TDS	285	4281	1000	1500
Na^{+}	19	1190	200	200
Mg^{+2}	7	115	200	150
Ca^{+2}	9	310	200	200
K^{+}	2	15	30	12
Cl^{-}	25	1284	250	600
HCO_3^{-}	126	318	380	500
SO_4^{-2}	45	1364	400	250

Generally, the water is not good for drinking. Wells # (4, 6 and 7) display salinity lower than 1000 mg/l and apply for the permissible limit of total dissolved salts. Same mentioned wells show permissible limit for sodium concentration unlike rest of the studied wells. Calcium ion is under permissible limit for all wells except for well #9.

Chloride ion is under permissible limit in wells # (4, 6, 7 and 8). Sulfate ion is under permissible limit in the studied samples except wells # (1, 3, 9 and 10). Potassium, magnesium and Hydrocarbonate ions are under permissible limits in the studied samples.

4.7.2.2 Suitability for Irrigation

The groundwater samples were assessed for irrigation suitability; US Salinity Laboratory methods were used for classification of groundwater. Salinity Laboratory Staff (1954) based on the Sodium Adsorption Ratio (SAR), which has long been used as a measure of sodium hazard.

The sodium adsorption ratio (SAR) is defined by the equation: SAR=Na / (Ca^{2+} + Mg^{2+})/2 - where the concentrations of the components are expressed in meq/L. High values of SAR is hazardous as the sodium replaces adsorbed calcium and magnesium, and this replacement is harmful to soil structure.

According to SAR value water can be classified into:

Excellent (0-10); Good (10-18); Fair (18-26); Poor (26-100) (Richards, 1954). We found that the studied samples are good to fair for irrigation uses.

The relation between SAR and EC according to Richards (1954) is used to assess both salinity and sodium hazards (Table 4.15)

Table 4.15: Standard classification according to sodium and salinity hazards.

Sodium (Alkali) hazard:	**Salinity hazard:**
S1: Low	C1: Low
S2: Medium	C2: Medium
S3: High	C3: High
S4: Very high	C4: Very High

The studied samples were plotted on the USSL diagram using Aquachem 4.0 software (Figure 4.17). It indicates that majority of the groundwater samples are plotted in C3S2 and C3S3 type, indicating high to very salinity and medium to high sodium hazard.

