Palacký University Olomouc

Faculty of Science

Department of Geology

Stable Isotopes in Precipitation and Groundwater in Iraqi Kurdistan Region: A Case Study in Sulaimani Governorate

Bachelor thesis

Salar Salam Smail

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Supervisor: Prof. Ing. Ondřej Šráček, Ph.D., M.Sc.

Advisor: Rebar Mahmmud M.Sc.

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Anotace:

Stabilní izotopy ve srážkách a podzemních vodách v subpovodí Sulaimani-Warmawa v irácké oblasti Kurdistán byly zkoumány pomocí stabilních izotopů kyslíku-18 (^{18}O) a deuteria (^{2}H). Studovaná oblast se nachází v provincii Sulaimani, v irácké oblasti Kurdistán, což je semiaridní oblast se sezónními srážkami v zimě. Podzemní voda je jedním z nejdůležitějších vodních zdrojů v region, zejména ve venkovských oblastech kvůli chybějícímu vodovodnímu systému. Hlavní řekou je Tanjero nedaleko města Sulaimani. Celkem bylo během dubna 2022 odebráno 10 vzorků podzemních vod na anion, kationty, stopové prvky a stabilní izotopy kyslíku-18 (^{18}O) a deuteria (^{2}H). Izotopová linie podzemní vody (GWL) byla vytvořena pro studovanou oblast a porovnána s globální linií meteorické vody (GMWL), místní linií meteorické vody (LMWL), která byla vyvinuta pro Zagros, a místní linií podzemní vody (LGWL). Podle výsledků má nová linie podzemní vody (GWL) vyšší sklon a průsečík než místní linie podzemní vody (GWL). Kromě toho má GWL pro vzorky podzemní vody ve studované oblasti vyšší sklon a protíná místní meteorickou vodní linii (LMWL) stanovenou pro Zagros. GWL pro studovanou oblast je téměř stejná ve srovnání s místní linií podzemní vody (LGWL). Lze uzavřít, že výsledek analýz deuteria (^{2}H) a kyslíku-18 (^{18}O) odhalil, že doplňování pochází ze zimních dešťových srážek s žádným nebo omezeným výparem před infiltrací.

Klíčová slova: stabilní isotopy, podzemní voda, srážky, irácký Kurdistán, Sulaimani City,

Annotation:

Stable isotopes in precipitation and groundwater in the Sulaimani-Warmawa Sub-basin in the Kurdistan Region of Iraq have been examined using stable isotopes of Oxygen-18 (^{18}O) and Deuterium (^{2}H). The study area is located in the Sulaimani Governorate, in the Kurdistan Region of Iraq, which is a semiarid region with seasonal precipitation in winter. Groundwater is one of the most important water resources in the region and especially in rural areas, due to the lack of a water distribution system. The main river of interest is the Tanjero River, close to the Sulaimani city. In total, 10 groundwater samples were collected during April 2022 for anion, cations, trace elements and stable isotopes of oxygen-18 (^{18}O) and Deuterium (^{2}H). The groundwater line has been created for the area and compared to the global meteoric water line (GMWL), local meteoric water line (LMWL), which was developed for Zagros, and local groundwater line (LGWL) in the study area. According to the result, the new groundwater water line (GWL) has a higher slope and intercept than the local groundwater line (GWL) in the study area. In addition, the GWL for the groundwater samples in the study area has a higher slope and intercepts the local meteoric water line (LMWL) established for Zagros. The GWL for the study area is almost the same when compared to the local groundwater line (LGWL). It can be concluded that the result of Deuterium (^{2}H) and oxygen-18 (^{18}O) analyses revealed that the recharge is from winter rainfall with no or limited evaporation before infiltration.

Keywords: Stable isotopes, Groundwater, Precipitation, Iraqi Kurdistan, Sulaimani City.

Number of pages: 54

Declaration

I declare that I have prepared the bachelor's thesis myself and that I have stated all the used information resources in the thesis.

In Olomouc, May 8, 202 … Salar Salam Smail …

Acknowledgement

I would like to acknowledge and give my warmest thanks to my supervisor (Prof. Ondřej Šráček) and especially my advisor (Rebar Mahmmud), who made this work possible. Their guidance and advice carried me through all the stages of writing my project.

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List of abbreviations

V-SMOW	Vienna Standard Mean Ocean Water
GMWL	Global meteoric water line
LMWL	Local meteoric water line
ICP-MS	Inductively Coupled Plasma
EC	Electrical Conductivity
TDS	Total dissolved solids
pH	Power of hydrogen

1. Introduction

In arid and semiarid regions, precipitation and evaporation are natural processes that directly influence the availability of surface and groundwater resources. Hydrologic cycle processes such as precipitation, evaporation and groundwater partly control flow variation. Groundwater is one of the most important and sometimes the only water resources in some regions, especially in the arid and semiarid regions. For instance, the Kurdistan Region, which is located in Iraq, is a semiarid region and groundwater is vitally important in rural areas. Natural processes such as precipitation and evaporation directly impact the availability of surface water resources. Several hydrogeological methods and standards can be used to manage groundwater and protect against contamination. For instance, groundwater stable isotopes ^{2}H and ^{18}O is valuable methods for determining the timing and amount of recharge to aquifers. The stable isotopes ^{2}H and ^{18}O exist naturally as part of the water molecule and have been used as tracers to provide information on physical, kinetic, and chemical alterations that influence water molecules as they flow through the hydrologic cycle. Because different isotopes exist and are available. Precipitation is a part of the hydrologic cycle in which water condenses to form rain, snow, or hail that falls to the ground (Al-Gburi et al., 2022). Several studies of groundwater have been carried out in such regions. The study area is a hydrologic Sub-basin that is a part of the Sulaimani Sharazoor basin and is located in the Iraqi Kurdistan Region near the city of Sulaimani (Stevanovic & Markovic, 2004). It has a semiarid climate resembling that of the Mediterranean, and precipitation generally falls in the winter. Since local streams are often perennial and dry out in the late summer, groundwater is a very important resource. In this study, the stable isotope of oxygen-18 ^{18}O and deuterium ^{2}H has been measured to know the source and time of groundwater recharge in the Sulaimani-Warmawa Sub-basin (SWSB) and compare the groundwater line to the global meteoric water line and available local water line in the Kurdistan Region of Iraq.

2. Aim of the study

The main aims of this study is to conduct the stable isotope analysis of Oxygen-18 (18O) and Deuterim (2H) in the area of interest are:

1- To stablish the groundwater line and compare to the Global Meteoric Water Line (GMWL)
2- To know the sources of recharge of groundwater in the study area
3- To estimate the groundwater residence time by using stable isotope data

3. Hydrologic Cycle

The hydrological cycle—also referred to as the "water cycle"—is the standard system for recycling water on Earth. Water evaporates from solar radiation, typically from the ocean, lakes, etc. As a result of transpiration, water also evaporates from plant leaves. The steam is cooling, condenses, and returns to the land and the sea as precipitation as it rises in the atmosphere. Rainfall forms the surface of the planet as surface water, forming streams of water that eventually become lakes and rivers. Aquifers are created when some of the precipitating water seeps into the Earth and flows downward through incisions. A portion of the surface and subsurface water finally flows into the sea (Inglezakis et al., 2016). Water undergoes all phases of transformation during this journey: gas, liquid, and solid. Water constantly transitions between the phases of liquid, vapour, and ice, with these processes taking place over millions of years and in the space of a single instant. Changes in the balance of radiation and temperature in the atmosphere have a direct impact on the hydrological cycle. It is now clear from measurements of increases in global average air and ocean temperatures, widespread melting of snow and ice, and global sea level rise that the climate system has been warming in recent decades. More precipitation and evaporation may strengthen the hydrological cycle, but the additional precipitation will be unevenly distributed throughout the world. It is anticipated that some regions of the world may experience precipitation decreases of some significance or even more severe changes in the timing of the wet and dry seasons (Inglezakis et al., 2016). The ability of the ground surface to hold moisture is increased by the presence of plants. When caught by the canopy, precipitation is then deflected by plants and evaporates immediately. Through evapotranspiration, the plants themselves produce a significant amount of water vapour through transpiration. The amount of surface runoff is significantly higher on bare ground than it is on vegetated regions. Plants are essential to the hydrological cycle's operation because they control the processes that exchange energy, water vapour, and carbon (Chakravarty & Kumar, 2019).

3.1 Isotopic Compositions in the Hydrologic Cycle

According to (Clark and Fritz, 1997), the isotopic compositions of the components of the hydrologic cycle, such as evaporation from ocean water, precipitation, snow, ice build-up, melting, and runoff, are distinctive to certain climate zones. These components include precipitation, snow, and ice accumulation. It is possible to track and identify the contributions of each of these hydrologic cycle components to a surface water body by using the distinctive isotopic compositions of each of these hydrologic cycle components.

3.1.1 Precipitation

Any product of the condensation of atmospheric water vapour that falls due to the gravitational attraction of clouds is referred to as precipitation in meteorology. Rain, sleet, snow, ice pellets, graupel, drizzle, and hail are the primary types of precipitation. When an area of the atmosphere reaches 100% relative humidity, or saturation with water vapour, precipitation occurs when the water condenses and "precipitates" or falls. Because the water vapour does not enough condense to precipitate, fog and mist are instead colloids rather than precipitation. Air can become saturated as a result of two processes, perhaps working in tandem: chilling the air or introducing water vapour. Smaller droplets collide with larger raindrops or ice crystals within a cloud to combine into precipitation. Precipitation is an essential component of the hydrological cycle, whereby water vapour condenses and forms precipitation in the form of rain, snow, or hail, which ultimately reaches the Earth's surface. The isotopic composition of precipitation is determined by the isotopic compositions of the parent cloud and the temperature at which condensation takes place (Kendall and McDonnell, 1998). The isotopic compositions of each parent cloud that produces precipitation will vary based on temperature, the distance the air mass has travelled from its origin, the change in altitude over topographic features, differences in latitude, and seasonal variations (Clark and Fritz, 1997). In general, the heavier isotopes ^{2}H and ^{18}O become enriched in the liquid or solid phase due to Rayleigh processes that take place while condensation takes place from the water vapour source. This is because mass differences will allow heavier isotope forms to precipitate first (Araguas- Araguas et al., 1997; Kendall and McDonnell, 1998). Even though Rayleigh processes are responsible for causing this enrichment-depletion tendency, the magnitude at which this behaviour is observed can be affected by factors such as altitude and seasonal changes. Isotope compositions in precipitation that originate from the same water vapour source with the same isotope composition will vary between highlands and lowlands, even if the water vapour source has the same isotope composition. More evaporation and re-evaporation processes take occur when moisture is transferred from a higher altitude to a lower one (Bowen, 1986). This results in a greater enrichment in the ^{2}H and ^{18}O compositions of the lowlands, while the mountainous regions experience a greater depletion of these elements. According to (Mazor, 2004), the isotope compositions exhibit variation in relation to the distance from the inland area. This is due to the precipitation of the heavier isotope forms, which occurs first, leading to an enrichment of the lighter isotope forms in the vapour as the distance from the source of the vapour increases. According to (Kendall and McDonnell, 1998), seasonal variations lead to evaporation, as the rise in temperature during summer causes precipitation to be more prone to fractionation processes compared to winter. The variations in isotope composition provide an input signal that is distinguished by Local Meteoric Water Lines that are specific to each region. This enables the identification of recharge sources (Clark and Fritz, 1997).

