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# Alkalinity, Major and Trace Elements as Hydrological Tracers in Different Seasons: Implications for the Origin of Hot Springs in Non-Volcanic Areas, Odisha, India

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## Abstract

During the rainy season, surface water can infiltrate and mix with groundwater, making it difficult to identify different groundwater sources. In addition, mixing of water from different sources over time can obscure the original characteristics of groundwater. In this study, we used geochemical analyses such as alkalinity, major elements, hydrological modelling and long-term monitoring before, during and after the rainy season to understand the changes in concentrations, and determine the origin of groundwater sources despite different seasonal conditions. The data from this study was taken from a previous study and examined 18 water samples with different locations and weather conditions. Determination of 9 elements including alkalinity and 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, Odisha, India. In the process, the water was put into two polypropylene bottles, and cation and anion analyses were conducted in the laboratory. The results showed that seasonal differences clearly affected the changes in alkalinity concentration of each hot spring. However, hot springs with higher alkalinity experienced larger changes. In contrast, the analysed chlorine (Cl) concentrations < 100 mg/L were more susceptible to shifts due to monsoon, whereas Cl concentrations > 100 mg/L were more homogeneous despite the influence of monsoon (seasonal differences). Differences in the rainy season affected the concentration changes in Attri, Tarabalo and Deulajhari hot springs. Meanwhile, hot springs dominated by meteoric water such as Badaberena, Taptapani and Boden are less affected. This proves that Attri, Tarabalo and Deulajhari hot springs originate and are dominated by deep groundwater.

**Keywords:** alkalinity; hydrological tracers; major elements; trace elements; hot springs; non-volcanic areas; different seasons

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## INTRODUCTION

Detecting groundwater sources can be challenging due to seasonal variations. In different seasons such as the dry and wet seasons, groundwater recharge rates can vary significantly between the dry and wet seasons, making it difficult to determine consistent recharge sources. Short-term monitoring can miss seasonal fluctuations, leading to incomplete data on groundwater sources (Blanchette et al., 2010; Dragon & Marciniak, 2010; Umar Kura et al., 2013).

During the rainy season, surface water can infiltrate and mix with groundwater, making it difficult to identify different groundwater sources. In addition, mixing of water from different sources over time can obscure the original characteristics of groundwater (Iqbal & Kusumasari, 2024; Khan Adnan & Rehman Yusra, 2017). Seasonal changes in groundwater levels can affect flow paths and water mixing, altering the geochemical signatures used to track water sources. Variations in hydraulic gradient and flow velocity can also change seasonally, impacting groundwater movement and mixing (Blanchette et al., 2010; Meredith et al., 2013a, 2013b; Vilomet et al., 2001). Seasonal changes in temperature and rainfall can affect isotopic composition, making it difficult to accurately interpret data. Similarly, seasonal variations in water chemistry, such as ion concentrations, can complicate groundwater source identification (Javino et al., 2010; Kusuhara et al., 2020). Under environmental conditions, seasonal changes in vegetation cover and evapotranspiration rates can affect groundwater recharge and flow patterns. Agricultural irrigation and other human activities can also vary seasonally, affecting groundwater recharge and quality.

Continuous monitoring equipment can be affected by seasonal weather conditions, leading to data gaps or inaccuracies. Limited resources for long-term monitoring can hamper the ability to capture seasonal variations in groundwater resources (Al-Khashman et al., 2017; Blanchette et al., 2010). Despite these challenges, researchers are using geochemical analyses such as alkalinity, major elements, hydrological modelling and long-term monitoring to better understand the origin of groundwater sources, changes in concentration and composition due to seasonal changes (McConnell et al., 2009).

## Theories

Alkalinity is an important parameter in analysing changes in groundwater composition. It measures the ability of water to neutralise acids, which is mainly due to the presence of bicarbonates, carbonates, and hydroxides (Acharya et al., 2018). Alkalinity indicates the buffering capacity of water against pH changes, which is essential for maintaining a stable environment for aquatic life. This indicator helps assess overall groundwater quality, identifying potential contamination or natural variations in water chemistry (Adejumo et al., 2018). Changes in alkalinity can signal water-rock interactions, such as dissolution of carbonate minerals. Elevated alkalinity may indicate contamination from agricultural runoff or industrial discharges. Monitoring alkalinity helps in understanding the health of aquatic ecosystems, as significant changes can affect species composition and biodiversity. Alkalinity measurements can provide insight into the impacts of climate change on groundwater systems. In use, alkalinity is also considered in water treatment processes to ensure water is safe for consumption and use (Dhaka & Bhaskar, 2017).