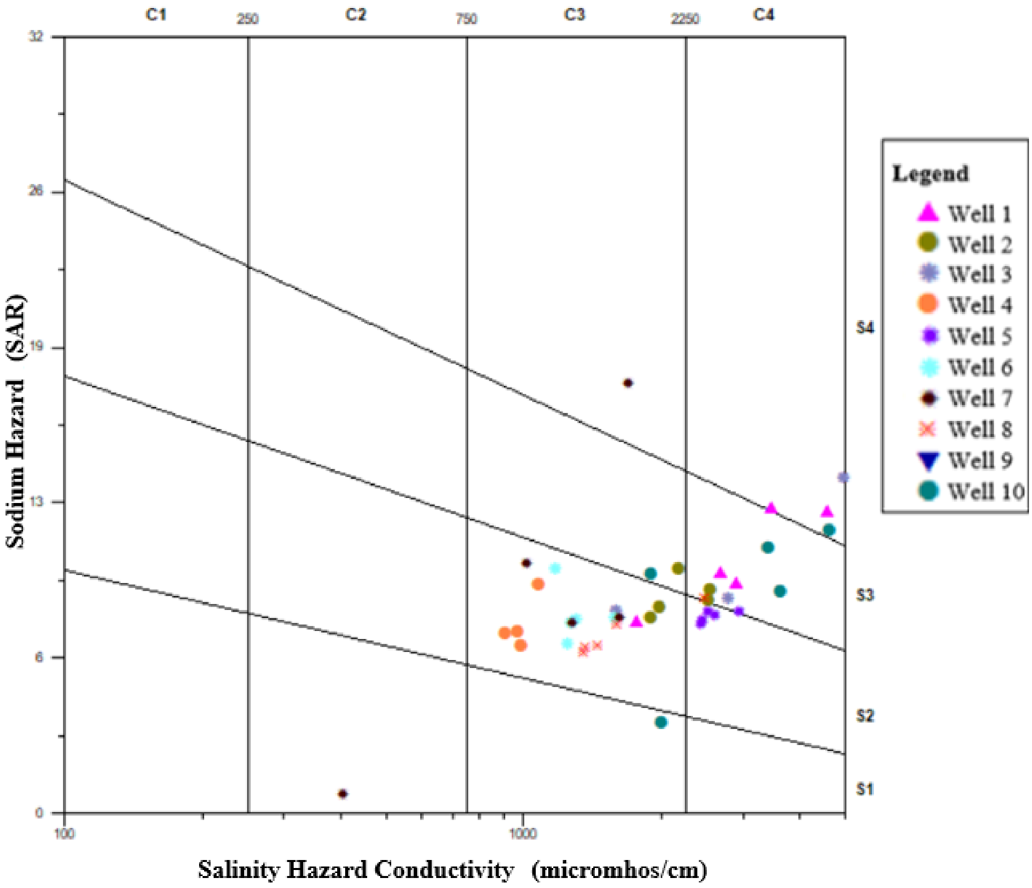


Figure 4.17: US salinity classification for irrigation.

4.7.2.3 Origin of Major Ions

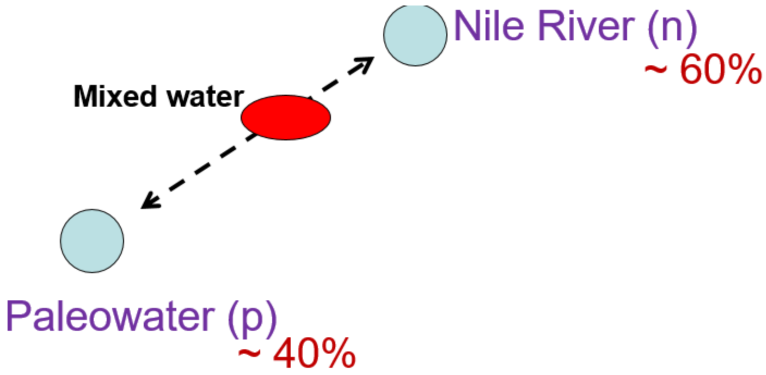
Concentration of ions dissolved in groundwater is generally controlled by the reservoirs minerals, groundwater flow rate, natural geochemical reactions, human activities, weathering of aluminosilicates and dissolution of evaporate and carbonate minerals and cation exchange reactions (Karanth, 1997; Bhatt and Salakani; 1996 Manno, *et al.*, 2007). High concentrations of calcium and sulfate in water indicate the possibility of dissolution of gypsum or anhydrite. The study of water quality is greatly concerned with sodium (Na^+) and chloride (Cl^-) ions as they are affected by halite mineral that may result from anthropogenic activities (D'Itri, 1992). According to Hem (1970), the natural concentrations are typically below about 15 mg/l for each ion and are highly variable. However, high concentrations may also result from natural resources because of interactions between water and soil, rocks, brines and salt deposits. The concentration of both Cl^- and Na^+ in the studied samples are higher than 15 mg/L.

Neal and Kirchner (2000) indicated that the ratios of sodium (Na^+) and chloride (Cl^-) ions are useful for identification of source. The molar ratio of Na^+ and Cl^- in the studied samples ranges from 1.1 to 1.6. The value (greater than 1) shows that the dominant process adding Na^+ to groundwater is silicate (Stallard and Edmond, 1983; Senthilkumar and Elango, 2013). Which is the case in wells (1, 3, 5, 8 and 9).

4.7.3 Source of Groundwater and Geographical Position

The presently isotopic contents of ($\delta^{18}O$, $\delta^{2}H$) of the collected groundwater samples indicate that there is indeed significant local recharge of the regional aquifers from the surface Nile water and paleowater and therefore, is a renewable resource.. The temporal variation of isotopic ratios during the five sampling seasons is not potentially high, especially isotope ratio of O, which shows stability along various periods of sampling.

Groundwater is generally enriched in ^{18}O and ^{2}H compared to paleowater. There is depletion in ^{18}O and ^{2}H on the peripheries of the depression. On the other hand, the isotopic content is similar to meteoric water. Most of the stable isotope values are negative and lie around the local meteoric water line whereas some samples are located between Nile water and meteoric water. The contribution of Nile water when paleowater is assumed to be the other end-member is calculated from the equation (Figure 4.18).



$$\text{Calculation Nile contribution (\%)} = \frac{C_m - C_p}{C_n - C_p} * 100$$

Figure 4.18: Water sources contribution in recharge of the studied wells.

The Nile water represents ~ 60% whereas the rest 40% is represented by paleowater. When Figure is scrutinized, however, the position of well water deviates slightly above from the linear line connecting the Nile water and paleowater. Therefore, a doubt remains that the Nile water is not a true end member. We consider that the oxygen isotope may not be as a good tracer as hydrogen isotope for the two reasons: one size of error in the oxygen isotope may be more significant that of hydrogen isotope in the spectroscopic isotope measurement and oxygen isotope can be subjected to exchange with that of silicate minerals. Hereafter, variation of hydrogen isotope is put more weight on than that of oxygen isotope.

