



Palacký University
Olomouc

Palacky University Olomouc
Faculty of Science
Department of Geology

Study programme: Geological Sciences (1201V022)

Field of study: Hydrogeology and Hydrogeochemistry

**Integration of Hydrogeology and Geochemistry for Sustainable
Groundwater Assessment, Modeling and Management in the
Zagros Basin, the Kurdistan Region of Iraq**

Doctoral Dissertation Summary

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Olomouc 2023

Abstract

The Sulaimani-Warmawa Sub-basin is in the Kurdistan Region of Iraq, which is part of the Zagros Basin and has been comprehensively studied. A combination of hydrogeology and geochemistry has been utilised for sustainable groundwater assessment, a better understanding of this vital water resource and the establishment of a scientific and standard plan for better management and protection against contamination. The region is semiarid with seasonal rainfall in winter and dry and warm summer. The field parameters such as pH, electrical conductivity and temperature were measured in water wells located in the study area. In total, twenty-six water samples, including two from rain and one from the Tanjero River, have been collected for cation, anion, trace element, stable isotope (^2H , ^{18}O and ^{13}C), $^{87}\text{Sr}/^{86}\text{Sr}$ and radioactive isotope (^3H) analysis.

In general, the water chemistry changes from Ca-HCO_3 groundwater type at the basin boundaries to Ca-Mg-HCO_3 groundwater type towards the Tanjero River along the axis of the basin. Concentrations of Na, Cl, and SO_4 increase in some samples due to halite and gypsum dissolution embedded in carbonates. Redox parameters indicate a moderately reducing environment; the pH values are neutral or alkaline.

Barium (Ba) is the principal geogenic contaminant with concentrations up to 0.383 mg/l. The other geogenic contaminants such as As, F, Mn and Cr have low or below the detection limit concentrations as predicted based on their low carbonate rock contents. Inverse geochemical modeling on selected profiles calibrated using ^{13}C values provided mass transfer coefficients for possible geochemical reactions.

The result of isotopes ^2H and ^{18}O indicate groundwater recharge from winter precipitation with no evaporation. Values of dissolved inorganic carbon $^{13}\text{C}(\text{DIC})$ correspond to equilibrium with carbonates and C4 plants as the source of CO_2 . Groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ values are consistent with carbonate dissolution as the primary process.

The tritium values of the rain sample were 7.3 TU and 4.4 TU for the Tanjero River inside Sulaimani City, respectively. The tritium values for groundwater samples were from less than 0.8 to 4.9 TU. Most groundwater samples do not seem to contain pre-bomb tritium, and the groundwater seems to be relatively young.

The most serious threat to groundwater quality are interactions of the studied aquifers with the heavily contaminated Tanjero River. Water treatment in the river is crucial and a water treatment plant should be built in Sulaimani. In addition, the determination of the depth and boundary of each aquifer, comprehensive hydrogeochemical and isotope study, water well monitoring system plan, and monitoring of geogenic contaminants of Ba, F and As are recommended for future research subjects.

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1. Introduction

Groundwater is one of the vital resources in the world, especially in arid and semiarid regions, and is used for drinking, domestic, agriculture, industrial, and other purposes. The effective management of groundwater resources in arid and semiarid regions through different hydrogeological and hydrogeochemical tools is crucial for protecting them from the viewpoint of both quantity and quality. Several groundwater studies have been conducted in such areas; for instance, in the Kalahari Desert located in Namibia (Ugulu & Wanke, 2020), and Botswana (Stadler et al., 2010) and in the northeastern region of Brazil (Halm et al., 2002), and central Australia (Harrington et al., 2002). The study conducted by Scanlon et al. (2006) revealed that groundwater quality in these regions is predominantly affected by intense evaporation and by the nature of recharge (diffuse vs. focused), in addition to the land use and land cover. Mountain front recharge is a commonly observed phenomenon in which the primary recharge zones of aquifers are in mountainous regions with higher precipitation levels. As a result, groundwater flows from these mountain areas towards lower-lying regions, where the primary extraction of groundwater occurs (Markovich et al., 2019).

The United Nations Sustainable Development Goal (SDG6) emphasises that “2 billion people are living with the risk of reduced access to freshwater resources, and by 2050, at least one in four people is likely to live in a country affected by chronic or recurring shortages of fresh water” (UNDP, 2017). Therefore, more than 2 million people die annually from waterborne infections; in addition, 4.3 and 6.4 per cent of Sub-Saharan African and Indian GDP is negatively affected by poor sanitation. Iraq and the Kurdistan region are ranked 105/166 and the SDG index score was 64.8. It means that most of the local population uses at least basic drinking water services. However, it ranks poorly in the effort to achieve Sustainable Development Goal 6 (SDG6), a challenge which involves a proper understanding of relationships between land use, sea level rise, climate change, and groundwater quality.

The study area, Sulaimani-Warmawa Sub-basin (SWSB), is a hydrological Sub-basin which is a part of the Sulaimani-Sharazoor Basin. The SWSB is located southeast of the Kurdistan Region, northwest of the Zagros basin. It is mainly in Sulaimani Governorate and Sulaimani City is a part of the study area. It is a semiarid region with a Mediterranean-type climate and precipitation occurs primarily in winter months. Groundwater is a crucial water resource because local streams are generally perennial and dry out during late summer. The region is

economically significant because of its huge oil reserves and several towns are booming due to the oil industry. Sulaimani is the principal city in the study area with about 800,000 inhabitants, primarily dependent on groundwater for water supply.

There is a lack of groundwater management in the Kurdistan Region of Iraq, especially in the SWSB. In addition, there is no clear management strategic plan from Kurdistan Regional Government and relevant authorities to preserve this vital water resource and protect them against contamination. Moreover, the unavailability of data and non-existence previous scientific study in the area of interest is another challenge in the Kurdistan Region of Iraq for establishing the scientific standard to preserve groundwater.

Monitoring of groundwater is crucial to identify contamination early enough to prevent resource damage, as cleanup is costly and almost impossible after water quality declines. This task requires adequate knowledge and information on groundwater chemistry to develop a novel approach to achieve an inclusive and efficient integrated water resources framework that will accelerate SDG6 in the Kurdistan Region, Iraq, the Zagros basin and the Middle East.

This dissertation deals with the identification of processes responsible for the formation of groundwater chemistry in the study area and special attention is paid to geogenic contaminants such as As and F. Several methods such as hydrogeology, hydrogeochemistry, geochemical modeling including speciation and inverse modeling, and stable isotope and radioactive isotopes are applied to improve existing hydrogeological and hydrogeochemical knowledge and to contribute to better groundwater management in the Sulaimani-Warmawa Sub-basin.

2. Study Area Description

2.1 Geography

The studied area Sulaimani-Warmawa Sub-basin (SWSB) is in the southeast of the Kurdistan Region, northwest of the Zagros basin, Figure 1. Meanwhile, it is located in the High Folded Zone (Buday, 1980; Buday & Jassim, 1987; Jassim & Goff, 2006; Al-Jiburi et al., 2015). The SWSB is mainly in Sulaimani Governorate and Sulaimani City is a part of the study area. The SWSB is placed within longitudes 45° 00' – 46° 00' east and latitudes 35° 00' – 36° 00' north. with an elevation range from 500 to more than 1250 meters (m). The SWSB covers an area of approximately 1500 km². It is a hydrological sub-basin which is a part Sulaimani-Sharazoor basin.

2.2 Climate

The SWSB in the Kurdistan Region of Iraq. It is a semiarid area characterised by a Mediterranean climate (Csa according to the Köppen climate classification) with relatively cold, humid winters and hot, dry summers. According to Stevanovic and Markovic (2003) findings, most of the precipitation occurs during the winter months spanning from October to May, with the highest amount of precipitation exceeding 100 mm in January. The average annual rainfall is 668.5 mm, the average annual air temperature is 21° C, and the annual evaporation is 2298.8 mm (Mustafa, 2006; Hamamin et al., 2018).

The principal river is the perennial Tanjero River, which is generally dry from August to the beginning of the precipitation season in October.

