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Application of Major and Trace Elements for Detecting the Origin of Groundwater: Lithium Enrichment in Ain Al-Harrah Hot Spring Influenced by Red Sea, Saudi Arabia

Rofiqul Umam*
Center for Research in Isotopes and Environmental Dynamics, University of Tsukuba,
JAPAN

Korhan Cengiz
College of Information Technology
University of Fujairah,
UNITED ARAB EMIRATES

Ahmad Said
[1]Department of Chemistry,
King Fahd University of Petroleum and Minerals,
SAUDI ARABIA

[2]Department of Industrial Engineering,
Sekolah Tinggi Teknologi Cipasung,
INDONESIA

***Correspondence: E-mail:** rofiqul.umam@ied.tsukuba.ac.jp

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Abstract

Major and trace elements are valuable tracers for understanding the groundwater cycle. In groundwater flow path applications, these elements help delineate groundwater flow paths and identify areas of recharge and discharge. While in geothermal systems, the major and trace elements can indicate the contribution of deep hydrothermal fluids. In this study, we used major and trace elements as a groundwater tracer used to determine the origin of the Ain Al-Harrah hot spring in Saudi Arabia. Water sample data collection was taken from previous studies. In the data collection process, pre-washed 0.5 L polyethylene bottles were used to collect a total of five water samples from Ain Al-Harrah hot spring, Saudi Arabia. To prevent contamination, all samples were stored in a refrigerated room to maintain their chemical composition until the analysis process. The analytical results of the study showed that most of the hot water samples from Ain Al-Harrah hot spring, Saudi Arabia had been influenced by seawater which exceeded the limit value of $x = 0.86$ in the Na/Cl ratio. In addition, the value of $y = 0.1$ at the SO_4/Cl ratio is the horizontal limit between the two. The interpretation of Cl against Cl/Li also confirms that the hot springs of Ain Al-Harrah, Saudi Arabia have been largely mixed with surface water. In addition, it is likely that the origin of the hot springs of Ain Al-Harrah, Saudi Arabia is also from seawater intrusion from red sea that has undergone mixing by meteoric water.

Keywords: hot spring waters; hydrological tracers; lithium enrichment; major elements; seawater influenced; trace elements

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INTRODUCTION

Ain Al-Harrah hot spring is a sulphurous hot spring located in Al-Laith Governorate south of Mecca, Saudi Arabia, is a famous natural health tourism destination. This sulphurous hot spring has a water temperature ranging from 80 to 85°C. At this location, there are 19 hot sulphur springs, providing ample space for relaxation and exploration. The springs cover an area of 49,000 square metres. The Ain Al-Harrah hot springs are part of the Al-Lith geothermal field, which is a medium-high enthalpy geothermal system associated with tectonic activity related to the rifting of the Red Sea (Rafiq et al., 2024; Stone et al., 2022).

Ain Al-Harrah Hot Springs is part of the Al-Lith geothermal field in western Saudi Arabia. The hot spring is associated with ancient Precambrian rocks, which provide the geological framework for the geothermal system. The region is characterised by tectonic activity associated with the Red Sea rift, which has created favourable conditions for geothermal systems (Basaham et al., 2015; Michelsen et al., 2015; Rafiq et al., 2024; Stone et al., 2022). The Ain Al-Harrah hot spring shows high concentrations of sodium (Na), bicarbonate (HCO_3) and chloride (Cl), indicating significant water-rock interactions. MT studies have revealed conductive anomalies at a depth of 3.5 km, which are likely related to geothermal resources. High resistive zones correspond to hard rock geological formations, while moderately resistive bodies indicate pathways for geothermal fluids (Ashadi et al., 2024).

The origin of Ain Al-Harrah hot springs has been extensively studied through hydrochemical characterisation and geothermometry. Collectively, the origin of Ain Al-Harrah hot springs is still a matter of debate. Some researchers say it originates from meteoric water that enters the depths and is then heated through geothermal processes. However, if this is the case then the discharge of Ain Al-Harrah hot spring would depend on the intensity of rainwater. Some researchers think there is a possibility of seawater contribution from the Red Sea. Therefore, in this study, we conducted a geochemical analysis based on major and trace elements that allows prediction of the origin of Ain Al-Harrah hot spring in Saudi Arabia.

Theories

The combination of concentrations and isotopes of boron (B), lithium (Li), and chlorine (Cl) is a powerful tool to trace the origin of hot water. By function, Boron is an indicator of water-rock interaction that is often used to show the level of water-rock interaction, as boron is often released from minerals during weathering. High boron concentration values can signal seawater intrusion into coastal aquifers (Amita et al., 2014; Millot et al., 2012; Tomascak, 2004).