4.7.4 Variation of Hydrogen Isotope and Salt Concentration

A relationship has been observed between ^2H and salinity (Figure 4.19): wells (1, 3, 8 and 10) show increase in TDS with change in ^2H whereas wells (2, 4, 6, 7 and 9) shows little change in TDS and small changes in ^2H value.

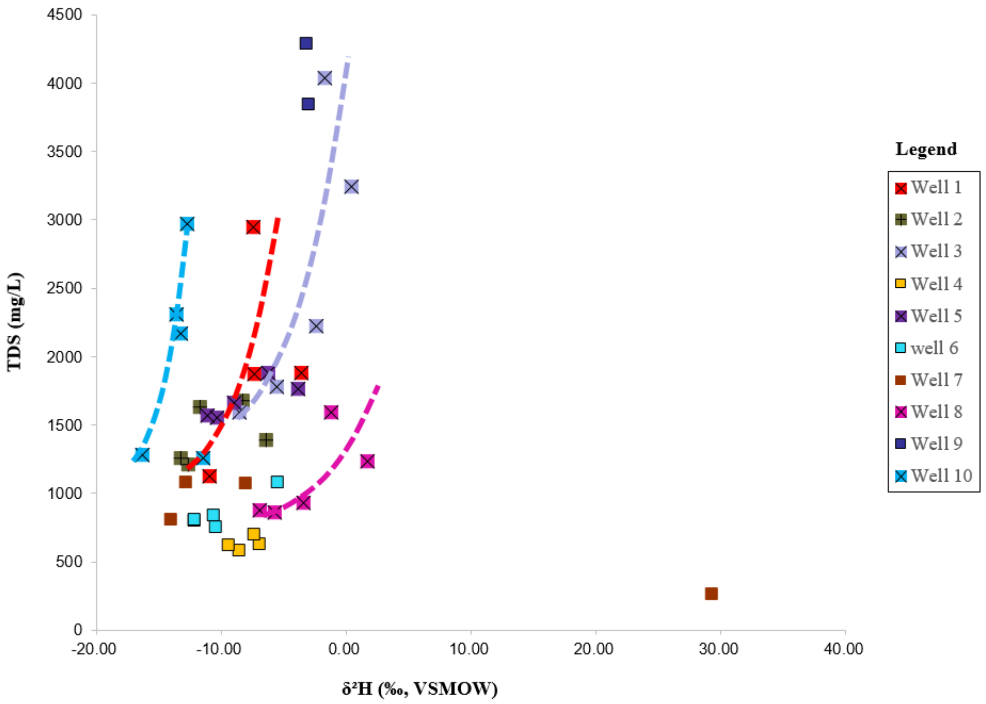


Figure 4.19: Relationship observed in variation of salinity and hydrogen isotopic content.

Although; the correlation between all the data of d²H and TDS is not significant (r^2= 0.0023), the significant correlation is seen between d²H and TDS for each of some wells (well # 1,3,10). Interestingly, the correlations are always of upward convex. The other wells do not show increase in TDS, but show a significant d²H increases (wells # 2 and 5) or only a small increase (wells #4, 6, 7 and 9).

Here we discuss the two features separately. We name the former well as unstable well and the latter as stable well.

1) Stable well (wells #2, 4, 5, 6, 7 and 9)

Probably some wells are in near steady state and no significant change both in chemistry and d²H is observed. Or water extraction rate is small for the wells. Such wells include wells #4, 6, and 9, but only number of data for some wells (2 or 3) is not enough to conclude this.

Some wells are likely to be recharged by inflow from Nile water. Such wells include well #7 and, to a smaller extent, well #2. Nile water has a high d^2H, but a low TDS concentration and the excursion to the right in the Figure. may be a reflection of inflow of the Nile water.

In the case of some wells, the same reason as discussed for unstable wells may be applicable. In this interpretation, they just look stable, because the water extraction is not s high enough to change the chemistry of water at the present stage.

2) Unstable well (wells #1, 3, 8 and 10)

Possible interpretation for this correlation, observed independently for each well, is water of aquifer at each well is isolated from one another in the time scale of observation (several years) and isotopically lighter water may be removed from the aquifer leaving salt. If the remaining water in the aquifer mixes well, and if water extraction is irreversible, this is the case of Rayleigh equation.