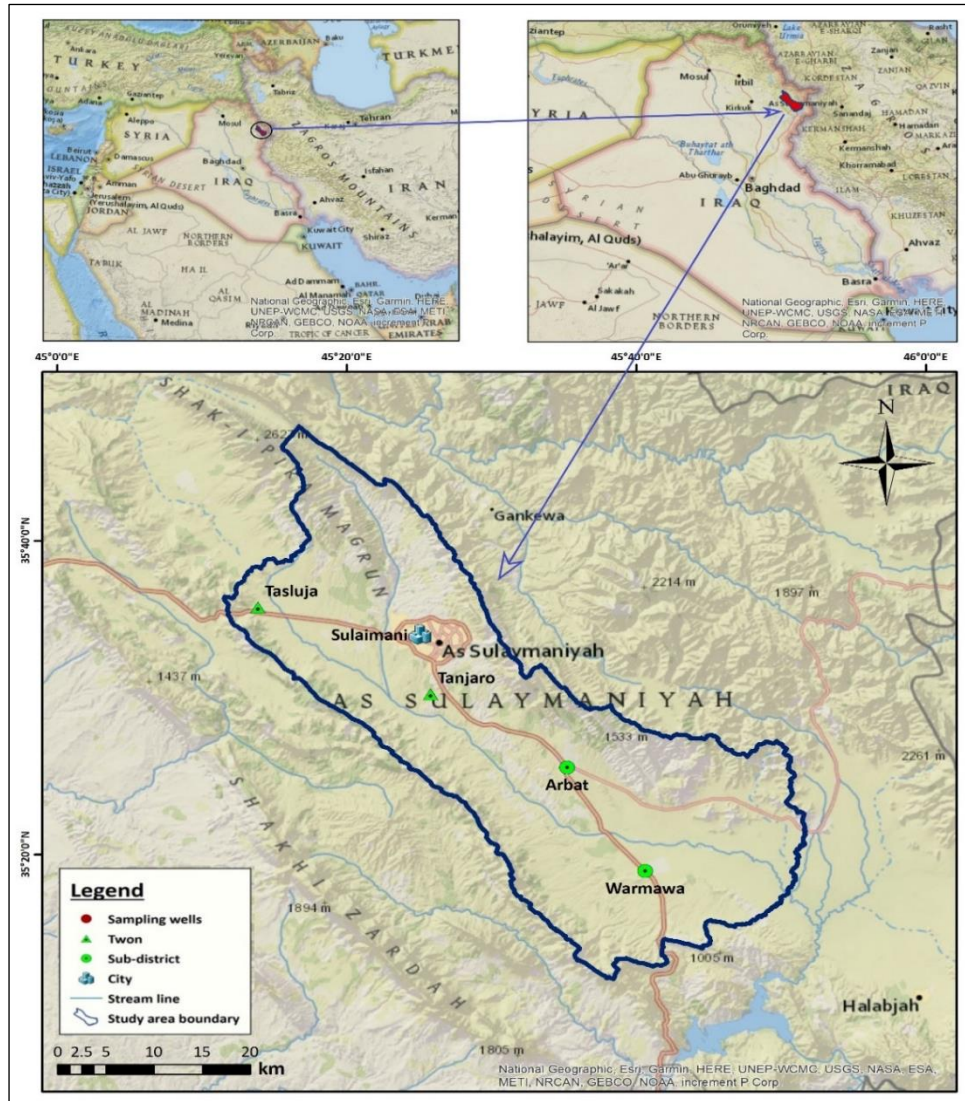


Figure 1. Location of the study area.

2.3 Geological setting of SWSB

The geological formations within the Sulaimani-Warmawa Sub-basin (SWSB) generally cover units from the Early Cretaceous to the Tertiary periods and Quaternary deposits (Table 1 and Figure 2). Hills around the basin are covered by grass and sparse vegetation of pine, *Pinus Sylvestris*, which are used for sheep and goat grazing.

The Cretaceous units within the research area include the Balambo, Qamchuqa, Kometan, Shiranish, and Tanjero Formations. In the Tertiary units that are visibly protruding in the SWSB, there are the Tanjero, Sinjar, Gercus, and Pila Spi Formations.

Moreover, within the Quaternary deposits, alluvial fans, polygenetic, and floodplain sediments are prominently found, indicating a high degree of geologic activity within the SWSB (Karim & Ali, 2004; Omar et al., 2015; Sissakian, 2015). It is notable that the

distribution of these units is not homogeneous. The Cretaceous formations predominantly emerge in the northeast, east, and southeast regions of the SWSB. In contrast, the Tertiary units are generally located in the western and southwestern areas of the studied region.

A particular presence of the Tanjero Formation and Quaternary deposits is observable at the centre of the study area, specifically around Sulaimani City and the Warmawa area. The Tanjero Formation demonstrates a broad presence throughout the Sulaimani-Warmawa Sub-basin, most notably surrounding the city of Sulaimani. The extent of the formation can be traced from the foothills of the Goizha Mountain in the north and northeast, proceeding towards the Tanjero Valley in the south and the Chaqchaq Valley in the northwest (Mustafa, 2006).

Table 1. Geological formations in the study area (after Karim & Ali, 2004; Omar et al., 2015; Sissakian, 2015).

Age	Geological Units	Lithological Composition
Quaternary	Quaternary deposits	Alluvial fans and flood plain sediments: Gravel, sand, silt, mud, sandy, and silty clay soil
Tertiary	Kolosh	Dark grey claystone, shale and siltstone with rare conglomerate
	Sinjar	Well-bedded limestone, dolomite, marly limestone and sandstone
	Gercus	Alteration of red claystone, marl, gypsum and sandstone few limestone
	Pila Spi	Cyclic deposits of claystone, marl, gypsum, and sandstone with occasional limestone
Late Cretaceous	Shiranish	Bluish-grey marl and marly limestone
	Tanjero	Silty marl, siltstone, shale, sandstone, conglomerate and sandy or silty organic detrital limestone
Lower Cretaceous	Balambo	Thin well bedded radiolarian limestone
	Qamchuqa	Grey massive dolomites and dolomitic limestone
	Kometan	White-weathering, light grey, thin bedded limestone and locally silicified