In contrast, Lithium is commonly used to trace the path and source of groundwater flow. Different sources (e.g. meteoric water, seawater, hydrothermal fluids) have different isotopic signatures. Li concentrations and isotopes help in understanding geochemical processes and fluid mixing. A recent study from the U.S. Geological Survey (USGS) estimated lithium concentrations in groundwater across the United States. The study found that lithium occurs naturally in groundwater at concentrations of 30 micrograms per litre or higher in many regions. These concentrations are different from lithium concentrations in deep groundwater. Thus, the significant difference between shallow groundwater and deep groundwater makes lithium used as a reliable tracer for thermal waters (Arevalo, 2013; Arienzo et al., 2020; Jan et al., 2021; W. Li et al., 2019).

On the other hand, chlorine (Cl) concentration can help determine the origin of hot water, with higher concentrations often indicating a seawater or evaporite source. Chlorine, along with other ions such as sodium and sulphate, is used to trace geochemical processes and fluid pathways. Chloride concentrations can help determine the origin of groundwater. High chloride levels often indicate a seawater or evaporite source, while lower concentrations may indicate meteoric water. Chloride, along with other ions such as sodium and sulphate, is used to trace geochemical processes and fluid pathways in groundwater systems (Hendry et al., 2000; Jalili et al., 2019).

Thus, in its application B-Li-Cl can help delineate groundwater flow paths and identify areas of recharge and discharge. In geothermal systems, B-Li-Cl concentrations can indicate the contribution of deep hydrothermal fluids. Some studies on shallow groundwater contamination, major and trace elements might be used to detect and trace the source of contamination, providing insight into the pathways and processes that affect groundwater quality.

METHOD

Methodology Research

In this study, we analysed the alkalinity, major and trace elements as hydrological tracers in different seasons. The data from this study was examined 5 water samples with different locations. Determination of 9 elements including trace elements was conducted as the main elements in this study. In the experiment, water temperature, pH, alkalinity, and free CO content were measured in situ from non-volcanic hot water, Ain Al-Harrah, Saudi Arabia. Water sample data collection was conducted by Rafiq et al., (2024) in December 2022. In the collection process, pre-washed 0.5 L polyethylene bottles were used to collect a total of five water samples from Ain Al-Harrah hot spring, Saudi Arabia. To prevent contamination, the samples were stored in a cooler to maintain their chemical composition until analysis. The data were processed and analysed using specialised software and tools to obtain accurate information about the study area.

Table 1. Physiochemical properties of the water samples collected from the Ain Al-Harrah hot spring, Saudi Arabia.

Sample ID	SO_4/Cl	Na/Cl	Na/(Na+Ca)	Cl/(Cl+HCO3)	B/4 (mg/L)	Cl/100 (mg/L)	Cl/Sr	Cl/Li	Cl/B
AH-01	0.80	0.86	0.61	0.88	0.03	5.39	183.49	1342.94	4373.94
AH-02	0.80	0.95	0.61	0.88	0.03	4.73	157.88	1212.21	3936.06
AH-03	0.80	0.87	0.62	0.84	0.04	4.87	162.48	1316.11	3392.03
AH-04	0.78	0.74	0.61	0.86	0.04	5.58	187.84	1394.40	3875.76
AH-05	0.78	0.70	0.61	0.87	0.03	5.82	192.44	1492.18	4263.68

Source : Water sample data collection was conducted by Rafiq et al., (2024) in December 2022.

Geology Setting

The geology of Saudi Arabia is quite interesting and diverse, reflecting its complex geological history **(Figure 1)**. The oldest rocks in Saudi Arabia date back to the Precambrian era, about 3 billion years ago. These rocks are mainly igneous and metamorphic rocks, forming the Arabian Craton, which is the ancient geological core of the Arabian Peninsula. Above the Precambrian basement is a thick sequence of sediments from the Phanerozoic era (541 million years ago to the present day). This sequence includes sandstone, anhydrite, dolomite, limestone, chert and marl. These sedimentary rocks hold significant oil and gas reserves (Ashadi et al., 2024; Sabir et al., 2020).

Saudi Arabia is affected by tectonic activity associated with the Red Sea Rift, which has created pathways for geothermal fluids and affected the geology of the region. A prominent geological feature is the west-facing slopes in central Saudi Arabia, which are lined with limestone. This vast desert region of Saudi Arabia is characterised by thick sedimentary sequences and significant oil reserves (Basaham et al., 2015; Rafiq et al., 2024).