$\alpha = R_{\mathrm{aquifer}}/R_{removed}$

The Rayleigh equation is typically applied to the vapor-condensation system. In the case of present aquifer system.

$R_{\mathrm{aquifer}=} R^0{}_{\mathrm{aquifer}}\ f$, where *f* is the proportion of residual water. Because only water is supposed to be removed, solute should remain in the aquifer. The concentration is expressed in terms of *f*.

To apply the two equations in the present groundwater system, the original water in the aquifer with *f* =1 is needed to assumed. Ideally, it is impossible to determine. However, the purpose of the application of Rayleigh equation is to determine the best fit for each well. The provisional original water is assumed to be the water with least TDS for each well (Figure 4.20).

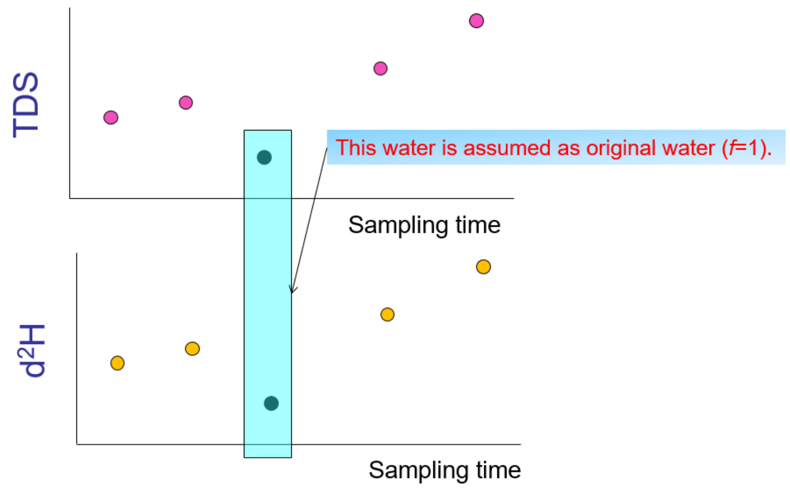


Figure 4.20: Schematic graph showing the variation between salinity and hydrogen isotopic content along different sampling periods.

The removed water equals (1- *f*).

The relative concentrations are plotted against Δ^2H (Figure 4.21) and this may have helped in determination fractionation factor (α) to control the change in both concentrations of ions and d^2H.

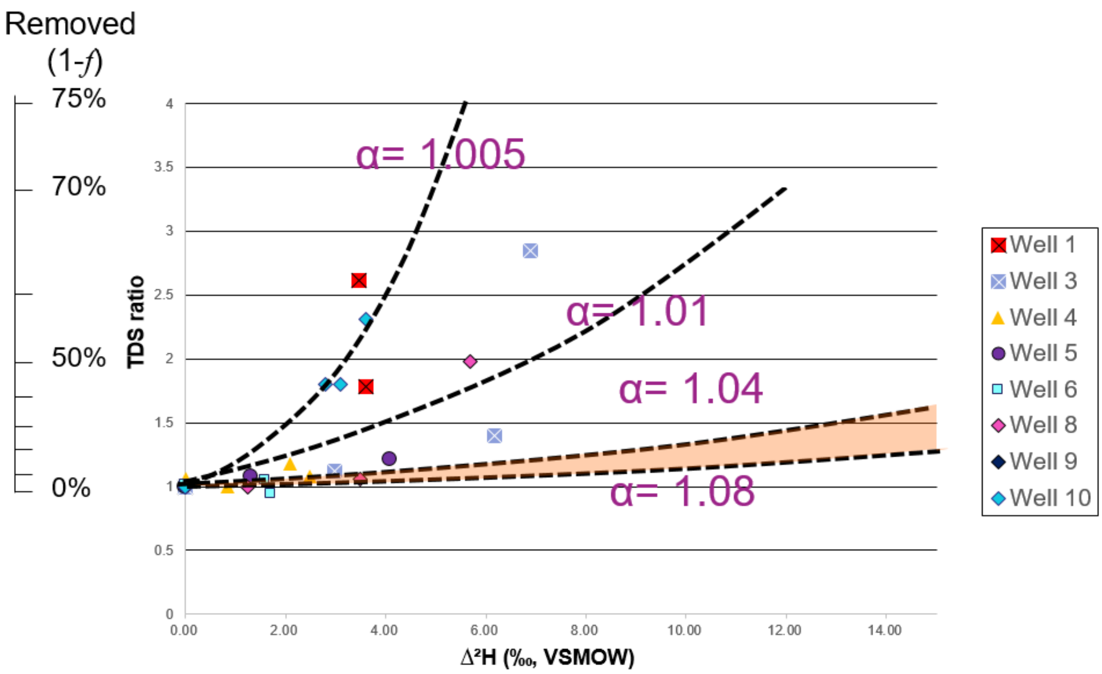


Figure 4.21: A relation found in the present study.