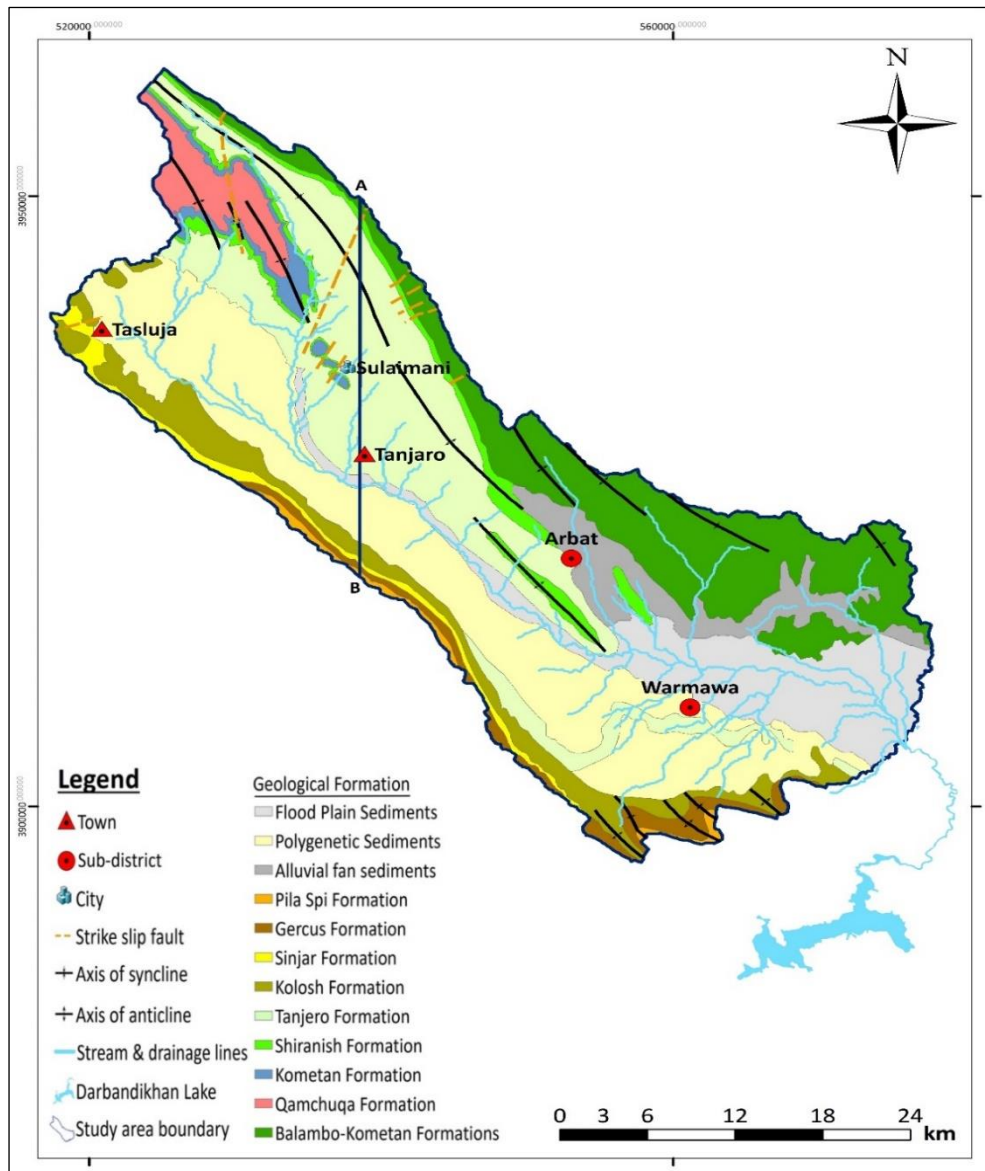


Figure 2. Geological map of the study area (after Karim & Ali, 2004; Omar et al., 2015; Sissakian, 2015).

2.4 Hydrogeological setting of the SWSB

In general, so far, there were no intensive hydrogeological studies conducted in the study area explaining the hydrogeology of the area in detail. Few studies have been conducted in Iraq and the Kurdistan Region. According to Stevanovic & Markovic (2004), the Kurdistan Region were divided into several hydrological basins and sub-basins. The division is based on the geology of the area, topography, stream and drainage pattern, the structure of the area and several other criteria. The Sulaimani Governorate is divided into southeastern Sharazoor, Dukan, Chamchamal-Sangaw, and Penjwin basins. The Sulaimani-Warmawa watershed is part of the southeastern Sharazoor.

Furthermore, the aquifer system in the Kurdistan Region has been classified into several aquifers due to formation age similarities, lithology, permeability and other hydrogeological characteristics.

The hydrogeological map has been created for SWSB (Figure 3) based on a prior Iraq, Kurdistan Region, and Sulaimani Governorate study. In addition to hydrogeological data from (DoGWS), hydrogeological data of 32 water wells in the study region were obtained from 24 to 450 m deep in July and August 2020 (Mahmmud et al., 2022). The hydrostratigraphic units in the study area have been grouped according to their lithology and hydrogeologic characteristics into the Karstic-fissured aquifer (KFA), the Kometan aquifer (KA), the Tanjero aquifer (TA), an Aquiclude, and a Quaternary intergranular aquifer (QIA) (Stevanovic & Markovic, 2004; Mustafa, 2006; Ali, 2007; Mahmmud et al., 2022). The type of aquifers and associated hydrostratigraphic information are summarised in Table 2. According to the hydrogeological data and report from the Directorate of Groundwater of Sulaimani (DoGWS), the main productive aquifers in the study area are the Quaternary Intergranular Aquifer (QIA) and the Tanjero Aquifer (TA) in terms of groundwater quantity and quality (Mustafa, 2006; Kareem et al., 2018; DoGWS, 2020). However, porous karstic formations at basin margins replenish them. The groundwater flow direction is generally from the north and northwest towards Sulaimani and the Tanjero River, which flows into the Darbandikhan Lake out of the basin in the southeast Figure 3.

Table 2. Aquifer types and lithostratigraphy in the study area (after Stevanovic & Markovic, 2004; Mustafa, 2006; Ali, 2007, SGI, 2011; Mahmmud et al., 2022).

Aquifer type	Geological Formation	Lithology	Hydraulic Conductivity K (m/s)
Quaternary intergranular aquifer (QIA)	Quaternary deposits	Sand, silt, rock fragments, mud, pebbly, sandy, silty and clayey soil	$9.83 * 10^{-6}$
Tanjero aquifer (TA)	Tanjero	Silty marl, siltstone, shale, sandstone, conglomerate and sandy or silty organic detrital limestone	$1.17 * 10^{-6}$
Aquiclude	Shiranish, Kolosh and Gercus	Claystone, shale, siltstone, sandstone, marl, marly limestone and rare conglomerate	Not available
Kometan aquifer (KA)	Kometan	Limestone	$2.3 * 10^{-5}$
Karstic-fissured aquifer (KFA)	Balambo, Qamchuqa, Pila Spi and Sinjar	Limestone, dolomite and dolomitic limestone and Chalky marl	$6.2 * 10^{-6}$

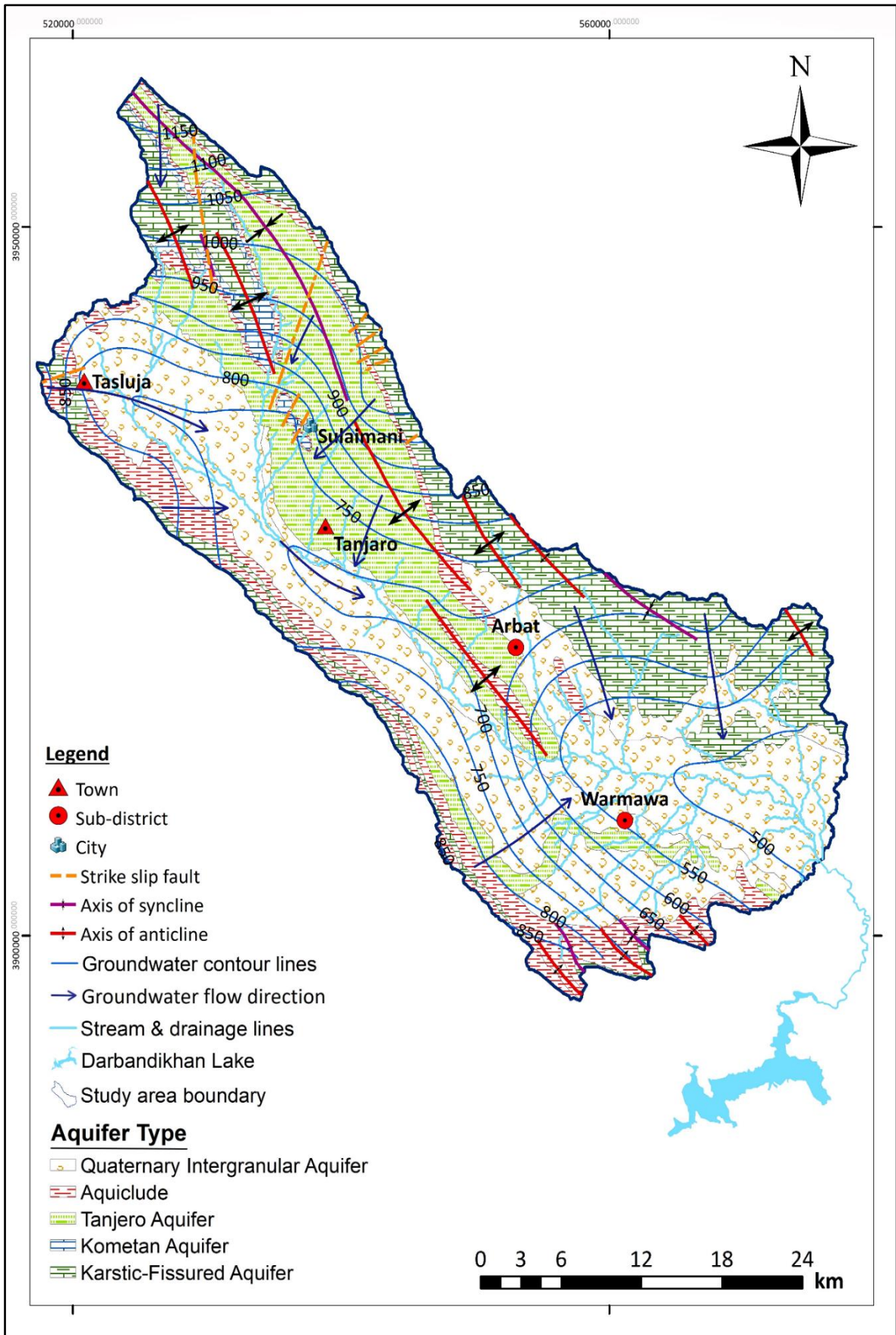


Figure 3. Hydrogeological map and groundwater flow pattern in the study area (Mahmmud et al., 2022).