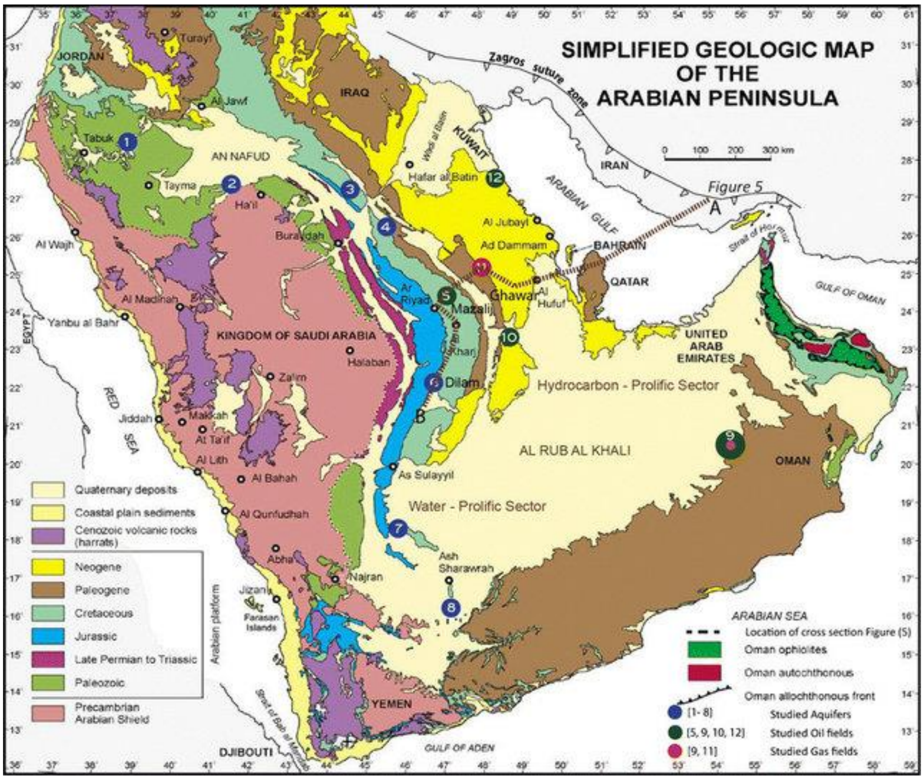

Figure 1. Map showing the countries in the Arabian Peninsula with the geological conditions of the rocks in the region. The black outline is the Ain Al-Harrah Hot Spring research site (Sabir et al., 2020).

In the Ain Al-Harrah region of Saudi Arabia, there is an emerging hot spring. Ain Al-Harrah is located in the Al-Lith geothermal field in western Saudi Arabia, which is part of a medium to high enthalpy geothermal system. The Al-Lith geothermal field is associated with tectonic activity related to the Red Sea Rift. This rift process created pathways for geothermal fluids and influenced the geology of the region. Geothermal systems are characterised by an open network of active faults and fractures, which allow the movement of geothermal fluids. Several researchers have used electromagnetic (EM) methods, such as magnetotelluric and transient electromagnetic, to explore and characterise geothermal reservoirs. The results of the magnetotelluric study revealed that underneath the Ain Al-Harrah area there is a high reservoir. It is possible that this high-temperature reservoir has a connection with faults or fractures in the Red Sea (Ashadi et al., 2024; Rafiq et al., 2024; Stone et al., 2022).

RESULTS AND DISCUSSION

The results of the hot spring data analysis from Ain Al-Harrah, Saudi Arabia show that in **Figure 2A** the lowest concentration value of major elements (cations and anions) is the concentration of Magnesium (Mg) in mg/L. While the concentration values of Chlorine (Cl) and Sodium (Na). Magnesium is one of the main constituents in seawater and plays an important role in the chemical processes of the ocean. Magnesium is present in seawater at an average concentration of about 1.284 mg/L. Magnesium helps maintain the alkalinity and buffering capacity of the ocean, which is crucial for regulating the pH of seawater. Magnesium is involved in the formation of marine minerals such as magnesium calcite and dolomite, which are important components of marine sediments. Magnesium ions (Mg) interact with other ions and compounds in seawater, affecting the chemical balance and overall stability of the ocean. The concentration of magnesium in seawater is affected by processes such as precipitation of magnesium-containing minerals and dissolution of rocks and sediments (Clow et al., 1997; Hendry et al., 2000; Idroes et al., 2019; Meju & Le, 2002). Chlorine, present as chloride ion (Cl), is a major component of seawater. The average concentration of chloride in seawater is about 19.353 mg/L. Chloride is the most abundant anion in seawater and, along with sodium, contributes significantly to overall salinity. Chloride ions interact with other ions and compounds in seawater, playing an important role in maintaining ion balance and overall chemical composition (Iqbal & Kusumasari, 2024; Wunder et al., 2005). While Sodium (Na) is one of the main elements in seawater, and is present in significant concentrations. The average concentration of sodium in seawater is about 10.781 mg/L. Sodium, along with chloride, contributes significantly to the salinity of seawater. Sodium ions interact with other ions and compounds in seawater, affecting various chemical processes and the overall ionic strength of seawater (M. Li et al., 2014; Luo et al., 2018; Michalski, 2010; Mousavi Mashhadi et al., 2016; Nazri et al., 2016). The high content of chlorine and sodium in the hot water samples in Ain Al-Harrah, Saudi Arabia has the same similarity with seawater as the initial assumption in this study.