From the graphical representation between salinity ratio and difference in hydrogen isotopic value Δ^2H. α value can be determined. In the case of the unstable wells (wells # 1, 3, 8 and 10), value to explain the groundwater should be values as small as 1.005 to 1.04. Especially the water from wells #1 and 10 gave the smallest around 1.005. The α values for some specific reactions have been given by various authors (Table. 4.16). Evaporation (α = 1.04-1.08) may explain the change observed in some stable wells (wells #5 and 6). We, however, consider that evaporation is unlikely to be a direct cause, as discussed above.

Table 4.16: Possible mechanisms of water removal

Mechanism	α value	Author
Evaporation	1.04-1.08	Kendall and Caldwell (1998)
Kaolinite-water	1.026± 0.001	Lawrence and Taylor (1972)
Smectite-water at 25°C	1.06	Sheppard (1986)
Clay-water at 27° C	1.058	Capuano (1992)
Kaolinite-water at 27° C	1.033	Sheppard and Gilg (1996)

Clay minerals in Wadi El-Natrun are mainly montmorillonite, a small amount of kaolinite and traces of illite associated with non-clay minerals (quartz, iron oxides and traces of plagioclase and K-feldspar). It is considered that water-soil interaction may explain the observed small α values. However, α values for smectite and kaolinite, which represents the main component of soil in Wadi El-Natrun, are greater than 1.03 and the equilibrium water-soil interaction is unlikely to explain the observed variation. It is suspected that the *non-equilibrium* water-soil interaction might be the case. Some of the wells can be explained by the water removal on the surface of kaolinite, which as a value around 1.03, but it is not possible to explain the water from wells #1 and 10. The interpretation is not clear in case of such low α value as small values are not reported for water-soil interaction. Non equilibrium mechanisms can explain the lower alpha values for wells showing (1.01-1.005), which are smaller than the α values for smectite (Sheppard, 1986) and kaolinite (α=1.02-1.04) (Sheppard and Gilg, 1996), which represents the main component of soil in Wadi El-Natrun. No equilibrium mechanisms can explain the lower alpha values.

Water-soil interactions and water-rock have a significant effect on groundwater major ions content (Purushothaman *et al.*, 2013). In the case of non-equilibrium interaction, surface of clay minerals cannot be renewed, because less time is given to remove once-exchanged water this should be caused by a higher water pressure gradient (Figure 4.22).

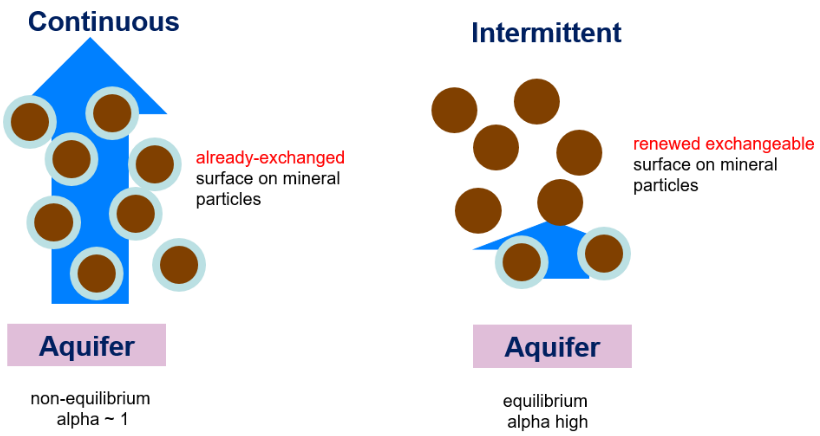


Figure 4.22: Showing difference between the two types of aquifers in water suction.

The wells that correspond to smaller α values (wells #1, 3, 8 and 10) might be interpreted as *non-equilibrium* water-soil interaction. On the other hands, wells with higher α values (1.04 – 1.08) undergoes higher rate of fractionation under an equilibrium condition, where salinity is relatively stable with a significant change in d2H. These wells are represented by wells #2, 4, 6 and 7.

In the current study, water loss was estimated from *f* value: removed water (water loss%) = (1- *f*). Water loss reaches up to 60%, whereas other wells show lower water loss around 10%.

Two types of ground water in Wadi El-Natrun.