3. Materials and Methods

3.1 Fieldwork and water sampling

Groundwater samples were taken in the study area at different times for data analysis. Sampling was conducted during July, August 2021, and April 2022 from 26 boreholes in the area of interest. In total, 96 samples were obtained including the samples from Erbil area (Mustafa et al., 2023). The samples were used for the examination of cations, anions, and trace elements, providing an understanding of the groundwater chemical constituents, cations, anions and trace element analysis. The samples were also taken for stable isotopes of oxygen-18 and deuterium analysis. The collected samples for cations and trace element analyses were filtered in the field with 0.45 mm Millipore filters, acidified with HNO_3 Suprapur, and stored in 50 mL HDPE bottles. Meanwhile, 15 water samples were taken in March 2022 for Tritium analysis, including one rain sample and one water sample from Tanjero River. The location sampling wells, and inverse geochemical modeling profiles is shown in Figure 4.

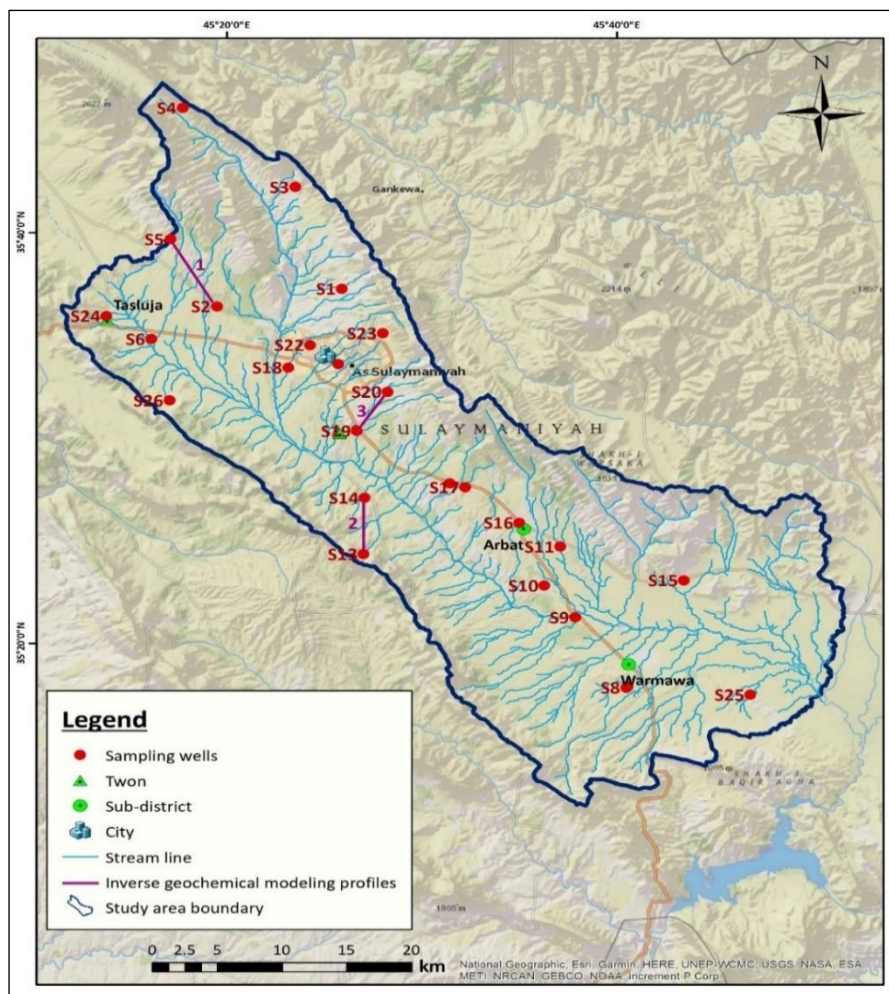


Figure 4. Sampling wells location and inverse geochemical modeling profiles.

3.2 Field and laboratory analyses

The field parameters such as pH, temperature, electrical conductivity (EC) and total dissolved solids (TDS) were measured on-site after pumping several well volumes during data collection. They were measured by the multi-parameter device Cyber Scan PC 300.

The collected groundwater samples have been stored and exported to the Czech Republic and France for laboratory analyses. Cations and trace elements measurements were conducted in the analytical facilities of Charles University in Prague using the ICP-MS technique. The analytical error of each solution analysis was less than 2%. Anions concentrations were measured using HPLC and Dionex ICS. The ferrous iron was determined by titration with potassium dichromate. Alkalinity values were obtained through HCl titration using the Gran plot to determine the endpoint. The QA/QC was carried out according to established protocols. About 10% of the samples were examined twice and obtained results were consistent.

The measurements of ^2H and ^{18}O isotopes were conducted at the Czech Geological Survey in Prague, Czech Republic, using an LWIA 3000 laser analyser (LGR). The accuracy of the analysis was 0.4‰ for ^2H and 0.12‰ for ^{18}O . The data were standardised in accordance with the international standard (V-SMOW) and presented using standard δ -notation (Clark and Fritz, 1997). For ^{13}C analyses, BaCl_2 was added to precipitate DIC as BaCO_3 . The precipitate was then decomposed in 100% H_3PO_4 under vacuum at 25 °C. The C isotope ratio in the generated CO_2 was determined by a Thermo Delta V mass spectrometer with a precision of ^{13}C values better than $\pm 0.1\%$. Results were expressed using the PDB standard.

Strontium (corresponding to at least 2 μg of Sr in solution) was isolated from water samples using exchange chromatography techniques based on Triskem's Sr resin (Pin et al., 1994). The isotopic composition was analysed using a Neptune Plus instrument (MC-ICP-MC; ThermoFisher Scientific) in the Stable and Radiogenic Isotope Research Laboratory at Charles University in Prague. Analytical mass bias was corrected to $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$ (defined as $\delta^{88/86}\text{Sr} = 0$ and related to NIST SRM 987, Nier, 1938). The analytical uncertainty was determined by repeated analyses of the SRM 987 standard, with the resulting $^{87}\text{Sr}/^{86}\text{Sr}$ $\text{Sr} = 0.7102777 \pm 0.0000099$ in (2 S.E.M; n = 8).

In addition, 13 groundwater samples were taken for tritium analysis in March 2022, one rainfall sample and one sample from the Tanjero River inside Sulaimani City. The tritium analyses were performed in the Mediterranean Environment and Modelling of Agro-Hydrosystems (EMMAH) of the University of Avignon in France. A Quantulus 1220 ultra-

low liquid scintillation spectrometer was used to measure the amount of tritium present in the water samples after electrolytic enrichment by low-level liquid scintillation counting with the detection level of 1 TU.

3.3 Software and data management

The ArcGIS has been used to prepare the maps and cross-sections for the study area. Statistica 13.3 were used for statistical analysis and for creating graphs. The USGS program PHREEQC (Parkhurst & Appelo, 1999) with the minteq.dat database was used to calculate speciation and saturation indices and to determine mass transfer between selected mineral phases and groundwater using the inverse geochemical modeling module. The program Geochemist Workbench was used to prepare the Piper diagram and Eh–pH diagram. The PAST program (Hammer et al., 2001) was used to prepare hierarchical cluster analysis (HCA), where samples and wells were grouped in the Ward's mode based on their similarity.

4. Results

4.1 Principal ions and trace elements

The Piper plot for the groundwater chemistry data is presented in Figure 5. The overall trend along the flow path is the evolution from Ca-HCO₃ groundwater type towards Mg-Ca-HCO₃ groundwater type with rising EC. However, there are some exceptions. Mainly, anomalous sample S14 presents a Na-Cl water type, and sample S24 is a complex mix of Na-Ca-HCO₃-SO₄-Cl type groundwater. Sample S18 is Ca-HCO₃-SO₄ groundwater type with elevated EC located close to the Tanjero River (Figure 4).