Visualising the relationship between sodium (Na) and chloride (Cl) concentrations in hot springs can provide valuable insights into the geochemical characteristics and processes affecting the hot water. By plotting Na against Cl can identify a linear or non-linear relationship between these two ions. A strong linear correlation may indicate a common source or a common geochemical process affecting both ions. Na vs Cl graphs can help trace the origin of geothermal fluids (Bhat et al., 2018; Gan et al., 2017; Luo et al., 2018; Morikawa et al., 2016; Umar Kura et al., 2013). For example, seawater-like Na and Cl ratios may indicate marine influence or saltwater intrusion. However, it can be seen in **Figure 2B** that the hot water data in the Ain Al-Harrah region of Saudi Arabia has a distribution close to the seawater dilution line. Variations in the Na/Cl ratio can provide insight into water-rock interaction processes, such as ion exchange, mineral dissolution, or precipitation. Anomalously high Cl concentrations may indicate contamination from anthropogenic sources such as seawater intrusion in coastal areas. Na and Cl concentrations can also reflect the temperature and solubility of minerals in geothermal reservoirs, providing insight into the thermal characteristics of hot springs.

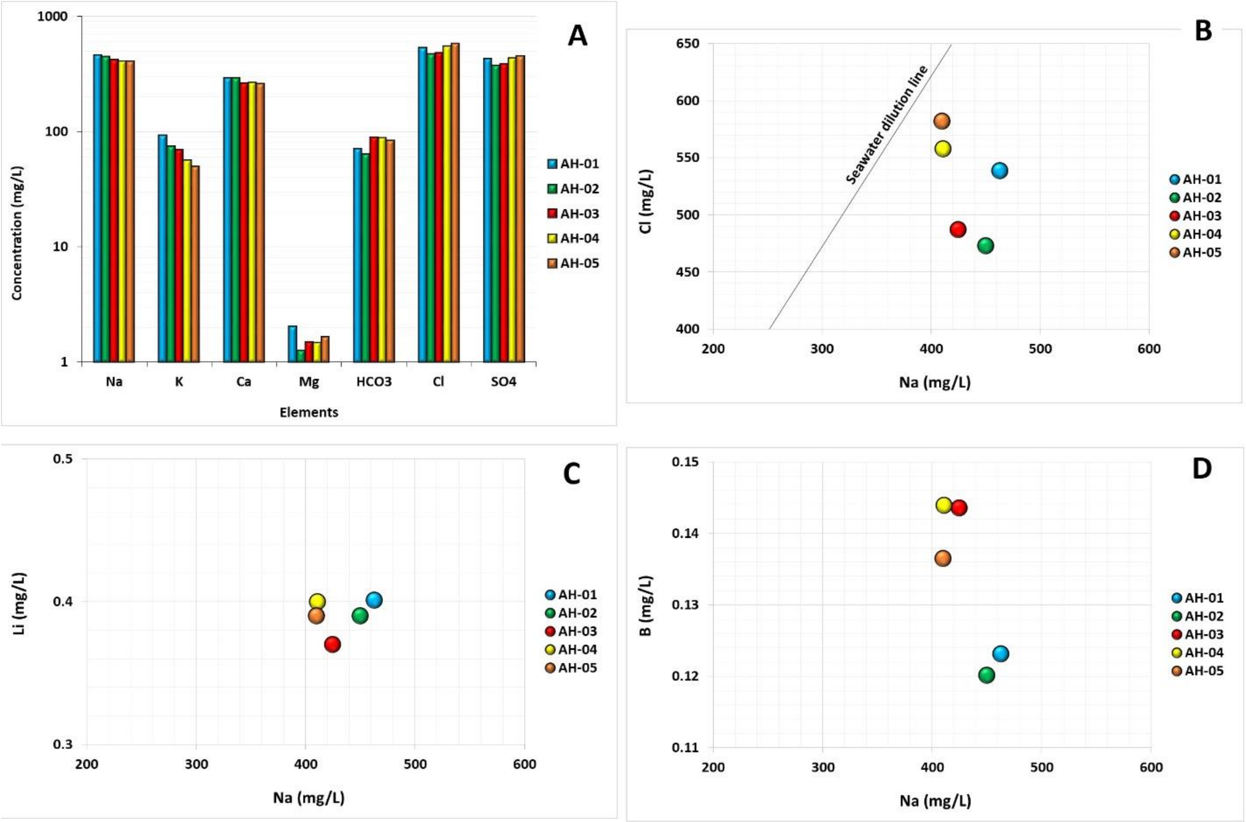

Figure 2. A. Distribution of cation and anion concentrations; **B.** Interpretation of Na vs Cl (mg/L) concentration with seawater dilution line; **C.** Interpretation of Na vs Li (mg/L) concentration; **D.** Interpretation of Na vs B (mg/L) concentration.