These applications frequently rely on records of precipitation isotope time series (hydrogen or oxygen isotope levels, respectively, in per mille relative to Vienna Standard Mean Ocean Water; ^{2}H or ^{18}O). A database of monthly precipitation ^{2}H and ^{18}O values (often referred to as "-values") has been compiled and maintained by the Global Network of Isotopes in Precipitation (GNIP) for more than 60 years. A very large scientific community has found and continues to find great value in this scientific resource (IAEA, 2014). Precipitation and groundwater are two of the most important sources of water for human and natural systems.

Precipitation falls to the Earth's surface and eventually infiltrates into the ground, where it is stored in aquifers. Groundwater is also a major source of water for plants and animals. Atoms in stable isotopes do not emit radiation. Although they don't produce radiation, they may be utilized in a wide range of applications, such as forensics, environmental research, nutrition evaluation studies, and water and soil management. Stable isotopes are atoms that have the same number of protons but different numbers of neutrons. This results in atoms with different masses but identical chemical properties. The most common stable isotopes found in precipitation and groundwater are hydrogen (H), oxygen (O), carbon (C), nitrogen (N) and sulfur (S). These elements make up over 98% of all living matter on Earth (IAEA, 2016).

There are stable isotopes for 80 of the first 82 elements in the periodic table. Numerous uses in real life can be made possible by measuring and analyzing their dispersion. Isotope-based approaches are used by Member States in a variety of fields, including hydrology, environmental research, and agriculture. Stable isotopes can be utilized by determining their concentrations and ratios in samples such as water samples. To understand the beginning, evolution, sources, sinks, and interactions in the water, carbon, and nitrogen cycles, stable isotopes of water and other naturally occurring chemicals are employed (IAEA, 2016).

In order to study a system, such as one in agriculture or nutrition, stable isotopes can also be introduced on purpose to that system. They need to be separated for this reason by utilizing extremely complex methods like mass spectrometry. While nitrogen-15 is the most widely utilized stable isotope in agriculture, Deuterium, an isotope twice as heavy as hydrogen, is mostly employed in nutrition studies. The usage of several additional stable isotopes is likewise rising (IAEA, 2016).

The relative abundance of stable isotopes can tell us a lot about the origins, history and evolution of our planet's waters. For example, studies have shown that certain types of H, O and C found in groundwater can be used to identify whether or not it came from rainfall or snowmelt runoff. This information is important because it helps us understand how quickly groundwater recharge occurs after precipitation events. Stable isotopes ^{2}H and ^{18}O in groundwater are an important tool for the determination of timing and amount of recharge to aquifers. They can be also used to determine processes during recharge, such as evaporation. The aquifers in Iraqi Kurdistan are frequently formed in carbonate rocks and sediments with a carbonate matrix derived from the Zagros Mountains. They can be important sources of water for local water supply. The data on stable isotopes in precipitation and groundwater in available databases and literature from Iraqi Kurdistan will be collected and reviewed. They will be plotted in diagrams and conclusions relevant for recharge to aquifers will be drawn.

3.1.2 Evaporation

The process of evaporation is a crucial component of the hydrological cycle, whereby liquid water undergoes a transformation into water vapour. The process of water molecules transitioning from the liquid phase to the vapour phase depends on various factors such as local temperature, humidity, and wind (Mazor, 2004). According to (Hoefs, 2004), there is variability in the isotopic compositions between surface water in its liquid phase and the vapour phase that occurs through evaporation, which is attributed to differences in vapour pressure. The isotopic compositions of water molecules exhibit mass differences, which result in the preferential evaporation of lighter isotopes of hydrogen and oxygen (^{1}H and ^{16}O) over their heavier counterparts (^{2}H and ^{18}O). This leads to an enrichment of lighter isotopes in the resulting water vapour and a corresponding enrichment of heavier isotopes in the residual water that remains behind, as noted by (Mazor, 2004).

In most cases, evaporation occurs from a surface water body into the surrounding atmosphere. However, it is possible for evaporation to take place during precipitation, which would result in an isotopic exchange between the precipitating liquid or solid water and the surrounding atmospheric water vapour (Hoefs, 2004). When evaporation takes place, the isotopic composition of precipitation will become enriched with decreasing elevation because lighter isotope forms are evaporated first (Hoefs, 2004). This is due to the fact that the isotopic composition of water vapour in the atmosphere is different than that of precipitation, such as rain or snowfall.

3.2 Isotopes

Isotopes are forms of an element that have the same number of protons and electrons but differing numbers of neutrons. There are many isotopes of an element that have varying weights depending on how many neutrons there are in each one. The isotope's total number of protons and neutrons is indicated by the uppercase number to the left of the element's designation. Deuterium, often known as ^{2}H or D, is an isotope of hydrogen that has one neutron and one proton. Protium (^{1}H) has around twice as much mass as this, but tritium (^{3}H) has roughly three times as much mass. The stable isotopes can make their own nuclei through the radioactive isotopes' decay, but on geologic periods, their nuclei do not decay to other isotopes. The nuclei of radioactive (unstable) isotopes naturally decay over time to produce other isotopes. For instance, the combination of stable ^{14}N and cosmic-ray neutrons in the atmosphere results in the production of ^{14}C, a radioisotope of carbon. By emitting a beta particle, ^{14}C decays back to ^{14}N with a half-life of approximately 5,730 years. Nitrogen that is created through nuclear reactions is referred to as "radiogenic" nitrogen. The stable, non-radiogenic isotopes are the main topic of this thesis (Kendall and Doctor, 2003)

3.2.1 Stable Isotope of Water

There are three naturally occurring isotopes of hydrogen: ^{1}H, ^{2}H (Deuterium), and ^{3}H (tritium). Oxygen also has three naturally occurring isotopes: ^{16}O, ^{17}O, and ^{18}O. Each isotope of hydrogen and oxygen is present on the Earth in varying quantities. The average percentages of these isotopes found in nature are approximately 99.985%, 0.015%, and 10-15% for hydrogen isotopes ^{1}H, ^{2}H, and ^{3}H, respectively, and 99.759%, 0.037%, and 0.204% for oxygen isotopes ^{16}O, ^{17}O, and ^{18}O, respectively. These percentages are based on the isotope (Bowen, 1986). Water molecules with different hydrogen and oxygen compositions are formed due to the presence and availability of the various isotopes. The four primary isotopic combinations forming water molecule compounds found in nature are $^{1}H_2$ ^{16}O, ^{1}H ^{2}H ^{16}O, $^{1}H_2$, ^{18}O and $^{1}H_3$ H ^{16}O (Araguas-Araguas et al., 1997; Singh and Kumar, 2005). The transition of water between gaseous, liquid, and solid states fractionates the isotopic components of water molecules, resulting in variations in the ^{2}H and ^{18}O

isotopic compositions of water molecules in any body of water. (Singh and Kumar, 2005) as shown in Figure (1).