The values of electrical conductivity range from 328 to 2460 $\mu\text{S}/\text{cm}$; the average is 757.28 $\mu\text{S}/\text{cm}$. The pH values are in the range from 7.02 to 8.75 and the average pH value is 7.56. The average value of Ca²⁺ is 72.14 mg/L with concentrations from 6.07 to 174 mg/L. Concentrations of Mg²⁺ range from 2.33 to 79 mg/L, with the average being 26.29 mg/L. Concentrations of Na⁺ are from 2.66 to 480 mg/L, with the average being 37.87 mg/L. The concentration of K⁺ ranges from 0.26 to 3.1 mg/L, and the average is 1.14 mg/L. Concentrations of HCO₃⁻ range from 140 to 320 mg/L, with an average of 222.76 mg/L. The concentration of SO₄²⁻ ranges from 7.34 to 200.7 mg/L, with an average of 52.1 mg/L. The concentration of Cl⁻ ranges from 1.88 to 462.37 mg/L; the average is 39.06 mg/L. The average value of NO₃⁻ is 34.28 mg/L with concentrations from 1.63 to 207.11 mg/L.

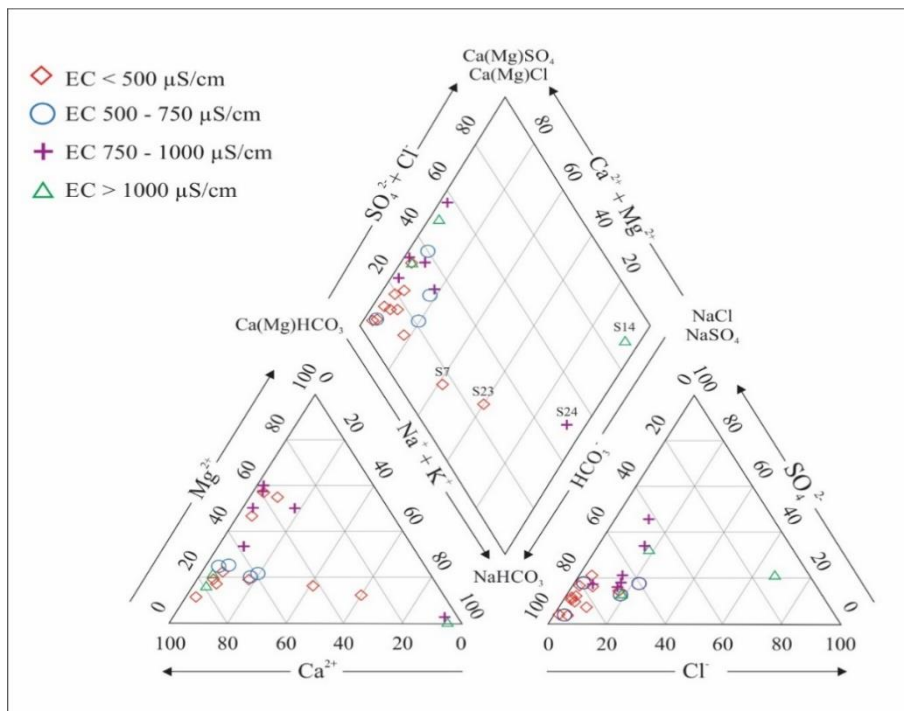


Figure 5. Piper diagram; samples are sorted based on their EC values, outliers S7, S23, S24, and S14 are marked.

The average concentration of Al is 12.5 µg/L with a range from 5.35 to 19.31 µg/L. Concentrations of Cr range from 0.08 to 7.29 µg/L, with an average of 2.26 µg/L. The average value of Fe is 310.96 µg/L with concentrations from 27.59 to 689.54 µg/L. Concentrations of Cr range from 0.08 to 7.29 µg/L, with the average being 2.26 µg/L.

Generally, the quality of water has been influenced by redox processes in addition to the mobility status of the toxic elements can be affected by redox processes that are naturally present in aquifer materials, along with organic and inorganic components. These processes in the aquifer contribute to the breakdown or preservation of anthropogenic contaminants (McMahon & Chapelle, 2008).

Regarding redox indicators, NO₃⁻ are from 1.63 to 207.11 mg/L, average 34.28 mg/L; concentrations of Fe are from 0.027 to 0.68 mg/L, average 0.31 mg/L; and concentrations of Mn generally in half of the groundwater samples were below the detection limit and maximum concentration reaches only 13.39 µg/L. Moreover, the concentration of Cl⁻ in the rain collected in the studied area out of Sulaimani was 2.2 mg/L.

4.2 Geogenic contaminants

Regarding the geogenic contaminants in the study area, barium, fluoride and arsenic are the most common in the semiarid area, including the area of interest. The concentrations of Ba range from 7.46 to 654.52 µg/L, with the average being 114 µg/L. Furthermore, the concentrations of F⁻ range from 0.2 to 0.63 mg/L, with an average of 0.44 mg/L. The average value of As is 0.64 µg/L with concentrations from 0.06 to 4.27 µg/L. The available groundwater data were used to make a geostatistical interpolation and construction of predictive maps for Ba, F and As concentrations in groundwater. The maps for Ba, F⁻, and As (Figure 6 A, B & C) indicate vulnerable areas. This can help authorities to become aware of potentially contaminated groundwater. The spatial distribution of As and F in the studied area is patchy, and different concentration hotspots are present. This may suggest the existence of local sources (Parrone et al., 2020).

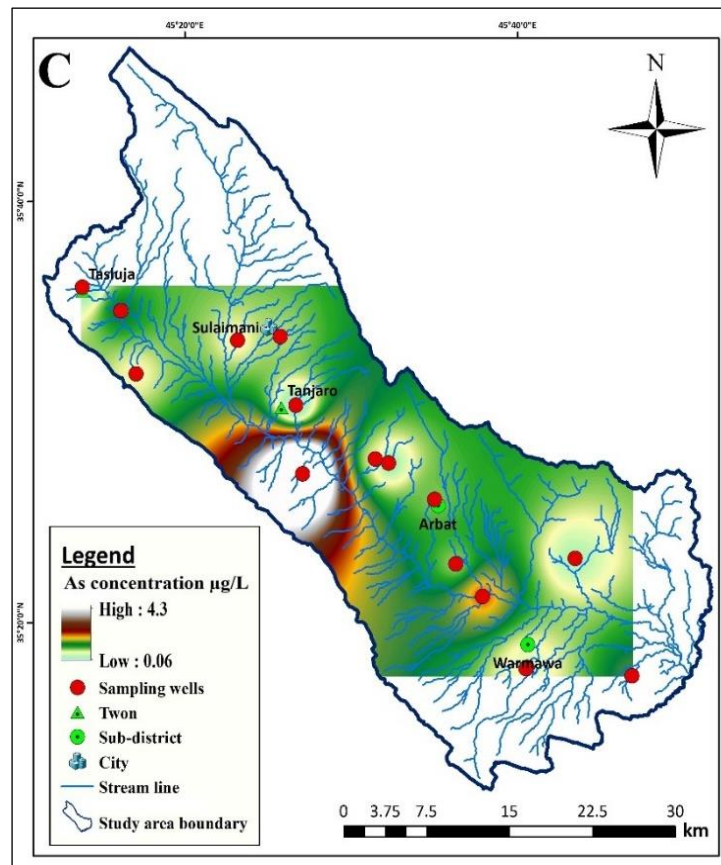
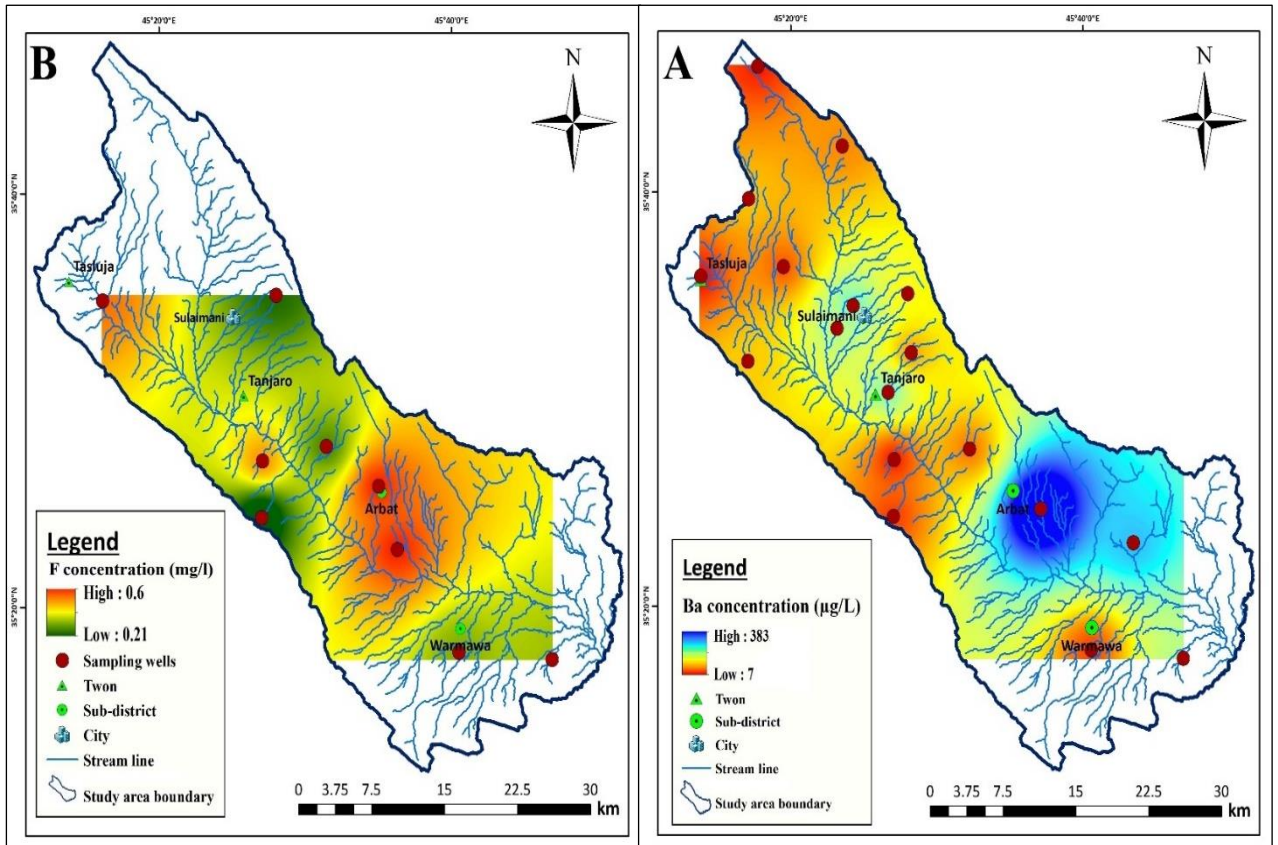