Visualising the relationship between sodium (Na) and lithium (Li) concentrations in a hot spring can provide valuable insights into the geochemical and process characteristics of the hot spring. By plotting Na against Li, we can identify a linear or non-linear relationship between these two ions. A strong linear correlation may indicate that the two ions are affected by the same geochemical process or have a common source. By analysing the relationship between Na and Li in hot springs, we can gain valuable information about the origin, evolution and current state of geothermal systems. Based on the analysis of **Figure 2C**, it can be seen that the hot spring water of Ain Al-Harrah, Saudi Arabia has high Li values ranging from 0.37 - 0.401 mg/L. These values are quite high for groundwater and may be derived from magmatic or evolved water (Hartmann et al., 2024; Kusumayudha et al., 2018; Négrel et al., 2010).

Graphs of sodium (Na) versus boron (B) concentrations in hot springs can be very informative for understanding geochemical processes and the origin of geothermal fluids. By plotting Na against B, you can identify linear or non-linear relationships between these two elements. A strong correlation may indicate that both ions are affected by the same geochemical process or have a common source. The concentrations of Na and B can reflect the temperature and geochemical conditions within the geothermal reservoir. Differences in the Na/B ratio can help trace the origin of geothermal fluids. For example, a high concentration of B relative to Na may indicate a significant contribution from deep magmatic or hydrothermal sources, while a lower ratio may indicate an influence from meteoric water or shallow groundwater (Oi et al., 1996; Williams & Hervig, 2004). Na vs B graphs can help identify mixing between different water sources, such as meteoric water, deep geothermal fluids and seawater. By analysing the relationship between Na and B in the hot springs of Ain Al-Harrah, Saudi Arabia, **Figure 2D** has a fairly high concentration of Boron (B) derived from water that has undergone a heating process at depth. The distribution of the plot data also looks homogeneous, indicating that it comes from the same reservoir.

Seawater Influence

The B-Li-Cl ternary diagram is a powerful tool used in geochemistry to analyse the chemical composition of hot water. This diagram helps identify the extent and nature of water-rock interactions, such as ion exchange, mineral dissolution, or precipitation. In **Figure 3**, this diagram can reveal mixing between different water sources, such as meteoric water, deep geothermal fluids, and seawater. The high Chlorine value in the hot water of Ain Al-Harrah, Saudi Arabia shows that the hot water originates from depth and undergoes a high Cl/B absorption process upon heating. The Ain Al-Harrah hot spring represents a moderately evolved (old) hydrothermal system (Arrofi et al., 2024; Rafiq et al., 2024).

Variations in B/Li and Cl/Li ratios can help trace the origin of geothermal fluids. For example, high B/Li ratios may indicate significant contributions from magmatic or deep hydrothermal sources, while lower ratios may indicate influences from meteoric water or shallow groundwater. The concentrations of B, Li, and Cl can reflect the temperature and geochemical conditions within the geothermal reservoir, thus providing information on the thermal characteristics of the hot spring (Kortelainen, 2011; Tabei et al., 2002).

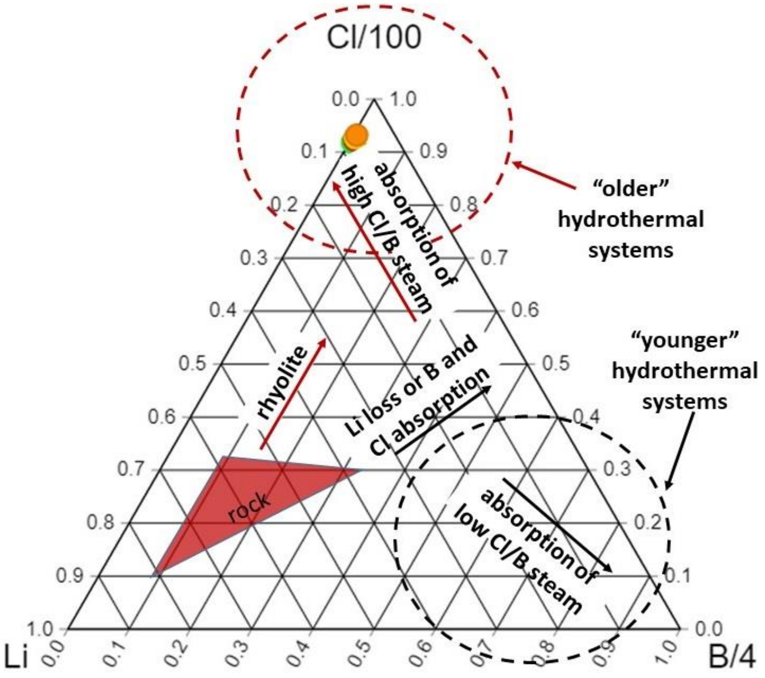

Figure 3. B-Li-Cl diagram for the hot spring water.