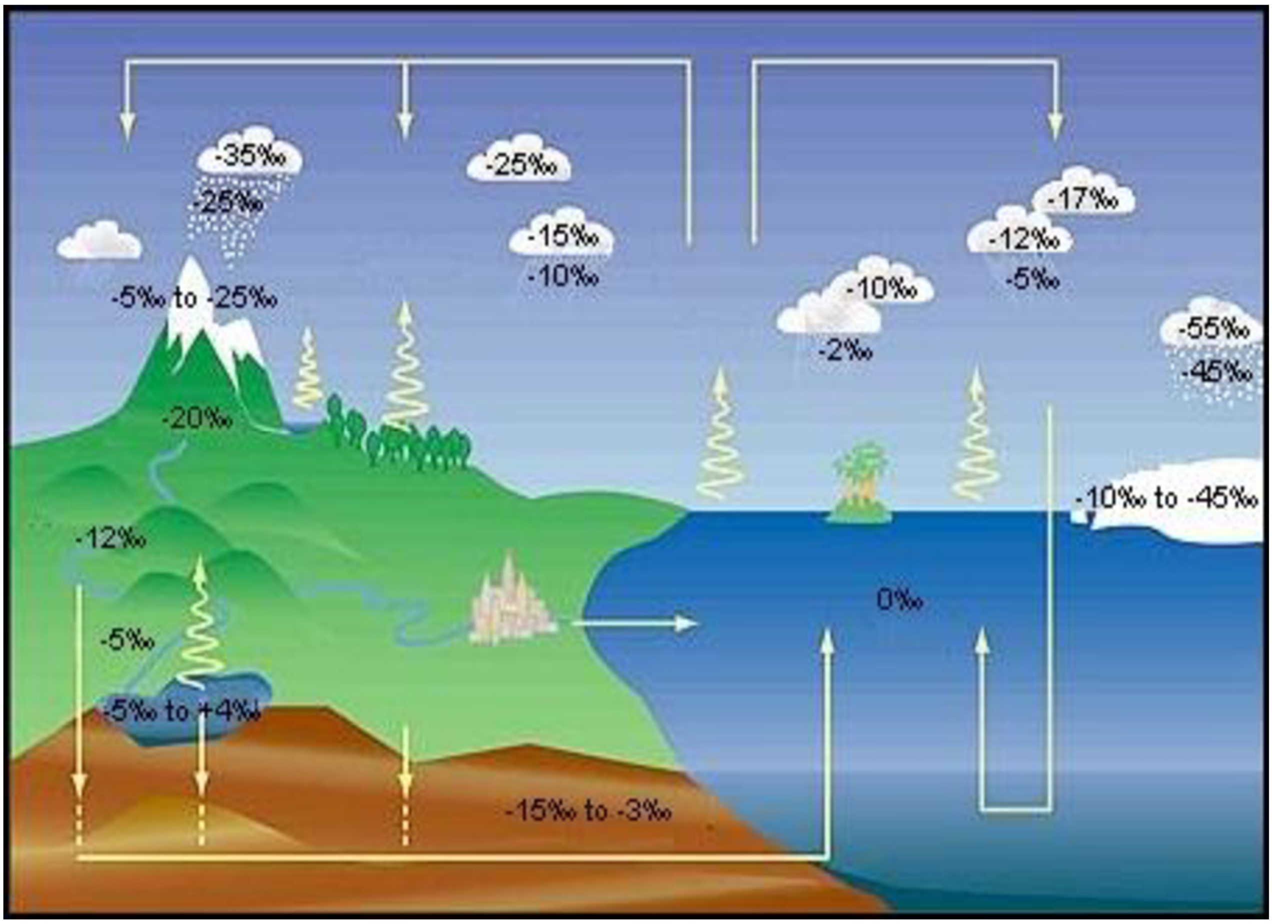

Figure 1 Isotope Compositions in the Hydrologic Cycle. Isotopic compositions of hydrogen and oxygen are partitioned differently under equilibrium and non-equilibrium conditions within the components of the hydrologic cycle. Illustrated is the change in isotope compositions of ^{18}O through the hydrologic cycle (http://atoc.colorado.edu: adapted from GNIP Brochure, IAEA, 1996).

(Kendall and McDonnell, 1998) stated that the fractionation processes are dependent on the mass differences of isotopes, which determine the composition of each individual water molecule. Stable hydrogen and oxygen isotope ratios may be used to infer the relative contributions of different water sources to a groundwater system, provided that the isotopic traces of the water sources do not change throughout the mixing process (Clark and Fritz, 1997; Liu et al., 2008).

The composition isotope of water molecules has been utilized as tracers in watershed systems (Clark and Fritz, 1997). In addition, utilizing information is crucial in determining water age and identifying mixing patterns between various water sources, as (Bowen, 1986) described. Additionally, it aids in characterizing flow paths that arise from precipitation to discharge in a stream and identifying contaminant sources for different solutes, as demonstrated by (Litke, 1994; Kendall and McDonnell, 1998). Furthermore, it helps determine flow velocity and direction, as evidenced by (Singh and Kumar, 2005). Lastly, it is useful in identifying water sources, such as groundwater and soil water content, for plants and crops during different seasonal periods (McCole and Stern, 2007).

In a semiarid environment like the SWSB, tracing the passage of water molecules and observing the fluctuations in their isotopic composition may be able to identify the primary sources of water (for example, snowfall, treated wastewater, and groundwater).

3.2.2 Deuterium Isotope ^2H

An isotope of hydrogen called Deuterium has one proton, one neutron, and one electron. A proton and a neutron make up the deuterium atom's nucleus. Deuterium is designated with the symbol ^2H. Deuterium has a mass number of 2 and an atomic number of 1. 2.014 amu can be used to represent the atomic mass. Even though it is less prevalent, this stable hydrogen isotope exists. Deuterium is estimated to be 0.015% abundant in the crust of the Earth. Deuterium is stable and has one proton and one neutron in its nucleus. Hence it is not radioactive. Deuterium can exist in two different states: gas and liquid. Diatomic gases containing Deuterium, like D^2 or HD, are present (in combination with hydrogen). Deuterium is present in heavy water if not. D^2O molecules are what make up heavy water. Deuterium frequently behaves similarly to protium in chemical reactions. There are, however, some other distinctions. Deuterium has a mass two times greater than protium because of the neutron. The bond length and bond energy are thus distinct from those of protium.

Furthermore, because of its great density, ice created from heavy water will plunge in liquid water (normal ice floats on the liquid water surface). Deuterium is used for several purposes as well. Instead of using hydrogen-only molecules as the solvent in NMR spectroscopy, deuterium-containing compounds are used. The solvent's atoms can then be used to discriminate between the peaks produced by the analyte's hydrogen atoms (Wiberg, 1955).

3.2.3 Oxygen Isotope ^{18}O

Examples of equilibrium fractionation processes include the precipitation of calcium carbonate from water. The fractionation factor, which depends on temperature and can therefore be used to estimate the temperature of the water in which the precipitation occurs, increases the abundance of oxygen-18 during this precipitation by a factor of 2.5 percent when compared to the lighter, more prevalent isotope oxygen-16. The potential of using chemicals tagged with stable isotopes effectively has been attained in many environmental applications thanks to the development of various isotopic analysis techniques. Acid rain's origins can be located, for instance, by using sulfur dioxide that has been tagged with oxygen-18 (Barbieri et al., 2005).

4. Literature review

For managing water resources and allocating resources in semiarid areas, stable isotope measurements of ^{2}H (Deuterium) and ^{18}O (oxygen-18) in precipitation and groundwater have been frequently used. Here are a few examples of research:

1- Stable isotope analysis of ^{2}H and ^{18}O in precipitation and groundwater was utilized in a study in the semiarid region of Kenya to identify the sources and mechanisms for groundwater recharge. The findings indicated that in the highlands, groundwater recharge was mostly caused by rainfall and that it was significantly reduced through the dry season (Aggarwal et al. 2005).

2- Stable isotope analysis of ^{2}H and ^{18}O in precipitation and groundwater was utilized in another study in the semiarid region of Tunisia to look into the sources of recharge and the impact of changing climates on groundwater resources. According to the findings, the groundwater was mainly replenished by winter precipitation, and during dry years, the recharging was substantially decreased (Mokadem et al., 2016).

3- Stable isotope analysis of ^{2}H and ^{18}O in precipitation and groundwater was applied in a study in the semiarid region of Western Australia in order to look into the sources of recharge and the age of the groundwater. The results from the study indicated that the groundwater was primarily recharged by winter precipitation and that its age ranged from less than five years to over a century old (Kendall and McDonnell, 2012).

4- The recharge sources and groundwater flow pathways were identified in a study carried out in the semiarid region of Mexico using stable isotope analyses of ^{2}H and ^{18}O in precipitation and groundwater. The findings demonstrated that the summer monsoon precipitation was the main factor for recharging the groundwater and that geological formations had a significant impact on the groundwater flow pathways (Mahlknecht et al, 2004).

In-depth research on the fluctuation of precipitation and groundwater in the Middle East has used stable isotopes of Deuterium (^{2}H) and oxygen-18 (^{18}O). Following are a few examples of research:

1- Stable isotope analysis of ^{2}H and ^{18}O was used in a study in the Jordan Rift Valley to look into where the area's groundwater is being recharged. The findings showed that climate variability had an impact on groundwater recharge and that winter precipitation was the primary source of recharge (Gat, J.R., 1971).
2- Another study examined the sources of recharge and the hydrologic connections between the various aquifer systems in the Gaza Strip using stable isotopes of ^{2}H and ^{18}O. The study discovered that the various aquifer systems were not well connected and that winter precipitation was the primary source of groundwater recharge (Al-Juaidi et al., 2014).
3- The recharge sources and groundwater flow patterns in the area were investigated in a study carried out in the United Arab Emirates using stable isotope analysis of the elements ^{2}H and ^{18}O. The findings demonstrated that the underlying geology had an impact on groundwater flow and that winter precipitation was mostly responsible for recharging it (Alsharhan & Rizk, 2020).
4- Stable isotopes of ^{2}H and ^{18}O were employed in a study carried out in Iran to look into groundwater recharge sources and flow patterns in the area. According to the study, the area's complicated geology had an effect on the groundwater flow and winter precipitation was the main source of groundwater recharge (Daneshian et al. 2021).

The variability of precipitation and groundwater in the Kurdistan area has been investigated using stable isotope analyses of Deuterium (^{2}H) and oxygen-18 (^{18}O). Following are a few examples of research:

1- Stable isotope analysis of ^{2}H and ^{18}O has been used in research in the Sulaimaniyah Governorate in the Kurdistan area to look at the sources and mechanisms of groundwater recharge. The study discovered that the groundwater was mostly replenished by winter precipitation and that the recharging was controlled by the local geography and geology (Mahmmud et al., 2022).

2- Another study in the Kurdistan area examined the sources of recharge and groundwater flow patterns in the Halabja-Said Sadiq Basin using stable isotope analyses of the elements ^{2}H and ^{18}O. The study concluded that faulting and the underlying geology had an impact on groundwater flow and that winter precipitation was the primary source of groundwater recharge (Abdullah et al., 2015).
3- In a study performed in the Kurdistan region's Erbil Governorate, stable isotope analysis of ^{2}H and ^{18}O was employed to look into the sources of recharge and the hydrologic connection between the various aquifer systems. The study discovered that there was little interconnection between the various aquifer systems and that winter precipitation was the primary source of groundwater recharge (Seeyan and Merkel, 2014).

Isotopic fractionation occurs when water moves from a gas to a liquid or from a solid to a liquid. Because the heavier isotopes (^{18}O and D) are more numerous in the condensed phase, fractionation changes the relative abundance of the isotopes. The heavier molecules $H_2\,^{18}O$ and HDO, for example, are more common in the water phase than in the vapor phase as water evaporates from the ocean (Schwartz and Zhang, 2003). These simple equilibrium models aid in explaining what occurs during fractionation. Natural processes, on the other hand, are more complicated, and isotopic ratios of water vapor in air masses near seas are not in balance with the water. In general, vapor levels are lower than anticipated. Rainfall collected at the equator has an isotopic composition that is most similar to that of seawater, but it is still significantly deficient. Both ^{18}O and D are fractionated in a consistent manner by evaporation and condensation processes, while the extent of fractionation varies. Water moving from the oceans into the sky and falling as rain has associated $\delta^{18}O$ and $\delta^{2}H$ values (Schwartz and Zhang, 2003). In other words, if one of the values is known, the other can be predicted. When isotope chemists began investigating rainfall samples from all around the world in the early 1950s, they discovered this feature.