The groundwater of the studied samples can be divided into two distinctive groups according to isotopic composition: Group I and Group II (Tables 4.17).

Table 4.17: Comparison between group I and group II wells from observed data.

Factor (observed)	**Group** I **1-5-3-8-10**	**Group** II **2-4-6-7**
TDS	High	Moderate
Salinity/δ²H variation	High	Small
W-E index	~1	>1
α values	low	High
Well depth	Generally shallow	Deep
Surface elevation	Generally High	Low
Farmland proximity	High	Low

Group I (unstable wells) displays higher water loss (Table 4.18), instability in both salinity and d²H. This group of water is also featured with W-E index being around unity. This group of wells tend to be located at higher elevation. Group II (stable wells) display lower water loss, stability in salinity and W-E index larger than 1. This group of wells tend to be located at lower elevation. Probably the wells grouped into type I is the input and output of water is too large compared with the size of its aquifer. Because water in group II well should have a longer residence time than the water in group I well and it stays in the aquifer long enough so that less dissolvable constituents were added from soil mineral via weathering.

Table 4.18: Comparison between unstable and stable wells

Factor	**Unstable** *Group I*	**Stable** *Group II*
Replenishment	Not enough	Occurs
Discharge	High Continuous withdrawal (non equilibrium)	Moderate Slow process and/or rapid water supply

α values show a variation in groundwater of the studied samples can be divided into two distinctive groups according to isotopic composition: Group I and Group II (Tables 4.17 and 4.18). Group I (unstable wells) displays overexploitation, instability and increase in salinity and possible soil interaction with aquifer and/or artificial discharge (irrigation). The second group (stable wells) show stability in total dissolved solids and under equilibrium conditions with continuous feeding for groundwater aquifer.

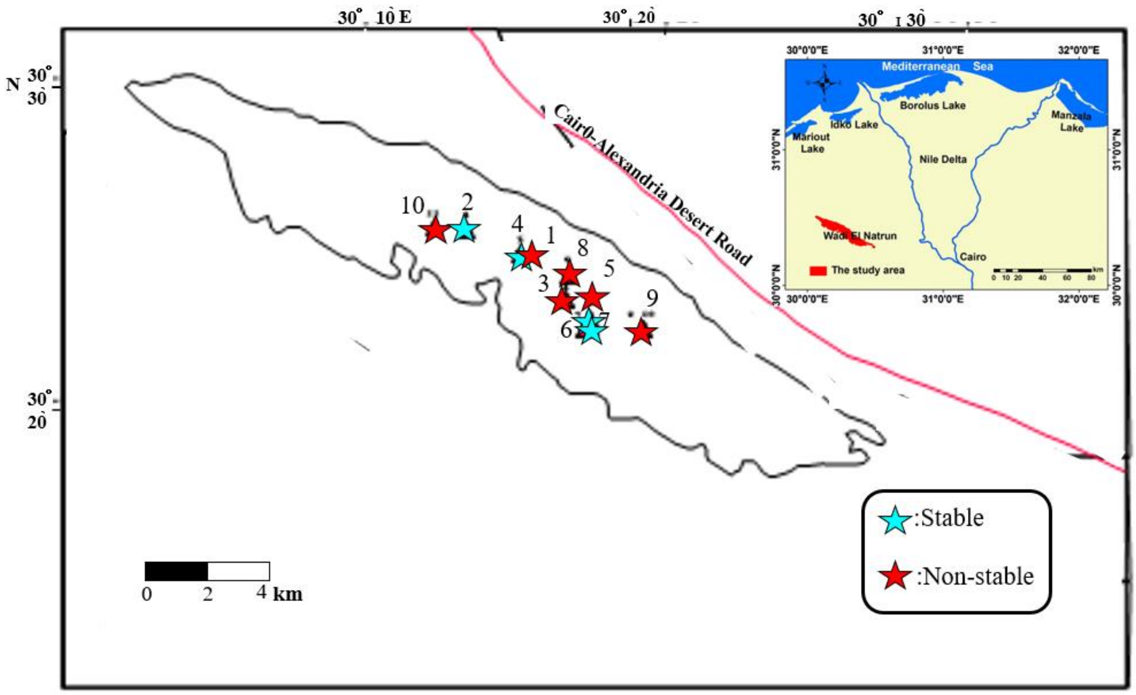


Figure 4.23: The geographic distribution of stable and nonstable wells in the study area.

4.8 Summary and Conclusion

The majority of samples are Na-Cl-HCO and Na-Cl-SO_4 water type (31%). The isotopic content showed roughly 60% contribution of Nile water and 40% of paleo-water. It is interesting to note that each aquifer seems independent of others within a time scale of a few years.