Gibbs diagrams are a valuable tool in hydrogeochemistry for understanding the chemical composition and processes of geothermal water. Gibbs diagrams help classify geothermal water based on its dominant ions (e.g., Na, K, Ca, Mg, Cl, SO_4, HCO_3) (Anthony, 2017; Arrofi et al., 2024; Chafa et al., 2022; Hwang et al., 2017; Luo et al., 2018). This classification can indicate geochemical processes affecting the water, such as water-rock interactions, evaporation, or mixing with other water sources. By plotting the concentrations of major ions, Gibbs diagrams can help trace the origin of geothermal fluids. In **Figure 4**, high concentrations of Na and Cl might indicate seawater influence, while high concentrations of Ca and HCO_3 might indicate water-rock interaction during heating process and upwelling to the surface.

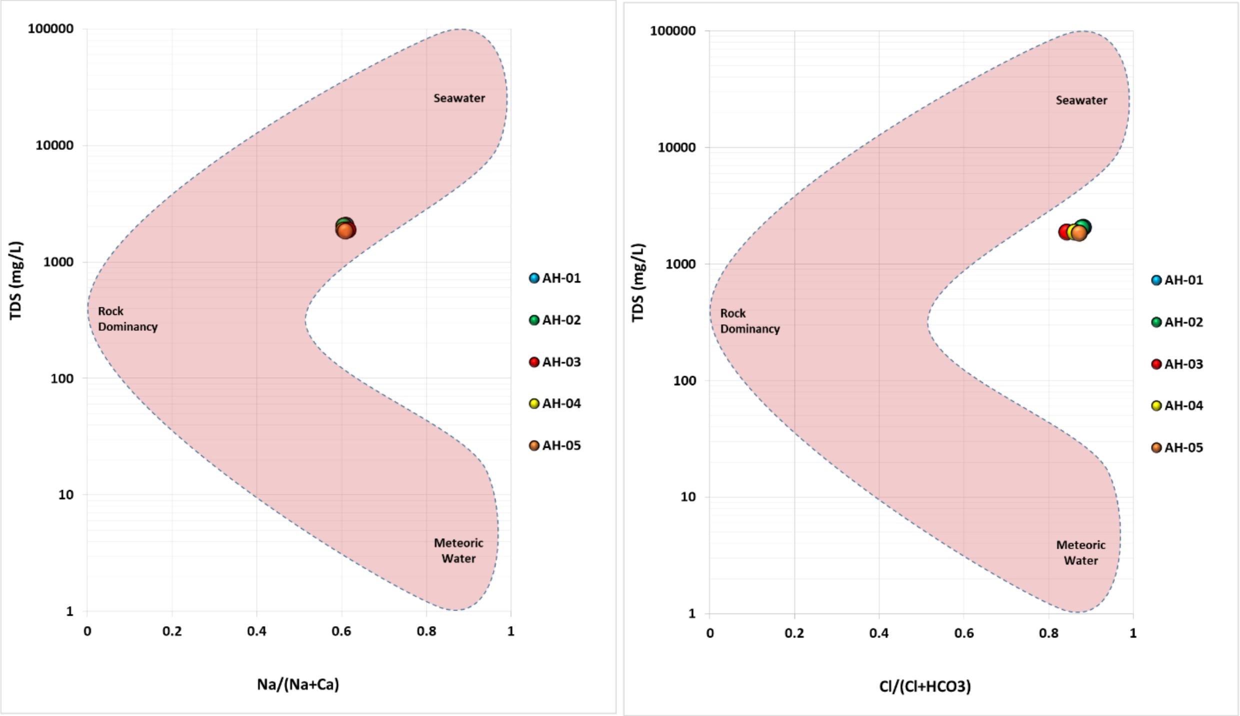

Figure 4. Gibbs diagrams of hot spring water samples collected in Ain Al-Harrah, Saudi Arabia.

The influence of seawater on hot springs can be demonstrated by analysing certain elemental ratios **(Figure 5)**. The Na/Cl ratio in seawater is about 0.86 (in molar basis). Ratios significantly higher or lower than this may indicate contributions from other sources, such as hydrothermal fluids or freshwater dilution. This ratio can help distinguish between marine and non-marine influences. Seawater typically has a higher Mg/Ca ratio compared to freshwater. In terms of mixing proportions, this ratio can be used to measure the proportion of seawater mixed with freshwater or hydrothermal fluids in hot springs. Elemental ratios are incorporated into geochemical models to understand the source and evolution of hot springs.