The most common technique to understand the results of ^{18}O and D analysis is to plot δD versus $\delta^{18}O$ (Craig, 1961). The location of the data in reference to the meteoric water line indicates what processes have transpired. Water with an isotopic composition that falls on the meteoric water line is thought to have formed from water vapor condensation and is unaffected by other isotopic processes. Temperature and other factors, which we shall investigate more, can cause the actual location on the meteoric water to change. Other isotopic mechanisms cause deviations from the meteoric water line. The position of the data points can help identify a process in most cases since these processes influence the link between δD and $\delta^{18}O$ in such a unique way. This depletion occurs more quickly if the rain falls at a colder temperature (Schwartz and Zhang, 2003). Water vapor can be added to the atmosphere by evaporating water from the ground and returning it to the atmosphere. However, due to evaporation-related fractionation, this water will be isotopically lighter. The δD and $\delta^{18}O$ values obtained for rainfall can be explained in terms of temperature and the air mass's transit history. There is more fractionation between phases at lower temperatures. As air masses move over continents, this temperature effect becomes more relevant since rain continues to deplete the air mass in terms of heavier isotopes. Write to this depletion occurs more quickly if the rain falls at a colder temperature. Water vapor can be added to the atmosphere by evaporating water from the ground and returning it to the atmosphere. However, due to evaporation-related fractionation, this water will be isotopically lighter. The concepts of a continental effect, an elevation impact, and a latitude effect represent these principles. The continental effect is the gradual loss of isotopic composition of water vapor as it travels from oceans to continents. Because the heavier isotopes (D and ^{18}O) are preferentially enriched in rain, the reservoir of heavier isotopes vapor is reduced. Each raindrop is isotopically lighter than the one before it. This effect has been thoroughly researched all throughout the world. The fall in δD when vapor from the Pacific Ocean flows over southern California is well illustrated by (Ingraham and Taylor, 1991). As it flows through mountains, the elevation impact accelerates the depletion of δD and $\delta^{18}O$ in water vapour. The tendency for greater rain at higher elevations as water vapour is transferred to higher elevations increases the pace of depletion. Furthermore, the temperature of condensation is lower at higher elevations, which promotes fractionation and accelerates the rate of depletion. The increase in elevation is accompanied by an increase in precipitation. The isotopic composition does not alter till you enter the Great Basin (around 350 kilometers) (Schwartz and Zhang, 2003). Precipitation in higher latitudes is disproportionately depleted in D and ^{18}O (that is, more negative) as compared to samples from lower latitudes, according to observations from around the world. Higher precipitation rates and cooler temperatures at higher latitudes explain this latitude impact. Moving north along the western coast of the United States to Canada, for example, values of δD drop from about to approximately while values of $\delta^{18}O$ drop from -4 to -14 (Gat, 1980). In groundwater, variability in ^{18}O and D along the meteoric water line, the usage of ^{18}O and D in groundwater applications is described in this section. It looks at circumstances where ground water's isotopic composition crosses the meteoric water line. Shallow groundwater has an isotopic composition in this type of situation. It is comparable to precipitation it is assumed that no processes modify the isotopic composition of precipitation once it recharges the groundwater in this simplest example. The following section addresses the more complex circumstances in which isotopic processes cause deviations from the meteoric water line. A groundwater system is more complex than the air systems that have been studied thus far. The reason for this is that a flow system can contain meteoric water that refilled ground water thousands, if not hundreds, of years ago. In effect, the groundwater system can serve as a repository for data on precipitation isotopic composition across time. Low-permeability units may also include the original formation water at the time the unit was deposited in a climate that was very different from today's (Desaulniers et al., 1981; Hendry and Wassenaar, 1999; Remenda et al., 1994). Several causes on the continents explain why the isotopic composition of rainfall at a given location may fluctuate over time. The most noticeable are continental glaciations that occur at regular periods throughout geologic time. Local rainfall was isotopically substantially lighter than current precipitation during the most recent glacier, which occurred 10,000 to 25,000 years ago. Consequently, the temperature in the Northern Hemisphere was colder on a continent-wide basis than today, resulting in increased loss of heavier isotopes as air masses moved across continents. A tectonic source of long-term changes in the isotopic nature of rainfall is another less obvious factor. Mountain ranges can grow and modify the pattern of vapour transfer throughout the continent over millions of years. An example is the Great Basin of the United States, where the Sierra Nevada's continued uplift has enhanced rainout while steadily decreasing the δD of rain. Groundwater ^{18}O and D measurements frequently map near the meteoric water line over a wide range. This pattern is typically explained as a long-term climate change, with old water from the last glacier being isotopically lighter (that is, more negative) than the current recharge. In the northern United States and Canada, for example, fine-grained glacial deposits (e.g., glacial tills) have frequently been discovered to contain water that was created thousands of years ago when the deposit was set down. The hydraulic conductivity of these deposits is so low that it has taken 10,000+ years of recharging to displace the formation water. This condition arose in a thick aquitard system in Saskatchewan, Canada, as described in Case Study 20-1 (Henry and Wassenaar, 1999) gathered along a 100 km flow line ranged from an outcrop value of roughly - 19% in D to -35% in the aquifer, considerably downgradient. The water at the down-angle end of the stream framework is assessed to be around 30,000 years of age. Sea levels decreased by 150 meters during the glacial maximum, shifting the shoreline 200 to 300 kilometres westward. Because of the increased journey time, the continental effect would cause metéoric water replenishing the aquifer to be reduced. Hendry and Wassenaar examined how ^{18}O and D varied within a thick aquitard. The aquitard is made up of 80 meters of Quaternary clay-rich till, which is overlain by 76 meters of Cretaceous coastal clay. Around 12.000 years ago, the glacier that deposited the till retreated from this portion of Saskatchewan (Hendry and Wassenaar, 1999). Sklash and colleagues studied hydrologic processes in Big Creek and Big Otter Creek, two tributaries of Lake Erie in southern Ontario, using ^{18}O as a tracer. Each watershed has an area of around 700 miles (1812 km2) and primary channel lengths of approximately 85 miles (137 km). The watersheds begin in a till highland and run across the Norfolk Sand Plain, which accounts for around 75% of the two watersheds. (Sklash et al., 1976) In Surprise Valley, California, this study tracks the changing isotopic composition of water as it moves through the hydrologic cycle. Melting winter snows entered the subsurface and flooded waterways. The creeks flowed into playa lakes, where much of the water evaporated during the summer. Snow samples have $\delta^{18}O$ and δD values that are near the meteoric water line, as expected.

Groundwater and creek water are heavier in isotopes, but they also lay along the meteoric water line. The creeks' relatively stable isotopic composition reflects the significant contribution of groundwater to the flow (Ingraham and Taylor, 1989). The Makook anticline's karst springs were studied to learn more about the complicated karst system's hydrogeologic, hydraulic, and hydrodynamic activity. Between September 2011 and November 2012, eight springs were investigated for hydrogeochemical constituents as well as ^{18}O and ^{2}H. The local meteoric water line was drawn for the first time for the area using precipitation data from November 2011 to April 2012. Between the global and Mediterranean meteoric water lines is the regional meteoric line. The majority of the spring samples fell between the local and Mediterranean meteoric water lines, indicating Mediterranean impacts, quick rainfall infiltration through the karst system, and a short residency time (shallow karst aquifers). The evaporation process in the area's karst waters was assessed using the correlation between d-excess and halite saturation index. The temporal variation in the isotopic composition of karst springs has been observed, allowing researchers to distinguish between different spring origins and indicating a possible connection between aquifers. Based on this, the karst system can be divided into three aquifers: Behkme aquifer, Kometan aquifer, and Shiranish aquifer. In Iraqi Kurdistan, the climate in the region is Mediterranean (Koppen climatic classification Csa), with chilly damp winters and scorching dry summers. The majority of precipitation falls between October and May, with a maximum of over 100 mm in January (Stevanovic & Markovic, 2003). The average annual precipitation is 668.5 millimetres, the average annual air temperature is 21 degrees Celsius, and the average annual evaporation is 2298.8 millimetres (Hamamin et al., 2018). By taking the data and creating a plot of δD versus $\delta^{18}O$, the outcomes of ^{18}O and D studies are often understood. Information about the processes that have taken place can be gleaned from where the data fall in reference to the meteoric water line. Supposed to have come from the condensation of water vapour and unaltered by other isotopic mechanisms, water with an isotopic composition falls on the meteoric water line. Temperature and other factors, which we shall go through in more detail, can change the precise location of the meteoric water. Several isotopic mechanisms cause deviations from the meteoric water line. Most of the time, these processes have a distinctive impact on the relationship between δD and $\delta^{18}O$, making it possible to identify a process by looking at the locations of the data points. The processes that shift water composition farther from the meteoric water line are shown in Fig (2) for clarity.