Among dissolve ionic species, HCO_3^- ion seems to be one of the most important ions to tell the nature of groundwater. Because HCO_3^- ion is supplied exclusively via weathering, the water influenced with weathering may be contact with soil minerals for a longer time and chemistry of water becomes stable. By integrating all pieces of information, two extreme types of wells have been identified. Unstable wells show greater variation in total dissolved salt concentration and are likely to undergo more intense water loss. The water of stable wells is recoverable due to continuous water supply and/or slow rate of withdrawal (Figure 4.24).

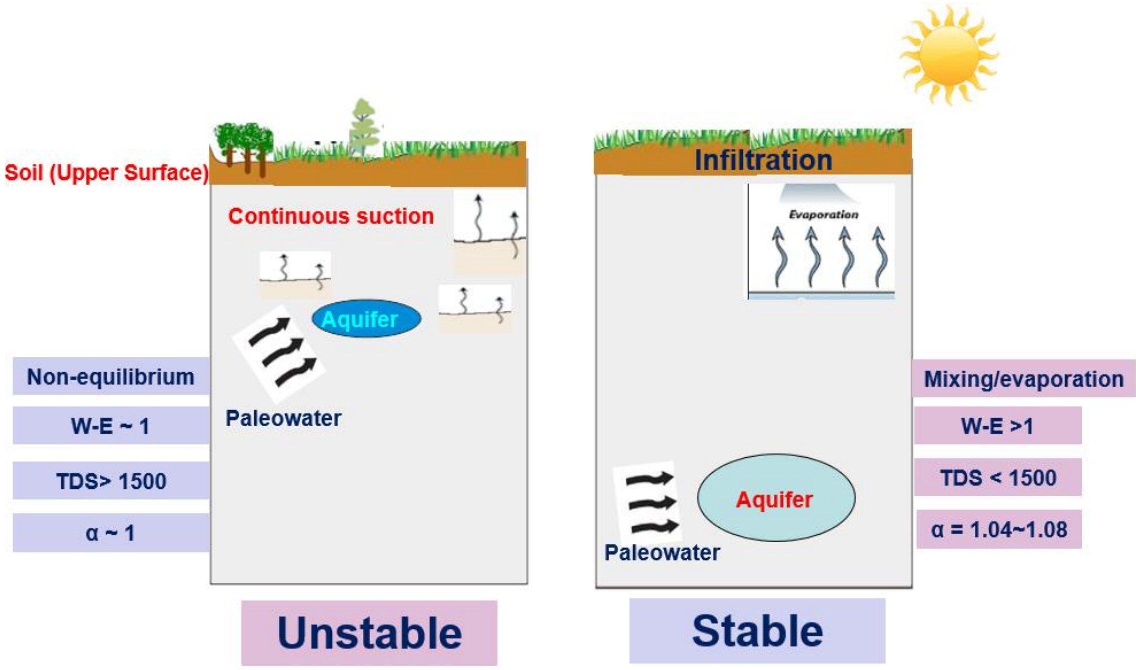


Figure 4.24: Schematic graph showing stable and nonstable wells.

Evaporation has a crucial role in water cycle. Heat from the sun certify the evaporation process. Among various factors affecting changes in water quality is the weathering of bedrock evapotranspiration (Stark *et al.*, 2000) and evaporation losses on the Egyptian water budget. The process of evaporation has been conventionally considered as direct cause of water quality change (El-Gamal, 2005; Omar and Moussa, 2016). From the isotopic fractionation factors during water loss, the current study shows that effect of evaporation may be not directly important, but that non-equilibrium interaction with soil mineral seems to be direct cause. Water transport should require water pressure gradient across the depth of well and surface of soil. The pressure gradient is likely to be produced by various ways including surface evaporation and plant uptake of water.

This pressure gradient lets water go through soil minerals, leaving dissolved salt behind. From the proximity of unstable wells to the farmland and their depth, one of the important cause of water pressure gradient is agro-activity. This explains very well the relationship between the recent deterioration of water quality and land greening. Some samples (20%) show a W-E index>1. Wells in the center (higher elevation) are generally subjected to evaporation W-E index ~1. The current study shows that effect of evaporation is not important and the direct cause of salinization of aquifer is water suction by agro-activity.