Analysing the key elements in groundwater is essential to understanding its composition and potential changes over time. The following are some of the main elements commonly analysed such as Cations and Anions (Tsay et al., 2017). For major cation elements, such as Calcium ($Ca^{2+}$) isoften derived from the dissolution of limestone and other carbonate minerals; Magnesium ($Mg^{2+}$) is generally found in groundwater due to the weathering of magnesium-containing minerals; Sodium ($Na^{+}$) can be derived from the dissolution of feldspar and other silicate minerals and Potassium ($K^{+}$) is usually present in groundwater due to the weathering of potassium-containing minerals. While anions such as Bicarbonate ($HCO_3^{-}$) is amajor component of groundwater, often resulting from the dissolution of carbonates; Chloride ($Cl^{-}$) can come from the dissolution of halite (rock salt) or from seawater intrusion. Sulfate ($SO_4^{2-}$) is often found in groundwater due to oxidation of sulfide minerals or dissolution of gypsum. Nitrate ($NO_3$-) is found due to agricultural runoff or oxidation of organic matter. For other parameters such as pH can be used to indicate the acidity or alkalinity of groundwater; Total Dissolved Solids (TDS**)** is used to measure the concentration of dissolved substances in water; and electrical conductivity (EC) is used to provide information on the ability of water to conduct electricity, which is related to its ion content. Applications using Major Elements can help determine the suitability of groundwater for drinking water, irrigation and industrial purposes. In addition, it tracks changes in groundwater composition due to natural processes or human activities and provides insight into the geochemical processes and geological history of the area (Adji et al., 2016; Millot et al., 2012; Zheng & Hermann, 2014).

Trace elements are present in very low concentrations in groundwater but can provide valuable insight into the composition and potential sources of contamination (You et al., 1996; Zhao et al., 2009). Arsenic (As) is an element that is naturally occurring in nature but can be toxic even at low levels; Lead (Pb) is an element that often comes from industrial activities and old pipe systems; Cadmium (Cd) is an element that can come from industrial discharges and agricultural runoff; Mercury (Hg) an element that can be found in areas with mining activities; Chromium (Cr): is an element associated with industrial processes; Copper (Cu) is an element that can come from natural sources or agricultural runoff; Zinc (Zn) often comes from natural sources but can increase due to human activity; Nickel (Ni) is an element that usually comes from natural sources but can increase near industrial areas; Manganese (Mn) is a naturally occurring element but can be affected by redox conditions; Iron (Fe) is an element that is commonly found in groundwater due to natural weathering processes; Lithium (Li) is an element that comes mostly from thermal processes and is associated with the mantle (Tang et al., 2007; Umam et al., 2022).

Trace element applications can be used in various scientific fields such as environmental monitoring which is very helpful in identifying sources of contamination and assessing their impact on groundwater quality. In addition, in the field of public health trace elements can be used to detect potentially harmful elements to ensure safe drinking water. In the field of geological studies, trace elements can provide insight into geochemical processes and aquifer history.

## 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 taken from a previous study by Zimik et al., (2017) and examined 18 water samples with different locations and weather conditions. Determination of 9 elements including alkalinity and 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, Odisha, India. In the process, the water was put into two polypropylene bottles, and cation and anion analyses were conducted in the laboratory. The next step is to understand the geological conditions to correlate with the analytical data that has been obtained.

### Geology Setting

Odisha, located on the eastern fringe of peninsular India, has a rich geological history and diverse mineral resources. Based on its geology, about 72.5% of Odisha is covered by Precambrian metamorphic rocks, including Archaean and Proterozoic formations. These ancient rocks have a wide variety of minerals (Acharya et al., 2018; Jamal & Singh, 2018; R. Kumar & Yadav, 2015; S. K. Kumar et al., 2009). Further, about 8% of the land area consists of Gondwana rocks, which are mainly associated with coal resources. The remaining area includes younger sedimentary formations that host minerals such as bauxite, chromite and iron ore **(Figure 1)**.