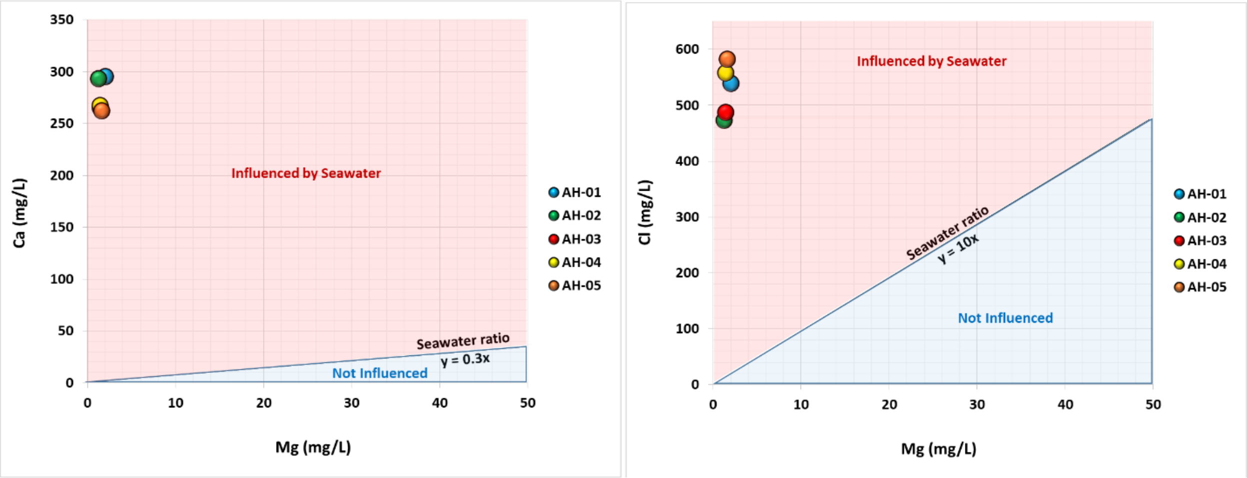

Figure 5. The ratio of the main elements indicates the influence of seawater. Pink-coloured areas indicate the presence of seawater influence.

The analytical results in **Figure 6A** show that most of the hot spring water samples from Ain Al-Harrah, Saudi Arabia have been influenced by seawater. The black line with a value of x = 0.86 is the Na/Cl ratio value which illustrates the boundary between groundwater that has the potential to be influenced by seawater and not influenced. The y = 0.1 in SO_4/Cl ratio is the horizontal boundary between the two. One of the hot water samples of Ain Al-Harrah, Saudi Arabia is included in the not influenced by seawater category allowing dilution or dilution by high meteoric water. So that the

Na/Cl ratio becomes above 0.86 (meq/L). In contrast to the analytical results in **Figure 6B**, the interpretation of the Cl vs Cl/Li ratios illustrates a small contribution from magmatic water. This interpretation confirms that the hot springs of Ain Al-Harrah, Saudi Arabia have been largely mixed with surface water. In addition, it is likely that the origin of the hot springs of Ain Al-Harrah, Saudi Arabia is also from seawater intrusion from red sea that has undergone mixing by meteoric water. The results of this analysis have a very strong correlation to previous research by Rafiq et al., (2024), although using different geochemical methods.