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CHAPTER 5
FUTURE ASPECTS

5.1 Introduction

A better knowledge of how the groundwater system operates and the prospects for improved groundwater management are of great importance in areas such as Wadi El-Natrun where exploitation of groundwater exceeds replenishment. The chemistry of groundwater is greatly affected by anthropogenic activities as agriculture and urbanization associated natural processes as soil nature, aquifer lithology and atmospheric effect (evaporation, precipitation and moisture). The quality of groundwater is significant in resolving the suitability of its usage for drinking, agriculture, and/or industrial usage. Monitoring of water quality is necessary to approach water management. In the present study, groundwater quality was evaluated temporally for drinking and agricultural purposes. The cultivated soil is vulnerable to reduction in crops production as a result of change in irrigation water chemistry and is hazardous for irrigation purposes due to high concentrations of salts.

The deterioration of groundwater quality and quantity of Wadi El-Natrun is a principal issue as a result of misuses and excessive agricultural activities, salinization, pollution from wastewater ponding and declining water levels. The current hydrogeochemical results together with previous studies along years shows that a number of groundwater wells have turned into saline most probably due to continuous discharge compared to insufficient recharge. Overexploitation of the fresh groundwater resources will be intensified in the future due to increasing demand for water. Over exploitation of the groundwater resources during the past few decades has increasingly affected the water quality and quantity.

5.2 Current Status and Challenges

Field measurements, personal communication with landholders and laboratory analyses clearly demonstrated that the studied wells had undergone salinization and that they were mostly not suitable for domestic use. Laboratory results provided evidence of the high concentration of sodium, which affects the soil and threatens agriculture activity. The increase of TDS that has been observed parts of the investigation area may be explained by the over pumping due to excessive irrigation and/or due to inherited salts within the aquifer deposits.

For effective management of groundwater, the analysis of stable isotopes and major ions in groundwater were carried out to identify the processes that may affect drinking water quality. It is important to determine the origin of groundwater in aquifers and the dominant geochemical reactions responsible for surface and groundwater quality in this type of environment.

The current study comes up with the result that two groups of wells are present in the depression. Stable wells, which are generally deeper wells with lower salinity, and unstable wells, which are shallower and provide water of higher salinity. Misuse of groundwater by landholders in many ways, as they operate wells around two hours daily to leach salts from soils and this practice represents great waste of water on daily bases. They as well grow crops with low salinity tolerance and do not care about amount of water wasted thinking that supply of water is limitless.

5.3 Proposed Solutions

There is urgent call for efficient tools for development of sustainable integrated water management policies based on sound scientific knowledge. To achieve comprehensive groundwater management and long-term sustainability, the followings are proposed as possible solutions for saving the current situation based on the mechanisms of water quality deterioration elucidated by this study:

1. The locals should learn and be aware of water crisis problems in Egypt. They also should know about the replenishment of water is not frequent and non-renewable. The source of groundwater is (40%) paleowater that would be no longer recharged to the aquifer.
2. Any actions that enhance water pressure gradient in soil would lead to deterioration of ground water quality. Among such actions development of farmland may be most problematic, because evapotranspiration from the vegetation from farmlands would be much greater than evaporation from barren lands. The planning of farmland may be critical and vegetation with less evapotranspiration should be carefully selected.
3. Flood irrigation must be banned, only drip and sprinkler irrigation should be allowed. Furthermore, the needed amount of water should be accurately determined and provided neither less nor more as the plant will not get benefit from any amount of water that exceeds its need.
4. Using crops that bears high salinity like olive for high salinity wells and salty soils
5. Planting alternative crops which tolerate higher salinity rather than its counterparts' species of lower salinity. For example: The Alfalfa (*Medicago stiva)* which tolerates salinity of 3000 ppm rather than Berseem Clover (*Trifolium sp.*) which needs lower salinity.
6. Deepening of shallow wells may permit reaching lower salinity levels for high saline shallower wells. The present study shows that wells in shallow wells is independent from one another. Therefore, running-out of a shallow well would not affect the quality of water of another shallow well. Deepening wells may solve the temporal problem in a short time scale (some 10 years), but, in a longer time scale (some 100 years), the deepening may cause an irreversible (unsustainable) deterioration of water of the deeper aquifer, which would never be recharged.

7. Using suitable crop for each soil rather than watering the area with water every day to leach salts from the planted area.
8. The expansion in using Casuarina trees as windshield, with a minimal spacing range between one and another would protect the planted area from windblown sand and strong winds that affect the plants and soil causing damage. In addition, the trees have economic value and can tolerate harsh and severe weather.
9. Egypt should take into consideration increasing the amount of water budget by considering political and economic cooperation with other nearby countries like Sudan that has wasted water by evaporation in the unused forest areas.