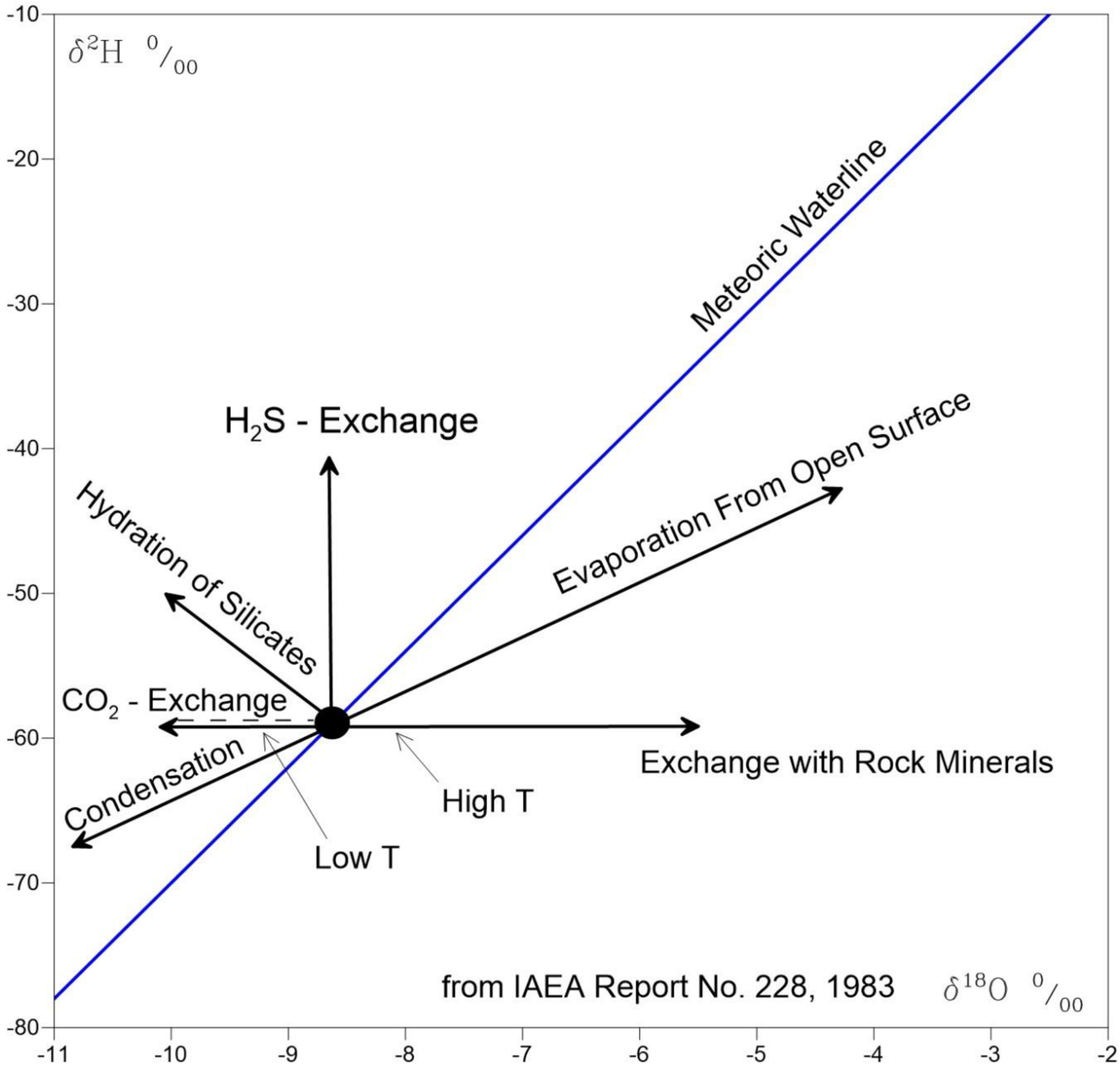

Figure 2 The effects of precipitation on hydrological investigations are shown by the global meteoric water line when combined with a local meteoric water line.

5. Study Area

The research area, which extends an area of approximately 1500 km2, is situated on the slopes of the Sulaimani governorate in the Iraqi Kurdistan Region. The Zagros Mountains are approximately between 700 m and 1200 m in elevation, figure (3). According to the Köppen climatic classification, the area has a Mediterranean climate (Csa), which is typified by moderately chilly, rainy winters and hot, dry summers. Most precipitation occurs between October and May throughout the winter, with a peak of more than 100 mm in January (Stevanovic & Markovic, 2003). The average annual temperature is about 21° C, with 668.5 mm for precipitation and 2298.8 mm for absorption (Mustafa, 2006; Hamamin et al., 2018). The perennial Tanjero River, which is the main river, is often empty from August to the start of the rainy season in October. The main city is Sulaimani, which is in the study area's westernmost corner and has a resource of garbage and waste dumped there (Rashid et al., 2018). The High Folded Zone contains the Sulaimani-Warmawa Sub-basin. Early Cretaceous to Quaternary geological formations make up the study area (Buday, 1980; Jassim & Gof, 2006; Al-Jiburi et al., 2015). The research region is a hydrological Sub-basin that is a section of the Sulaimani Sharazoor basin and is located in the Iraqi Kurdistan Region near the city of Sulaimani (Stevanovic & Markovic, 2004).

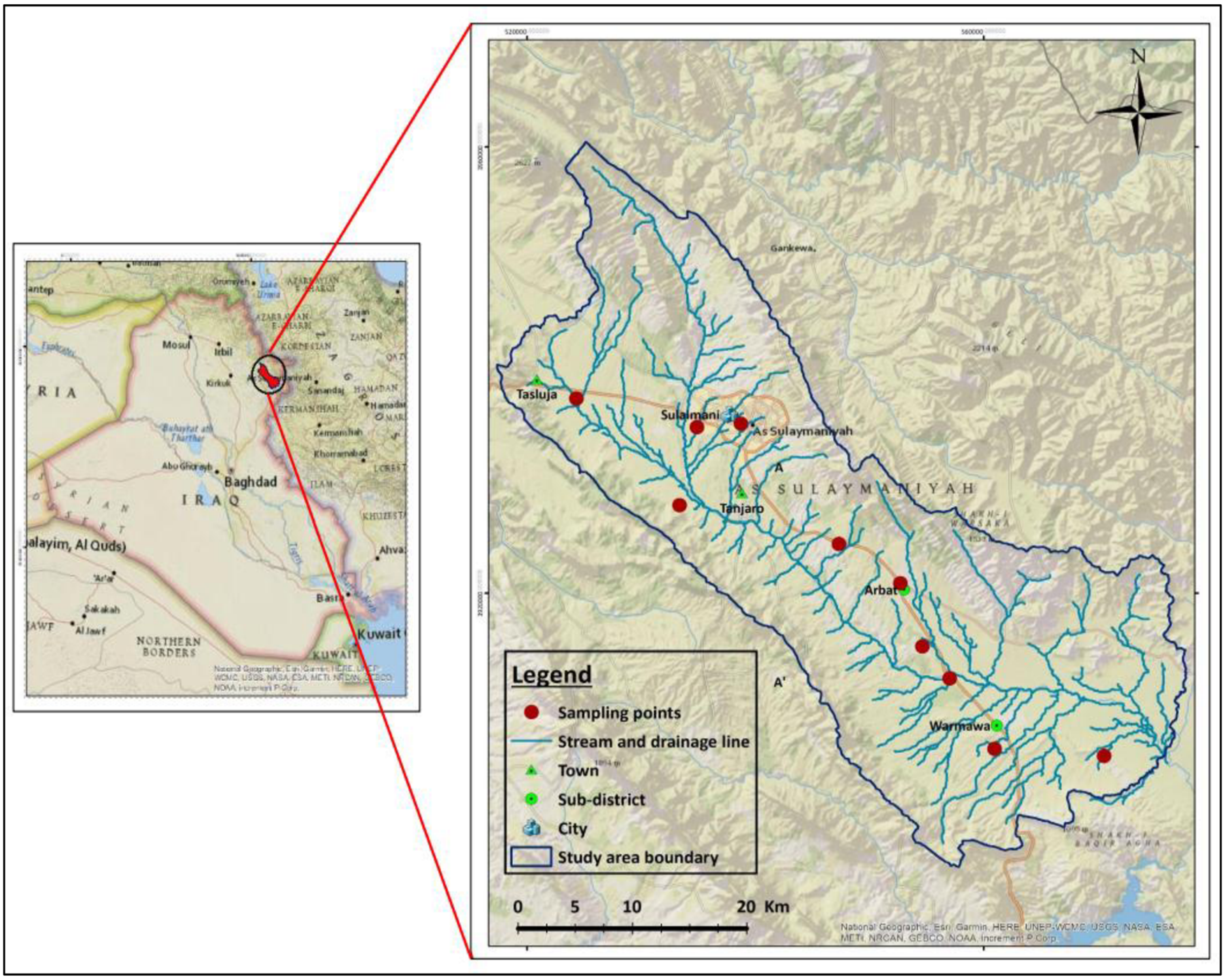

Figure 3 Study area location and sampling points

5.1 Geological Formation of the study area

5.1.1 Balambo Formation

The Balambo Formation, the oldest Formation in the examined area, is one of many rock units that are present within and around it that date from the Lower Cretaceous, as shown in Figure (4). The sequence below this Formation is represented by unknown Jurassic rocks, and the newest unit is characterized by recent Pleistocene (Quaternary) deposits that may encompass a portion of the study region (Mustafa, 2014). Formations are

1,000, 120, 70, and 60 meters thick. The study area's oldest exposed Formation was dated to the Valanginian to Turonian period (Lower Cretaceous). The Formation has two portions, each of which is 762 meters thick on average. The lower part of (259) m is made up of thin-bedded blue ammonitiferous limestone with chemical interaction of olive-green marls and dark-blue shales, both of which were deposited in a miogeosynclinal trough in a deep-marine bathyal environment. The upper part of (503) m is made up of thin-bedded grey globigerinal-radiolarian limestone. Most of the Balambo Formations are outcrops and are located to the east and southeast of the research area of radiolarian limestone that is thin and well-bedded (Mustafa, 2014).

5.1.2 Kometan Formation

Dunnington, who first researched the Formation in 1950 near the Kometan village in NE-Rania (North Iraq), identified it as (Turonian). The Kometan Formation is defined as globigerial-oligosteginal limestone, white-weathering, light grey, thin-bedded, and sometimes silicified. Additionally, well-bedded fne crystalline limestone is another way to define it (Bellen et al., 1959). The Formation is located near Sarchinar in the northwest of the examined area and has complete (90 m) thickness stylolite, pyrite, and chert nodules.

5.1.3 Qamchuqa Formation

Wetzel first identified the type of the Formation in 1950 in the vicinity of Qamchuqa Gorge in the Sulaimani region; the age of the Formation is (Albian-Barremian). Additionally, the Qamchuqa Formation, which is made up of dolomitic limestone and massive grey dolomites, predominantly outcrops in the northern section of the Sub-basin (Ali, 2007). The Formation was deposited in a miogeosynclinal trough (Buday, 1980) in a neritic to pseudobathyal marine environment, in which underlying by Sarmord Formation conventionally and overlying unconformably by Kometan Formation (Bellen et al., 1959). (Karim and Ali, 2004) claims that the Qamchuqa Formation is a Lowstand System Tract (LST) that was deposited in a shallow maritime reef environment.

5.1.4 Shiranish Formation

The Shiranish Formation is Late Cretaceous strata in the research region. The main elements of the Shiranish Formation are marly limestone and bluish-grey marl. The lithology of Shiranish Formation is Claystone, shale, siltstone, sandstone, marl, marly limestone, and rare conglomerate (Sissakian, 2015). Early High-stand System Tract (HST) in a Shelf to Basin environment which is analogous to a shelf in depth, is the sequence of deposition of the Formation (Karim and Ali, 2004).