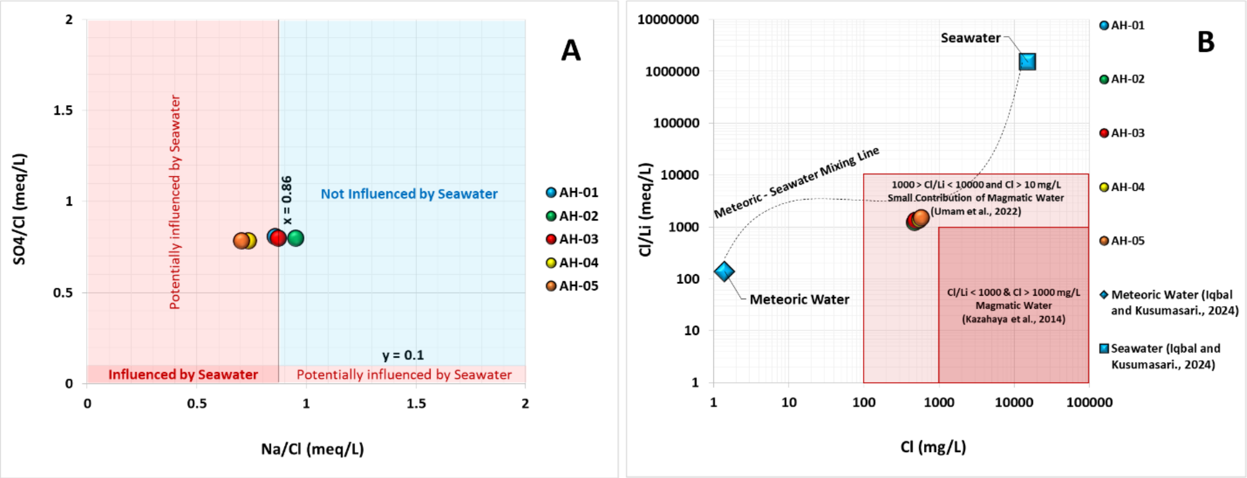

Figure 6. A. Na/Cl vs SO_4/Cl ratio denote the indicatore of influenced by seawater in hot spring water samples; **B.** Cl vs Cl/Li ratio is indicator of small contribution of magmatic water.

Table 2. Estimated reservoir temperature of each hotspring. Temperature are measured in °C.

Sample ID	Na/K					
	Truesdell (1975)	Fournier (1979)	Tonani (1980)	Nieva (1987)	Arnorsson (1983)	Giggenbach (1988)
AH-01	277.80	285.23	324.79	270.58	277.48	295.02
AH-02	250.31	265.08	293.49	250.85	259.34	276.68
AH-03	248.46	263.71	291.39	249.50	258.10	275.42
AH-04	224.80	245.85	264.57	232.02	241.92	259.04
AH-05	210.87	235.12	248.84	221.53	232.15	249.15

*The equation for each calculation can be seen in (Arrofi et al., 2024)

Estimating reservoir temperature is a fundamental aspect in geothermal exploration and development. Understanding reservoir temperature helps in managing geothermal resources sustainably. Chemical geothermometers, such as Na-K, Na-K-Ca, and silica geothermometers, are commonly used to estimate reservoir temperature based on the chemical composition of geothermal fluids. **Table 2** is the calculation result based on the formula from each source (Arrofi et al., 2024)**.**

CONCLUSION

The results of the hot spring data analysis from Ain Al-Harrah, Saudi Arabia show that the lowest concentration value of major elements (cations and anions) is the concentration of Magnesium (Mg) in mg/L. While the concentration values of Chlorine (Cl) and Sodium (Na). Visualising the relationship between sodium (Na) and chloride (Cl) concentrations in hot springs can provide valuable insights into the geochemical characteristics and processes affecting the hot water. By plotting Na against Cl can identify a linear or non-linear relationship between these two ions. A strong linear correlation may indicate a common source or a common geochemical process affecting both ions. Na vs Cl graphs can help trace the origin of geothermal fluids. In B-Li-Cl diagram can reveal mixing between different water sources, such as meteoric water, deep geothermal fluids, and seawater. The high Chlorine value in the hot water of Ain Al-Harrah, Saudi Arabia shows that the hot water originates from depth and undergoes a high Cl/B absorption process upon heating. The Ain Al-Harrah hot spring represents a moderately evolved (old) hydrothermal system. High concentrations of Na and Cl might indicate seawater influence, while high concentrations of Ca and HCO_3 might indicate water-rock interaction during heating process and upwelling to the surface. The interpretation of seawater influenced using Major and Trace elements confirms that the hot springs of Ain Al-Harrah, Saudi Arabia have been largely mixed with surface water. In addition, it is likely that the origin of the hot springs of Ain Al-Harrah, Saudi Arabia is also from seawater intrusion from red sea that has undergone mixing by meteoric water.

This study provides a comprehensive analysis of the geochemical and isotopic characteristics of the Ain Al-Harrah hot springs within the Al-Lith geothermal field in Saudi Arabia. Through detailed hydrochemical analysis and the application of isotopic evolution models, we have traced the origins and geochemical processes influencing these thermal waters. The results indicate that the hot springs are predominantly fed by meteoric water, which undergoes extensive water-rock interaction and mixes with deep hydrothermal fluids. Elevated concentrations of boron (B) and lithium (Li) suggest contributions from magmatic sources, while the sodium (Na) to chloride (Cl) ratios hint at minor seawater intrusion. Understanding these processes is crucial for effective geothermal resource management and sustainable exploitation of geothermal energy. The findings enhance our knowledge of geothermal systems in tectonically active regions and provide a framework for future studies on the geochemical behavior of thermal waters. By elucidating the complex interactions between different water sources and geological processes, this research contributes to the broader field of geothermal energy and supports efforts to harness this renewable energy source sustainably.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest concerning the publication of this article. The authors also confirm that the data and the article are free of plagiarism.

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