Odisha, India, lies on the Indian Plate, which is a minor tectonic plate straddling the equator in the Eastern Hemisphere. The Indian Plate moves in a north-easterly direction at a rate of about 26-36 mm per year. It was once part of the ancient supercontinent Gondwana, which began to break apart about 100 million years ago. The northward movement of the Indian Plate caused a collision with the Eurasian Plate, which resulted in the formation of the Himalayas (Guo & Wang, 2012; Lin et al., 2014; Zhu et al., 2025). The Indian region is characterised by numerous faults and fractures, which play an important role in the movement of geothermal fluids and the formation of mineral deposits (Blanchette et al., 2010; Haines & van der Pluijm, 2012; Huh et al., 1998; Purnomo et al., 2016; Saparun et al., 2022; Schleicher et al., 2015; Zheng & Hermann, 2014). Tectonic activity has created favourable conditions for geothermal systems, including hot springs in Odisha. Recent studies have shown that the Indian Plate is undergoing dramatic structural separation, with some parts fragmenting about 100 kilometres below the surface (Adimalla & Venkatayogi, 2018; Muthamilselvan et al., 2019; Zimik et al., 2017).

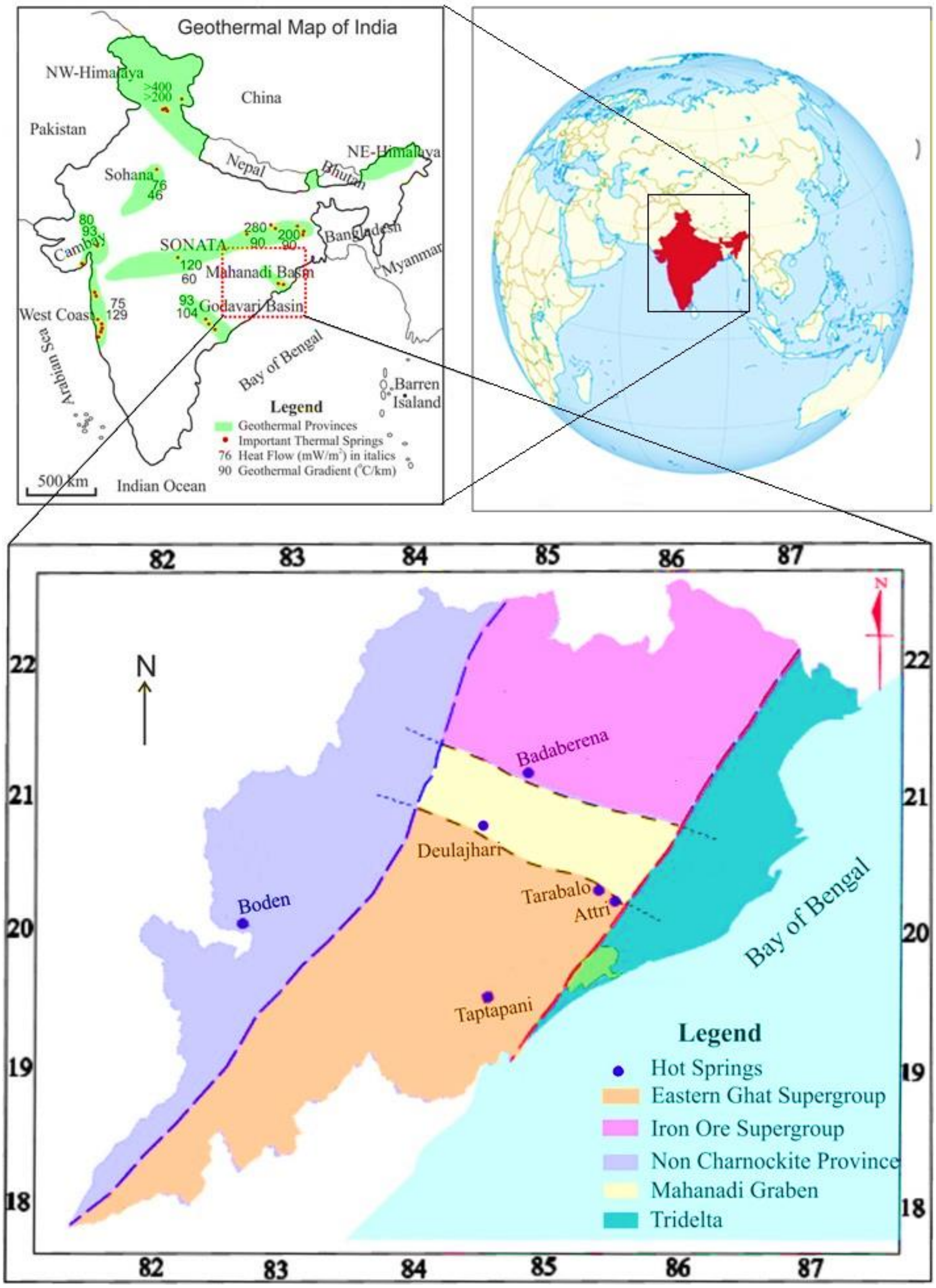

**Figure 1.** The distribution of geothermal springs in Odisha taken from the previous study by Zimik et al., (2017). The figure has been edited and taken from Zimik et al., (2017)

The hot waters in Odisha, India, are mainly located in the Mahanadi Geothermal Province, which is part of the Archean/Pre-Cambrian Geothermal Province. In its Precambrian geologic formation, the hot springs that appear in this region are associated with