5.1.5 Tanjero Formation

In the Sulaimani-Warmawa Sub-basin, particularly in the area surrounding the city of Sulaimani, the Tanjero Formation is widespread and stretches from the foothills of Goizha Mountain in the north and northeast towards the Tanjero valley in the south and the Chaq-Chaq valley in the northwest (Mustafa, 2006). It is made up of organic detrital limestone that is sandy or silty, as well as silty marl, siltstone, shale, sandstone, and conglomerate (Bellen et al., 1959). Based on its lithological makeup, the Tanjero Formation has been classified into three sections: the Lower, Middle, and Upper sections. The alteration of thin sandstone wedged between thick dark grey calcareous shale, which transitions to a thick bed of boulders and coarse gravel conglomerate strata, makes up most of the lower section. The upper portion is made up of mixed siliciclastic-carbonated layers that are depicted as the modification of thick-bed biogenic limestone and calcareous shale on the shelf. The middle portion is made up of bluish marl. Kolosh, Sinjar, Gercus, and Pila Spi are the region's Tertiary geological formations. Dark grey siltstone, shale, and claystone make up the Kolosh Formation, together with rare conglomerate (Karim and Ali, 2004).

5.1.6 Kolosh Formation

Studied for the first time by Dunnington in (1952) NE-Iraq at Kolosh village. A region from the foot of the cliff to the right bank of the stream is cropped out of the Kolosh Formation, which is intermittently covered by enormous quantities of thick-bedded limestone. The outcrops run along this homocline from Tasluja Town in the northwest to the Sirwan River in the southwest, south of Halabja Town.. Dark grey claystone, shale, and siltstone make up the Kolosh Formation, and there is infrequent conglomerate (Sissakian, 2015).

5.1.7 Sinjar Formation

The Formation was described by Keller (1941) near Mamissa village in Sinjar Mountain NW-Iraq and dated the Formation as (Paleocene-Lower Eocene) (Bellen et al., 1959). The Formation, according to Surdashy (1988), is made up of white to grey limestone that has been dolomitized in certain places and skeletal brown to dark-grey hard limestone that has resulted in the development of cliffs. Baranan Mountain is composed of dolomitic-limestone at the summit and white-grey limestone with nodules of chert, iron oxide, and limestone. The Formation was formed in a shallow maritime habitat called a reef (Buday, 1980) and Gercus Formation lies on top of the Formation (Bellen et al., 1959).

5.1.8 Gercus Formation

Based on stratigraphic location, the Gercus Formation is a Middle Eocene formation that is exposed in northern Iraq's High Folded Zone. It extends as a confined northwest-to-southeast band from Dohuk to the Darbandikhan region (Buday, 1980; Jassim and Goff, 2006). The Formation mostly comprises conglomerate along with clastic rocks such as claystone, sandstone, marl, and calcareous shale. Gypsum lenticles, especially at the top. Rare lignite occurs in the base of the sandstone and rock salt occasionally (Bellen et al., 1959).

5.1.9 Pila Spi Formation

Low-thickness outcrops of the Pila Spi Rock Formation are primarily found in the northwest and southwest of the study region. They are made up of cyclic Formations of claystone, marl, gypsum, and sandstone with occasional limestone as well as well-bedded limestone, dolomite, marly limestone, and sandstone, as well as altered red claystone, sandstone, and conglomerate. Most of the Quaternary deposits are sediments from flood plains and alluvial fans. Gravel, sand, silt, mud, sandy, and silty clay soil make up the majority of their material (Mustafa, 2006; Sissakian, 2015). Iraq geological map is shown in figure (3).

5.1.10 Fatha Formation

Busk and Mayo (1918) were the first to define and describe the Fatha Formation (formerly known as the Lower Fars Formation), which was later reassessed by (Bellen et al., 1959), in Iran, as part of the Fars Group. The Lower, Middle, and Upper Fars formations constituted the Iranian Fars Group. The Lower Fars Formation (also known as the Fatha Formation) is lithologically related to its Iranian counterpart and was also recognized in Iraq (Bellen et al., 1959). A variety of mud rocks, limestones, and gypsum make up the Fatha Formation sequence. It consists of two separate rock units. The Lower Member is composed of a basal unit of organo-detrital limestone, thin limestone, and green dolomitic marl, as well as gypsum, green marl, and limestone are cyclically interbedded (Alsultan & Awad, 2021). Gypsum, thin grey limestone layers, and cyclic red-and-green mudstones with calcarenite beds on top make up the Upper Member. The findings suggest that the four major lithofacies that can be distinguished between the Fatha Formation are based on the dominant lithology (Alsultan & Awad, 2021).

5.1.11 Quaternary deposit

Quaternary deposits in the region are typically made up of floodplain deposits from the Qiliasan and Tanjero Rivers, which range in thickness from 10 to 15 meters and range from coarse gravel to fine silt and clay. The second major Pleistocene deposit that covers both sides of the Qiliasan and Tanjero Rivers with a thickness of (5–10 m) is represented by river terraces. In the examined area, alluvial deposits that form fans along the foothills of the Goizha, Piramagroon, and Baranan mountains range in size from boulders to sand and clay particles. Some areas of Sulaimani City are situated above the Goizha Mountain alluvial fans (Mustafa, 2014).

Figure 4 The Balambo Formation showing well bedded and highly deformed nature of layers (Sissakian et al., 2016).

5.2 Hydrogeology of the study area

The hydrogeological map has been created for the study area based on the previous study which conducted in Iraq and Kurdistan Region. In addition, Mahmmud et al., (2022) prepared and updated the hydrogeological map, especially for the Sulaimani-Warmawa Sub-basin. The hydrogeological map of Sulaimani sub-basin is shown in fig (6). According to the classification, their lithology and hydrogeologic properties, the hydrostratigraphic units in the study area have been divided into the karstic fissured aquifer (KFA), the Kometan aquifer (KA), the Tanjero aquifer (TA), an aquiclude, and a sedimentary intergranular aquifer (QIA) (Mahmmud et al., 2022). The primary productive aquifers in the research region, in terms of groundwater quantity and quality, are the Tanjero Aquifer (TA) and the Cretaceous Intergranular Aquifer (QIA). However, they receive their replenishment from karstic formations that are relatively porous and located close to the basin margins. The Tanjero river, which flows into the Darbandikhan Lake out of the basin in the southeast, and Sulaimani are the general groundwater flow directions (Mahmmud et al., 2022).

The high discharge capacity is frequently present in deep drilled wells with 100–150 m depths. The measured yields during pumping experiments occasionally approached 40–50 l/s with minimal drawdown. The final sedimentary phase of the Cretaceous was characterized by flysch formations (Tanjero, Shiranish Fms.) Alternating carbonate and flysch layers were formed during the Paleogene epoch as a result of lateral variation and various depositional conditions (neritic and bathyal) (Kolosh Formation, Red bed series). Similar conditions persisted during the Neogene: impervious clastic rocks predominate in the Gercus Formation, while the "Pila Spi" karstic-fissured aquifer, created in the limestone, contains significant reserves (in certain cases, the well capacity may reach 40 l/s with high artesian pressure) (Stevanovic & Iurkiewicz, 2009).

The karstic aquifers' primary method of drainage is by spring discharge. The locations of the outlets are influenced by several factors, including the contact between water-bearing layers and impervious rocks, the presence and distribution of tectonic elements, and climatic conditions. The resources of the aquifer system determine how much water is discharged through springs. The High Folded zone is where many of the huge springs are found. The area's great unpredictability in terms of both the area and quantitative distribution of recharge is one characteristic that directly represents the karstic aquifer regime. The rainy season typically ends in April, and until late September, there are no wet days. Therefore, the spring hydrographs show a typical monotone loss of the accumulated resources throughout a recessionary phase. The growth of underground drainage is mostly dependent on effective porosity, the karstification of the subsurface, and accumulated nonrenewable (static) groundwater reserves. As a result, while many springs abruptly dried out or significantly reduced their supply, others gradually discharged by slightly decreasing spring flow. Middle and upper Miocene periods saw the continuation of the sedimentation cycle in the Low Folded zone, which resulted in the deposition of substantial layers of

Lower and Upper Fars sediments. Their facies, which consist of marls, sandstones, anhydrite, gypsum, conglomerates, clays, and sand, is highly diverse. The Formation's diverse lithology represents negligible groundwater supplies that could only locally address the issue of supplying water to tiny communities (Stevanovic & Iurkiewicz, 2009). The Shiranish formation is in contact with the second aquifer, the Kometan formation, which is a well-karstified and heavily fissured aquifer with confined to semi-confined characteristics. The Kometan aquifer has a pore- and conduit-controlled flow regime and varies in depth from moderate to high. The Kometan aquifer is made of carbonate rocks and contains a significant volume of groundwater that varies in location and time (non-homogenous aquifer with seasonality affecting the available amount of water). During the Paleocene and Miocene eras, the aquifer system underwent intense karstification cycles. The Kometan aquifer contain rocks with varying degrees of karstification, from mild to well-karstified. While the Shiranish aquifer is distinguished by poorly karstified rocks, karst maturity ranges from young to mature karst. Although depressions and sinkholes are a rarity among karst features, remote sensing studies show that the cores of some of the largest anticlines are pitted as a result of karstification. Iraq hydrogeological map is shown in Figure. 5.