Figure 6. Spatial distribution of (A) Ba, (B) F and (C) As.

4.3 Stable isotopes

The groundwater samples from the Sulaimani-Warmawa Sub-basin reveal their stable isotopic compositions through the δ -notation, representing per mil deviation from the globally recognised standard, V-SMOW (Vienna Standard Mean Ocean Water). This data is outlined in Table 3 and visualised in Figure 7.

Table 3. Isotopes in groundwater samples from the Sulaimani-Warmawa Sub-basin, Kurdistan Region, Iraq, during the period July–August 2020 and March–April 2022.

Sample No.	$\delta^2\text{H}$ (‰)	$\delta^{18}\text{O}$ (‰)	Deuterium excess	$\delta^{13}\text{C}(\text{DIC})$ (‰)	$^{87}\text{Sr}/^{86}\text{Sr}$
S1	-28.5	-6.1	20.0	-2.4	N/A
S2	-25.5	-5.6	19.2	-1.6	0.7082
S3	-32.9	-6.6	19.6	-1.5	0.7078
S4	-34.7	-7.0	21.7	-1.8	N/A
S5	-30.3	-6.3	20.4	-1.7	0.7079
S6	-26.2	-5.4	17.1	N/A	N/A
S7	-26.2	-5.5	18.0	-2.5	0.708
S8	-24.0	-4.9	15.6	N/A	N/A
S9	-24.4	-4.6	12.6	N/A	N/A
S10	-27.0	-5.0	13.4	N/A	N/A
S11	-28.7	-5.7	16.9	-3.4	0.7082
S12	-27.5	-5.1	12.9	N/A	N/A
S13	-33.7	-6.5	18.4	-1.7	0.7081
S14	-39.5	-6.7	13.9	-4.3	0.7076
S15	-29.8	-6.5	22.1	-1.3	0.7081
S16	-38.2	-6.7	15.2	N/A	0.7082
S17	-29.1	-5.6	16.0	-1.6	N/A
S18	-30.2	-5.5	13.6	N/A	N/A
S19	-28.5	-5.5	15.2	-1.6	0.7082
S20	-27.5	-6.2	22.1	-1.5	0.7082
S21	-30.7	-5.4	12.6	N/A	N/A
S22	-29.9	-6.2	19.3	-1.2	0.7081
S23	-36.9	-6.9	18.4	-1.4	0.7078
S24	-36.9	-6.9	18.1	-2.3	0.7077
S25	-24.0	-4.5	11.6	N/A	N/A
S26	-27.4	-5.6	17.7	N/A	N/A
N/A= Not available					

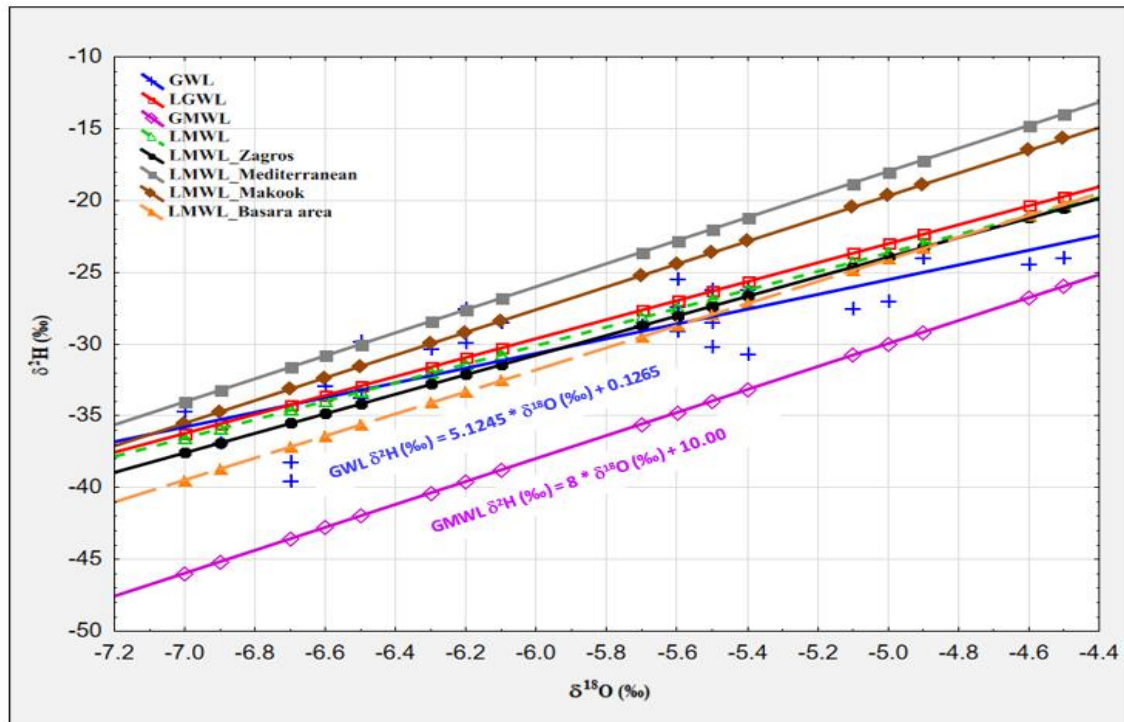


Figure 7. Diagram of ^2H vs ^{18}O , GWL is groundwater line for the study area, LGWL is the local groundwater line for the study area (Mahmmud et al., 2022), LMWL (Total) is average local meteoric water line for Zagros, LMWL (Zagros) is local meteoric water line for winter precipitation in Zagros, LMWL (Mediterranean) is local meteoric water line for precipitation in Mediterranean Sea, LMWL (Makook) is local meteoric water line for precipitation in Makook anticline area (Mustafa et al., 2015), LMWL (Basara) is the local meteoric water line for precipitation, springs, wells and streams in Basara (Hamamin and Ali, 2013), and GMWL is the world global meteoric water line.