ancient Precambrian rocks, which provide the geological framework for geothermal systems. The region is characterised by a complex tectonic framework with numerous faults and fractures that facilitate the movement of geothermal fluids. The province includes several hot springs such as Attri, Tarabalo, Deulajhari, Magarmuhan, Bankhol, Badaberena, Taptapani, and Boden. The hot water in the region exhibits a wide temperature range, from 28°C to 58°C, and a varied chemical composition. Hot springs can be categorised into three types based on their chemical composition: Na-Cl, $Ca\text{-}HCO_3$, and $Na\text{-}HCO_3$. In previous studies, the chemical signatures of hot springs, especially those from Attri, Tarabalo, and Deulajhari, show that they rise rapidly and can be used to estimate reservoir temperatures (Brindha & Elango, 2012; Zimik et al., 2017).

## RESULTS AND DISCUSSION

### Alkalinity

Alkalinity is an important parameter in hot water analysis, as it provides insight into the buffering capacity of the water and the geochemical processes occurring within the geothermal system. Alkalinity measures the water's ability to neutralise acids, which is critical for maintaining pH stability in geothermal systems. High alkalinity often indicates the presence of bicarbonates and carbonates, which can result from water-rock interactions. Alkalinity can help track the extent of water-rock interactions, providing information on the dissolution of minerals such as calcite and dolomite. Monitoring alkalinity can indicate changes in water chemistry due to geothermal exploitation or natural processes (Acharya et al., 2018; Adejumo et al., 2018; Dhaka & Bhaskar, 2017).