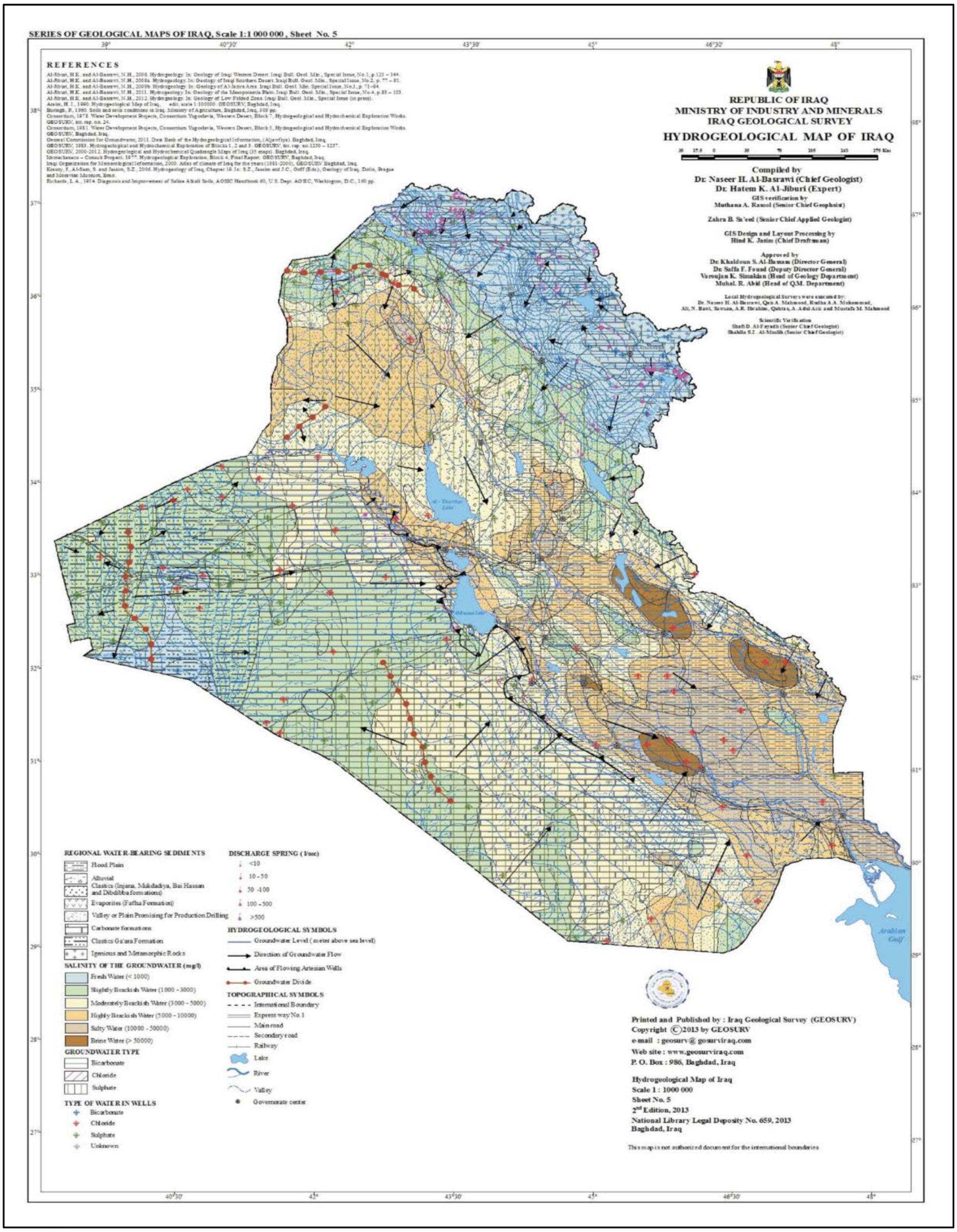

Figure 5 Hydrogeological map of Iraq and Kurdistan Region (Al-Jiburi & Al-Basrawi, 2015).

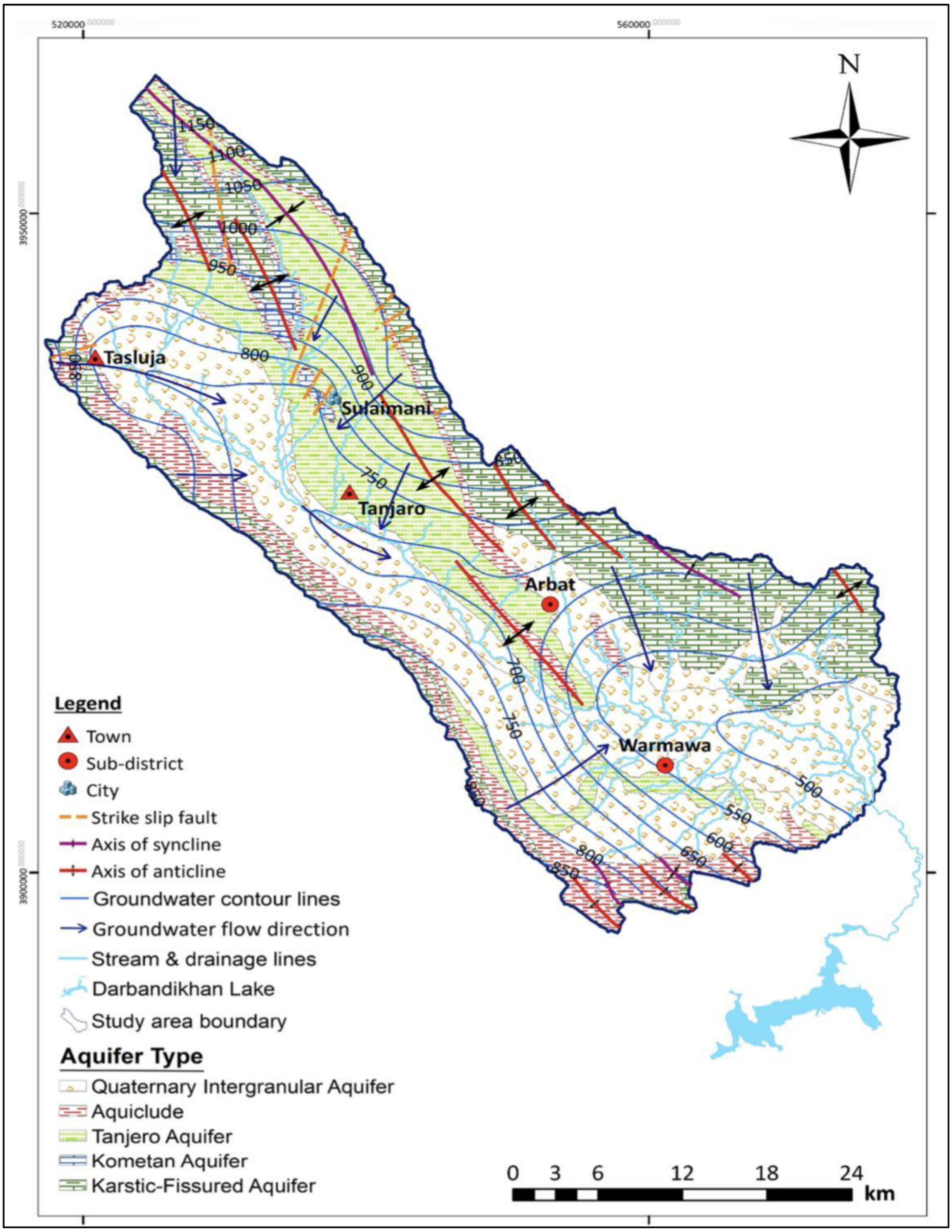

Figure 6 Hydrogeological map of Sulaimani-Warmawa Sub-basin (after Mahmmud et al., 2022)

6. Material and Methods

6.1 Field works and data collection

In April 2022, the data were collected from several groundwater wells in different locations in the study area. Groundwater samples have been taken from 10 different wells. Physical parameters of water such as pH, TDS, electrical conductivity, and temperature, have been measured in the field (Fig. 7, Fig. 8), and the samples were taken from each well after 10-15 minutes of pumping. Samples were collected in the standard plastic bottles. The volume of bottles was 100 ml. These samples have been used for stable isotope analysis in Czech Geological Survey in Prague.

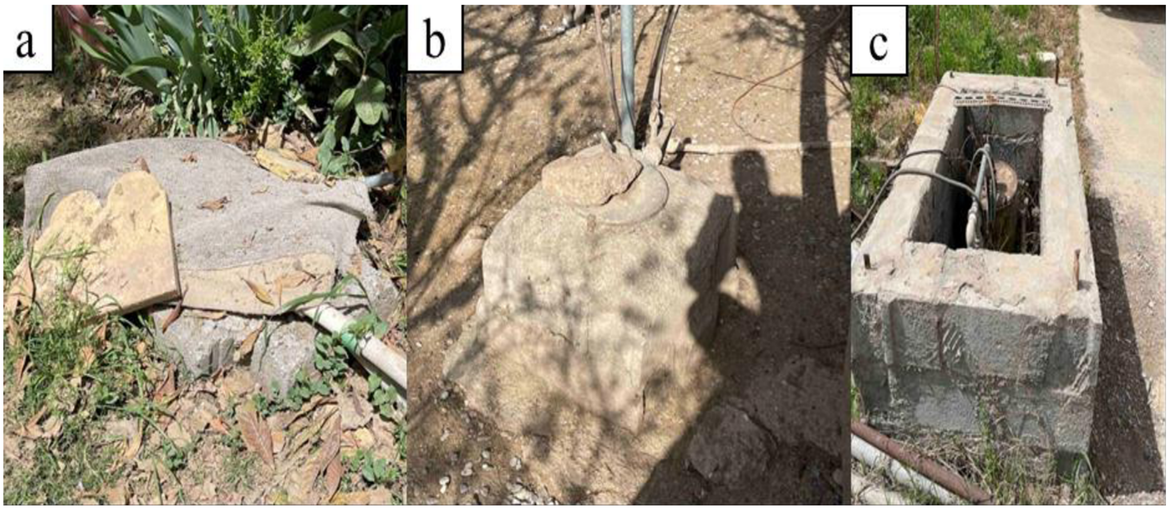

Figure 7 Three of sampled wells. Wells are in Sulaimani in different locations: a) Bakrajo, b) Weladar, and c) industrial area of Sulaimani.

Figure 8 Measurement of pH, TDS, electrical conductivity EC, and temperature in the field

6.2 Data analysis

Using a LWIA 3000 laser analyzer, the isotopes δ^2H and δ^{18}O were measured at the Czech Geological Survey in Prague (LGR). For δ^2H and δ^{18}O, respectively, the analysis' resolution was 0.4 and 0.12. The data were provided in common δ- notation after being standardized to the global standard (V-SMOW) (Clark and Fritz, 1997).