The value of ^{18}O ranges from (-7.0‰) to (-4.5‰) and the value of ^2H ranges from (-39.5‰) to (-24‰). Values of deuterium excess are high, in some samples more than 20‰ . The local rainfall isotopic composition can be influenced by several factors such as humidity, surface air temperature, geographic location (longitude and latitude) and altitude (Mook, 2001; Mazor, 2004; Al-Charideh, 2011). According to the results of the isotopic composition of the groundwater samples in the area of interest, the most negative value ($^{18}\text{O} = -7.0\text{‰}$) was measured for the highest altitude sample, which is 1224 m above sea level (Mahmmud et al., 2022). The sample collected in the Alan village near Warmawa sub-district (altitude 527 m) had more positive value of ^{18}O , which was (-4.5‰). The groundwater line (GWL) for the study area is ($\delta^2\text{H} (\text{‰}) = 5.1245 * \delta^{18}\text{O} (\text{‰}) + 0.1265$). The global meteoric water line (GMWL) has a higher slope and intercept than the local groundwater line (GWL) for the

collected sample in the SWSB (Craig, 1961; Gat & Carmi, 1970) (Figure 7). The local GWL for the groundwater samples in the studied area has a higher slope and intercepts the local meteoric water lines (LMWL Zagros) developed for the Zagros by Osati et al. (2014).

The local GWL for groundwater samples in the research area shows slope and intercept between local meteoric water lines (LMWL) calculated for the Zagros by Osati et al. (2014) ($\delta^2\text{H} = 6.80 \cdot \delta^{18}\text{O} + 10.1$) and Mohammadzadeh et al., 2020 ($\delta^2\text{H} = 6.44 \cdot \delta^{18}\text{O} + 8.514$). Nevertheless, there is a strong concurrence between the local GWL and the Local Meteoric Water Line (LMWL) in relation to winter precipitation, as indicated by the equation $\delta^2\text{H} = 6.67 \cdot \delta^{18}\text{O} + 9.766$ (Mohammadzadeh et al., 2020).

The result of stable isotope data shows that the groundwater in the study region was nearly entirely recharged by winter rainfall, with little evaporation impact during infiltration. This contrasts with groundwater data from western Iraq, where there was a strong evaporation effect with a slope of the groundwater line 5.19 (Ali et al., 2015).

The values of carbon isotope composition of dissolved inorganic carbon ^{13}C (DIC) are in Table 3. Additionally, the relationship between ^{13}C (DIC) and bicarbonate (HCO_3) is in Figure 8. The majority of ^{13}C (DIC) values fall within the range of -3.0 to -1.0‰. The samples S10 and S13 show exceptional values of -3.4 and -4.3‰, respectively. The presence of high values suggests that there is a state of equilibrium with carbonate rocks in a closed-system environment. This is further supported by the high saturation index (SI) values for calcite, particularly in wells located near Sulaimani. The primary plant species found in the recharge areas surrounding Sulaimani are grasses, specifically C4 plants. These grasses show high ^{13}C values, approximately -12‰, (Clark and Fritz, 1997). These plants serve as the source of CO_2 that interacts with Cretaceous carbonate rocks, which typically possess ^{13}C values ranging from -1 to -2‰, (Razmjooei et al., 2020).

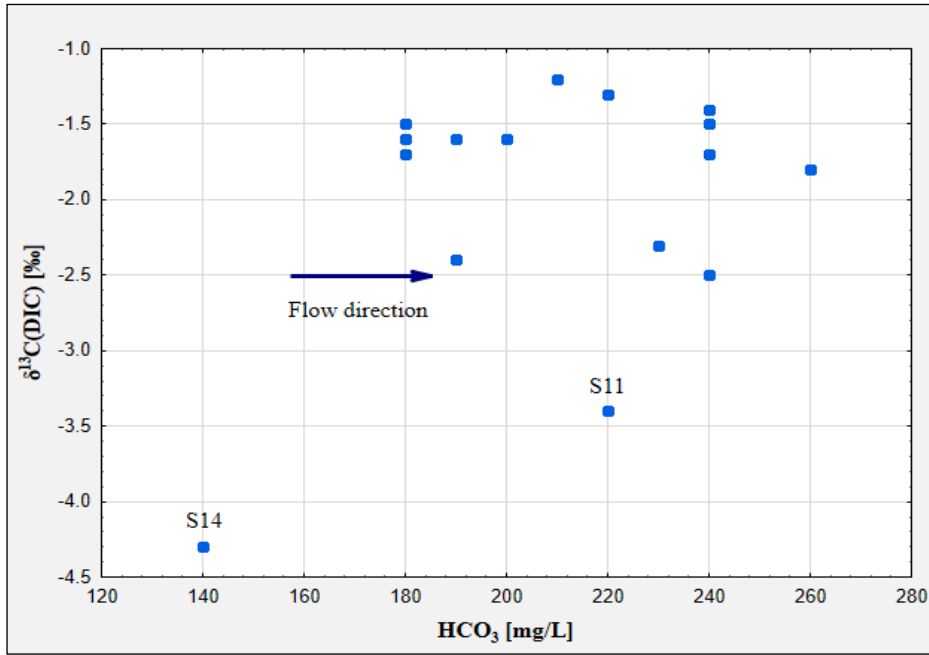


Figure 8. The $^{13}\text{C}(\text{DIC})$ vs HCO_3^- concentration, outliers are marked.

The values of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in groundwater are in Table 3, while a relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentration is provided in Figure 9. Most $^{87}\text{Sr}/^{86}\text{Sr}$ ratios fall within the range of 0.7081 to 0.7082. Samples S3, S5, S23, and S24 obtained from wells in proximity to recharge areas near the groundwater divide (Figure 8) show values slightly below 0.708. The groundwater from well S14 shows anomalous water chemistry, as indicated by its lowest recorded value of 0.7076. Nevertheless, the values are representative of groundwater in contact with Cretaceous carbonates (Veizer, 1989).

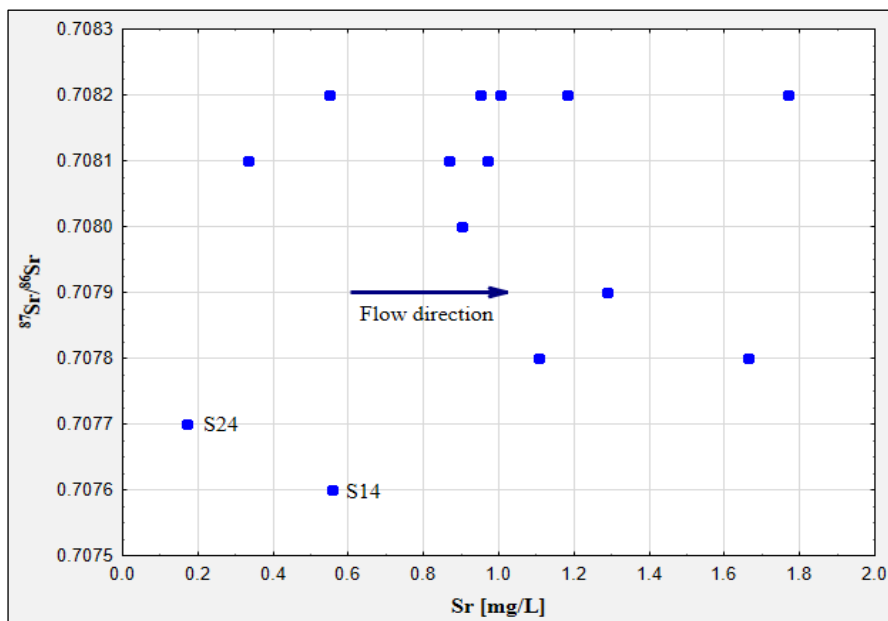


Figure 9. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio vs Sr concentration, outliers are marked.

4.4 Tritium (³H)

The result of tritium analysis for groundwater samples, one rainfall sample and one water sample from Tanjero River near Sulaimani City are in Table 4.

Table 4. Tritium analysis result of water samples in the SWSB.