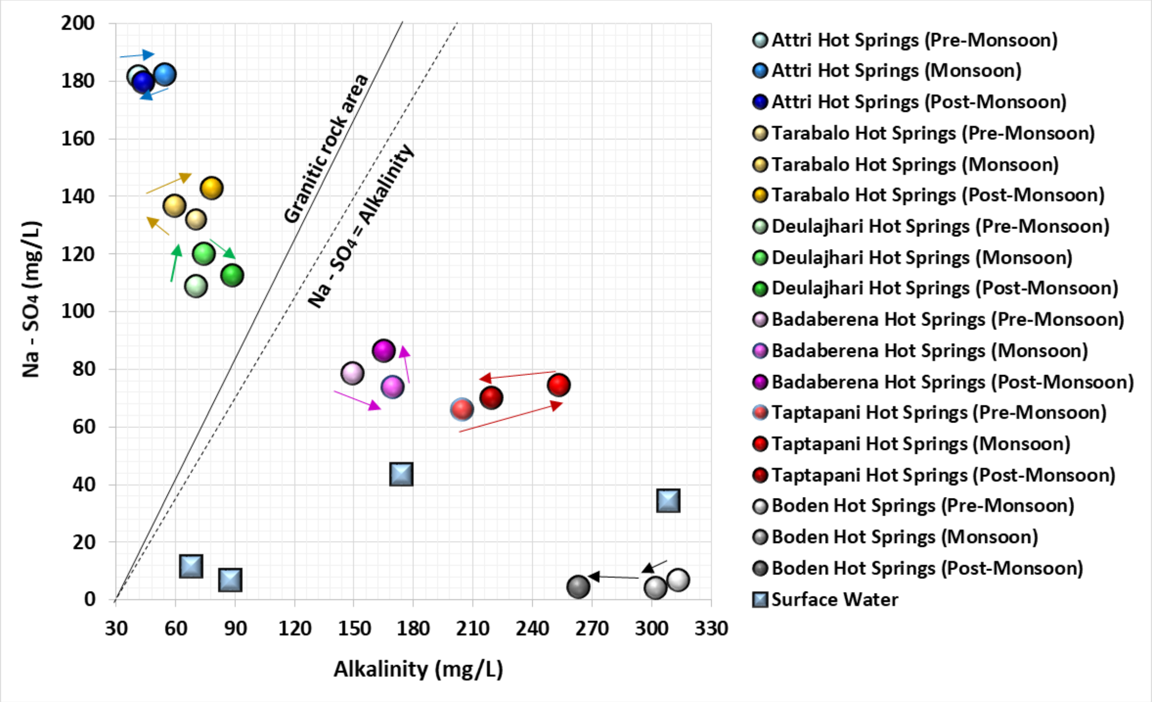

**Figure 2.** Interpretation of Alkalinity vs Na-$SO_4$ in thermal waters from Odisha, India

The formation mechanism of hot spring quality can be estimated based on the analysis of Na and alkalinity as the main components. Weathering plagioclase in hot springs usually has Na and alkalinity as the main chemical components, with low concentrations of Mg. In addition, particularly in areas of granitic rocks, water samples show a strong correlation between Na and alkalinity (**Figure 2**). These chemical properties suggest that the quality of hot water in the granitic rock area is influenced by plagioclase montmorillonisation. Plagioclase is a series of solid solutions between albite and anorthite end members that react with rainwater and $CO_2$. The plagioclase series can be written with the following equation (Yaguchi et al., 2014):

$$6CO_2 + 6H_2O \rightarrow 6H+ + 6HCO_3^- \quad ... (1)$$

$$7NaAlSi_3O_8 + 6H^+ + 20H_2O \rightarrow 3Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 6Na^+ + 10H_4SiO_4 \quad ... (2)$$

$$7CaAl_2Si_2O_8 + 12H^+ + 8H_4SiO_4 \rightarrow 3Ca_{0.33}Al_{4.67}Si_{7.33}O_{20}(OH)_4 + 6Ca^{2+} + 16H_2O \quad ... (3)$$

The interpretation of **Figure 2** shows that high alkalinity values were obtained from Badaberena, Taptapani and Boden hot springs. While low alkalinity values were obtained from Attri, Tarabalo and Deulajhari hot springs. The impact of seasonal differences clearly affects the changes in concentration of each hot spring. However, the hot springs with high alkalinity had a larger shift.

Analysing the concentration of sodium ($Na^+$) and calcium ($Ca^{2+}$) in thermal water is essential for understanding its geochemical characteristics and potential applications. The concentration of $Na^+$ and $Ca^{2+}$ helps classify thermal water into different types, such as Na-Cl, Na-$HCO_3$, and Ca-$HCO_3$, based on their dominant ions. These cations are used in geochemical tracing to understand fluid-rock interaction and mixing of different water sources. In estimating reservoir temperature, $Na^+$ and $Ca^{2+}$ concentrations, along with other ions, are used in geothermometry to estimate geothermal reservoir temperature.