6.3 Vienna Standard Mean Ocean Water (V-SMOW)

Vienna Standard Mean Ocean Water is a water-specific isotopic reference. The VSMOW, despite its name, is for pure water that doesn't include any salt or other substances that are present in oceans. In 1968, the Vienna-based International Atomic Energy Agency (IAEA) published the VSMOW standard, and since 1993, the IAEA, the European Institute for Reference Materials and Measurements, and the American National Institute of Standards and Technology have all continued to evaluate and research the standard. The standard includes both the determined concentrations of stable isotopes that are present in waters as well as calibration materials for standardization and laboratory-to-laboratory comparisons of the devices used to measure these concentrations in experimental materials. When comparing hydrogen and oxygen isotope ratios, usually in water samples, the VSMOW is used as a reference standard.

6.4 Global Meteoric Water Line (GMWL)

Comparison with the global meteoric water line is the accepted method for interpreting results of measurement of oxygen-18 (^{18}O) and Deuterium (^{2}H) stable isotopes in water. The plot compares Craig's (1961) world global meteoric water data displayed on the x-axis and the y-axis, respectively, and the data from studied areas.

The following equation commonly describes the global meteoric water line (GMWL), which is based on the stable isotopes in naturally occurring meteoric fluids (water produced from snow, rain, and other types of precipitation):

$$\delta^{2}H = 8 * \delta^{18}O + 10 \text{ .... Equation (1)}$$

7 Results and Discussions

7.1 Results

7. 1.1 Stable isotopes

The composition of a stable isotope of the groundwater from the Sulaimani-Warmawa Sub-basin stated in δ-notation per mil deviation from the internationally accepted standard V-SMOW (Vienna Standard Mean Ocean Water) are illustrated in Table 1 and Figure 9. The range of $\delta^{18}O$ is from (−6.7‰) to (−4.5‰) and for $\delta^{2}H$ from (−38.2‰) to (−24‰) for the water sampling in April 2022. The deuterium value excess is high in some samples, reaching more than 20‰. The isotopic composition of local rainfall might be affected by several factors, such as geographic location (longitude and latitude), altitude, surface air temperature and humidity (Mazor, 2004; Charideh, 2011). As per the result of the isotopic composition of groundwater samples in the study area, the most negative value was obtained in the groundwater sample (WS06) which was (−6.7‰) and the most positive value was in the groundwater sample (WS09) which was (−4.5‰) The sample is located in the lowest altitude in the area.

Table 1 The results of isotope in groundwater samples in the study area during April 2022

Samples	$\delta^{2}H$ (‰)	$\delta^{18}O$ (‰)	Deuterium excess
WS01	-27.0	-5.0	13.4
WS02	-26.2	-5.4	17.1
WS03	-24.0	-4.9	15.6
WS04	-24.4	-4.6	12.6
WS05	-27.5	-5.1	12.9
WS06	-38.2	-6.7	15.2
WS07	-30.2	-5.5	13.6
WS08	-30.7	-5.4	12.6
WS09	-24.0	-4.5	11.6
WS10	-27.4	-5.6	17.7

7.1.2 Discussion

According to the result of isotopic data analysis and after comparing the results to the global meteoric water line (GMWL), it can be concluded that the (GMWL) has a higher slope and intercept than the local groundwater line (GWL) in the study area (Craig, 1961; Gat & Carmi, 1970) (Fig. 9). The GWL for the groundwater samples in the study area also has a higher slope and intercept than the local meteoric water line (LMWL) which was established for Zagros by (Osati et al., 2014). This suggests that the groundwater in the area of interest has been recharged mostly from winter rainfall with limited of evaporation during infiltration as found in previous study by (Mahmmud et al., 2022). In addition, the GWL for the study area almost the same slope when compared to the local groundwater line (LGWL) which was developed by (Mahmmud et al.,2022). However, this is different from the groundwater data from western parts of Iraq where evaporation influence with resulting groundwater line slope of 5.19 was detected (Ali et al., 2015).

The highest altitude sample, which is 717 m above sea level, had the greatest negative value ($\delta^{18}O = -6.7‰$), Table 1, as a consequence of altitude effect (Clark and Fritz, 1997).

The equation for groundwater data is δ^2H ($\delta^2H = 6.3442 * \delta^{18}O + 5.474$) has lower slope compared with GMWL ($\delta^2H = 8 * \delta^{18}O + 10$), i.e., as shown in Fig. 9. Also, the slope is slightly lower compared with local meteoric water line (LMWL) made for Sulaimani sub-basin ($\delta^2H = 6.6055 * \delta^{18}O + 10.04$). It is similar compared with LMWL for spring and winter precipitation in the study area ($\delta^2H = 6.44 * \delta^{18}O + 8.514$) (Mohammadzadeh et al., 2020). The data again correspond to winter/spring precipitation with limited evaporation. The large deviation observed for precipitation isotopic data in the Iraqi and Irani Kurdistan LMWL from the global meteoric water line (GMWL) seems to be caused by the mixing of air masses from the Eastern Mediterranean with high deuterium excess and the Persian Gulf air masses. The latter process is more important in Fall when the slope of the Kurdistan LMWL decreases to 6.08 (Mohammadzadeh et al., 2020).

In the study area, the flow system is a gravity-driven flow system in the sense of (Toth, 2009). Mineralization is expressed as EC and pH increase along the direction of flow in such systems and Eh values decrease (Toth, 2009). There is a possibility of limited evaporation impact in the Tanjero Formation due to slow infiltration in lower permeability marly limestone (Mustafa et al., 2015).

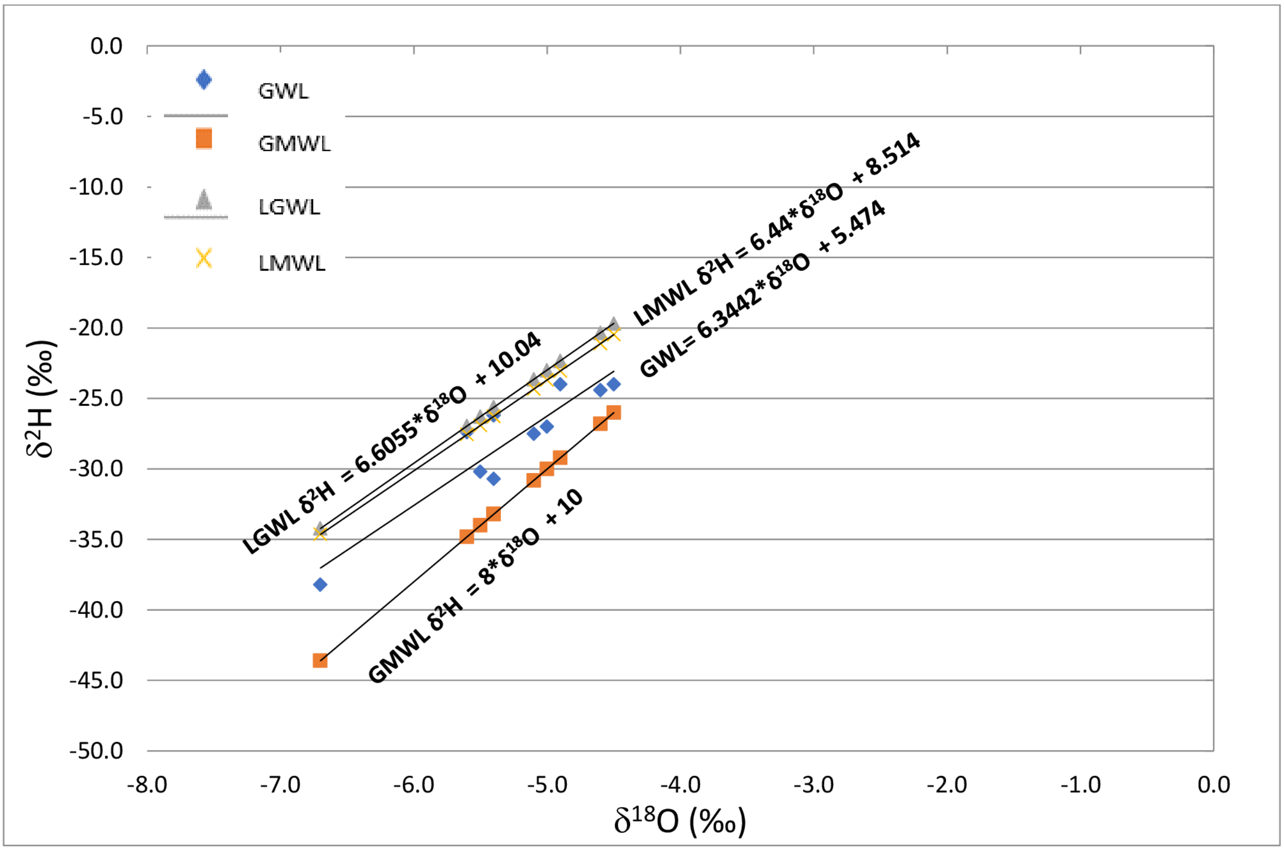

Figure 9. Diagram of δ^2H vs. $\delta^{18}O$, the GWL is the groundwater obtained in this study, LGWL is from Mahmmud et al. (2022), GMWL is global meteoric water line, and LMWL is local meteoric water line for Zagros from Mohammadzadeh et al. (2020).

8. Conclusion

The main conclusions of this study are:

The stable isotope study for precipitation and groundwater has been conducted in the Sulaimani-Warmawa Sub-basin using isotope analysis of Oxygen-18 (^{18}O) and Deuterim (^{2}H). The area of interest is located in the Kurdistan Region of Iraq, which is a semiarid region characterized by hot dry summers and cold winter. The winter in the area is cold and most of the precipitation occurs during this season with a maximum of over a hundred mm in January. The stable isotope has been analyzed for 10 groundwater samples which were taken in April 2022. According to the results, isotopic compositions ranged from (−38.2‰) to (−24‰) $\delta^{2}H$ and from (−6.7‰) to (−4.5‰) $\delta^{18}O$. The higher value of $\delta^{18}O$ is -4.5 ‰ and the higher value of $\delta^{2}H$ is -24 ‰. The groundwater line has a slightly higher slope than the local meteoric water line.

The groundwater line compared to the local meteoric water line in the area shows that the recharged groundwater faced no or limited evaporation before infiltration.

The groundwater in the area of the study has been recharged almost completely from winter rainfall and there is an altitude effect with more depleted isotopic values in samples collected in the mountains at the boundary of the catchment.

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