No.	Samples	pH	EC (µS/cm)	Activity (TU)	Aquifer
1	S1	7.5	350	3.5	Tanjero Aquifer
2	S3	6.3	560	4.1	Tanjero Aquifer
3	S4	8	550	3.9	Tanjero Aquifer
4	S5	7.8	340	2.6	Tanjero Aquifer
5	S11	8.3	350	3.2	Quaternary Intergranular Aquifer
6	S12	7.9	440	2.7	Karstic-Fissured Aquifer
7	S13	8.4	2980	≤ 0.8	Quaternary Intergranular Aquifer
8	S14	7.5	370	3.2	Quaternary Intergranular Aquifer
9	S17	7.8	990	3.4	Tanjero Aquifer
10	S18	7.4	650	4.3	Tanjero Aquifer
11	S21	7.4	890	4.9	Tanjero Aquifer
12	S22	6.03	490	1.7	Tanjero Aquifer
13	S23	8.5	870	0.7	Aquiclude
14	Rainfall	N/A	N/A	7.3	N/A
15	Tanjero River	5.4	540	4.4	N/A
N/A= Not available					

The tritium value of the rain sample was 7.3 TU, the tritium value of the river sample was 4.4 TU and the mean values of the groundwater samples were 3.2 TU for Quaternary Intergranular Aquifer, 3.55 TU for Tanjero aquifer, 2.7 and 0.7 TU for Karstic-Fissured Aquifer and Aquiclude, respectively, Table 8. The tritium concentration in the groundwater samples was from less than 0.8 to 4.9 TU. In general, there were higher values close to the catchment boundaries (except for wells S22 and S23) and lower values in the lowlands.

4.5 Speciation modeling

Speciation modeling reveals that the Eh values, determined using the Fe(II)/Fe(III) pair, suggest post-oxic, mildly reducing conditions. Total carbon C, expressed as CO₂, generally increases along the flow path, with low values near the groundwater divide (e.g., wells S5 and S24) and high values along the valley axis (e.g., wells S18 and S20). The log P_{CO2} values follow a similar pattern, except for well S14 showing unusually low values for both. Most groundwater samples are either supersaturated or in equilibrium with calcite, and some with dolomite. However, all samples are undersaturated with respect to gypsum, strontianite SrCO₃, all manganese minerals, barite, and amorphous silica. Groundwater typically surpasses saturation concerning quartz and exhibits supersaturation with kaolinite, although values for the latter are uncertain due to potential colloidal aluminium presence.

4.6 Inverse geochemical modeling

Inverse geochemical modeling was used to understand the evolution of groundwater chemistry across three selected profiles and the results are shown in Table 5. Profile 1, near the recharge zone, exhibited minimal chemical change along its flow path, with minor calcite dissolution and a slight increase in Na⁺ due to the dissolution of Na-silicate. Profile 2 saw substantial dissolution of halite and some gypsum, leading to marked changes in Cl⁻ and SO₄²⁻ concentrations; there was also dolomite precipitation. Profile 3 had less dramatic changes than Profile 2, with minor dissolution of halite and gypsum and some calcite precipitation. Additionally, small amounts of organic matter CH₂O were introduced in Profile 3, influencing the redox state and iron concentrations. Amorphous quartz precipitated in Profiles 2 and 3, and cation exchange was noted in all profiles (Razmjooei et al., 2020; Clark & Fritz, 1997).

Table 5. Transfer of phases calculated by inverse geochemical modeling. Mass transfer coefficients in mmol/L.

Profile	Calcite	Dolomite	Halite	Albite	Gypsum	Fe(OH) ₃	CH ₂ O	SiO ₂ (a)	NaX	CaX2	MgX2	δ ¹³ C	δ ¹³ C
												calc.	meas.
1	+0.104	-	-	+0.001	-0.009	+0.001	+0.0003	-	+0.67	-0.1	-0.24	-1.6	-1.6
2	-	-1.286	+12.96	+3.40	+1.84	+0.027	-	-6.84	+1.85	-1.22	+0.29	-4.1	-4.3
3	-0.03	-	+1.11	-	+0.382	+0.004	+0.001	+0.31	-0.79	+0.07	+0.34	-1.6	-1.6

+ dissolution, - precipitation, X cation exchange

5. Conclusions

Groundwater in the Sulaimani-Warmawa Sub-basin in the Kurdistan Region of Iraq was examined using hydrogeology and geochemistry, revealing a conceptual model for groundwater chemistry evolution, recharge timing, and age determination. This area, part of the Zagros Basin, is semiarid and experiences peak precipitation in January. The hydrogeological map for the SWSB shows groundwater flowing from the north and northeast to the south and southwest, heading from the mountains to the Tanjero River and Darbandikhan Lake. Water chemistry shifts from a Ca-HCO₃ type near recharge zones to a Ca-Mg-HCO₃ type closer to the Tanjero River. Dissolution processes in the recharge area, especially involving halite and gypsum in carbonate rocks, have led to varying concentrations of sodium, chloride, and sulfate. The pH is generally alkaline, and the environment is moderately reducing. Notably, certain samples indicated a possible groundwater mixing due to the co-existence of iron and nitrate. Ba concentrations can reach 0.383 mg/L, while other contaminants are either low or undetectable. Speciation modeling indicated moderately reducing conditions, and along the flow path, carbon content increases. Geochemical modeling was done on select profiles, showing carbonate interactions being less significant than halite and gypsum. Stable isotopes revealed winter precipitation as a primary recharge source, with CO₂ likely originating from decomposition of C4 plants. Groundwater's tritium concentration ranged from <0.8 to 4.9 TU, with some variations noted across regions. The water samples were split into two groups: Group I, with recent precipitation recharge, and Group II, containing older water.

6. Recommendations

Based on the results of the study, the following recommendations are proposed for future studies for establishing better management plan of groundwater resources:

1. A comprehensive hydrogeological study should be conducted to determine the depth and boundary of each aquifer.
2. More detailed hydrogeochemical and isotopic studies should be conducted in the area for a better understanding of geochemical processes.
3. Well monitoring system plan should be prepared to obtain continuous hydrogeological and hydrogeochemical data.
4. Future work should focus on interactions in the hyporheic zone of the Tanjero River and the impact of seasonal cyclic drying and flooding of river sediments.
5. Comprehensive monitoring of geogenic contaminants of Ba, F and As is needed to consider potential contamination sources.

Probably, the most severe threat to groundwater quality are interactions of the studied aquifers with the heavily contaminated Tanjero River. Treatment of water in the river is very important and a water treatment plant should be built in Sulaimani.

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Appendix

Publications related to PhD Study

- Mahmud, R., Sracek, O., Mustafa, O., Čejková, B., Jačková, I. and Vondrovicová, L., 2022. Groundwater geochemistry evolution and geogenic contaminants in the Sulaimani-Warmawa Sub-basin, Sulaimani, Kurdistan Region, Iraq. *Environmental Monitoring and Assessment*, 194(5), p.352.
- Mustafa, O., Mahmud, R., Sracek, O. and Seeyan, S., 2023. Geogenic Sources of Arsenic and Fluoride in Groundwater: Examples from the Zagros Basin, the Kurdistan Region of Iraq. *Water*, 15(11), p.1981.

Publications unrelated to PhD Study

- Mansurbeg, H., Mohialdeen, I., Al-Juboury, A., Salih, N., Alsuwaidi, M., Shahrokhi, S., Al-Aasm, I., Mahmud, R. and Permanyer, A., 2023. Meteoric Water Incursion, Crude Oil Degradation and Calcite Cementation of an Upper Cretaceous Reservoir in the Zagros Foreland Basin (Kurdistan Region of Iraq). *Water*, 15(10), p.1953.

Conference Presentation

- Integration of Hydrogeology and Geochemistry for Sustainable Groundwater Assessment, Modeling and Management in the Zagros Basin, the Kurdistan Region of Iraq. (XXII International Conference of Young Geologists, 20 – 22.04.2023, Smolenice, Slovakia).

Research Stay and Training Courses

- Research stay activity at the University of Tours, France, for one month, May-June 2022.
- Participation in the International German Summer School on Hydrology (IGSH), Groundwater and Urbanisation, Ruhr University Bochum, Germany, September 2021.
- Participation in the Geospatial Technologies in Hazard Research and Response, University of Iceland, Iceland, August 2022.

Teaching Activities

- Teaching activities conducted for Petroleum Engineering Program students.
- Supervised bachelor thesis of Petroleum Engineering Program students during the academic year 2021-2022 and 2022-2023.
- Working as Education & International Relations Officer for Petroleum Engineering Program, December 2021-Present.