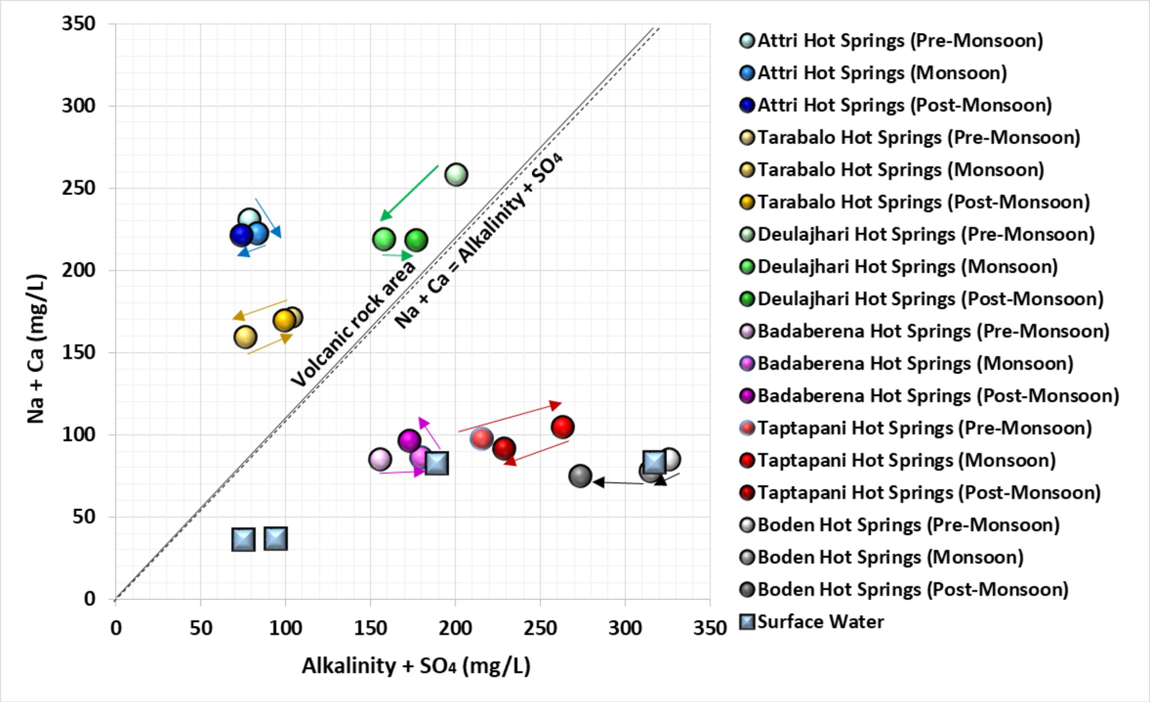

**Figure 3.** Interpretation of Alkalinity + $SO_4$ vs Na+Ca in thermal waters from Odisha, India

The Na+Ca interpretation results in **Figure 3** show that the hot springs with higher Na+Ca have little change in concentration due to seasonal differences. However, one of the hot springs originating from Deulajhari has high concentration changes before and during the rainy season. On the other hand, those with high alkalinity + $SO_4$ values have high concentration changes except for the hot spring from Badaberena.

## Major and Trace Elements

Cl/Li ratio and temperature are important parameters in geothermal water analysis. Cl/Li ratio helps determine the origin and evolution of geothermal fluids. A low Cl/Li ratio often indicates a meteoric water origin, while a high ratio indicates a deeper magmatic source. However, in a study conducted by Kazahaya et al., (2014), it was explained that this parameter needs to be supplemented or supported by other parameters such as outlet water temperature. This ratio is used in geochemical tracing to understand fluid-rock interaction and mixing of different water sources. In reservoir temperature estimation, geothermal water temperature measurements help estimate reservoir temperature, which is crucial for assessing geothermal potential. In thermometry, various geothermal thermometers (e.g., silica, Na-K-Ca) are used to calculate subsurface temperature based on the chemical composition of the water.

The results of the Cl/Li ratio vs water temperature analysis showed **(Figure 4)** that the hot spring plots were divided into two distinct groups. The first group is hot water taken in the Attri, Tabarabalo, and Deuljahari areas. This group has water temperatures higher than 50 degrees centigrade with Cl/Li ratios between 1000 - 10000. The location of the plots in the first group is similar to hot springs that appear in the Non-Volcanic Kii Peninsula region, Southwestern Japan (Umam et al., 2022). The second group of hot springs is taken from Badaberena, Taptapani, and Boden. This group has a water temperature that is quite cold to warm. However, this second group has a Cl/Li ratio between 10 - 1000. The Cl/Li ratio plot in this second group is thought to have been mixed by shallow groundwater/surface water very much. In other words, the proportion of water coming from depth is very small compared to group 1. When correlated to **Figure 1**, the group with high water temperature is located close to the fault. These results provide evidence that the presence of faults can cause deep groundwater or thermal water to come to the surface. In addition, faults can also minimise the process of dilution or mixing by surface water or shallow groundwater.

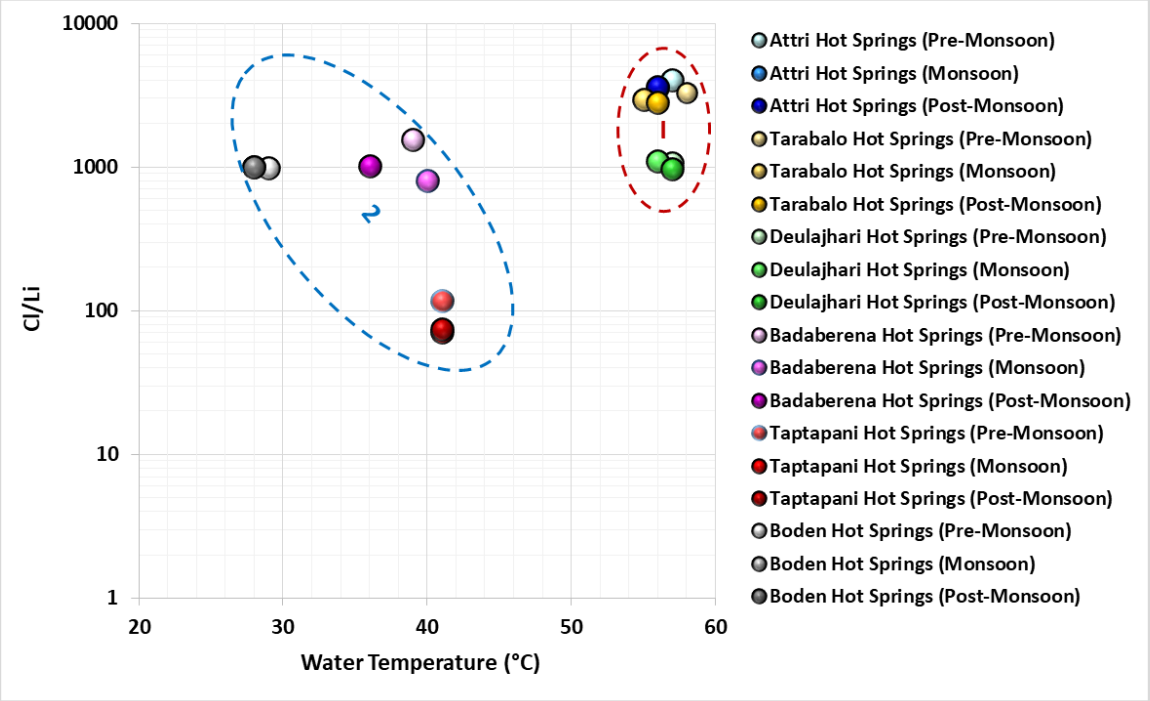

**Figure 4.** Interpretation of Cl/Li ratios vs water temperature in celcius. The first group is hot water taken in the Attri, Tabarabalo, and Deuljahari areas. The second group of hot springs is taken from Badaberena, Taptapani, and Boden

Chlorine concentration is a key parameter in geothermal water analysis, as it can provide insight into fluid origins, interactions, and potential sources of contamination. High chlorine concentrations often indicate seawater or evaporite sources, while lower concentrations may indicate meteoric water. The analysis results shown in **Figure 5** provide the same information as **Figure 4**, that clustering also occurs based on chlorine concentration. Chlorine (Cl) concentrations < 100 mg/L are more easily shifted due to the rainy season, while Cl concentrations > 100 mg/L are more homogeneous despite the influence of the rainy season (seasonal differences). The interpretation of **Figure 5** also shows that there is a suspected contribution of magmatic water from deep down that enters and mixes with Attri, Tarabalo, and Deuljhari hot springs.

In geochemical tracking, Chlorine along with other ions such as sodium and sulphate, can be used to track geochemical processes and fluid pathways in geothermal systems. Chlorine concentration, when combined with other geochemical parameters, can help estimate the temperature of geothermal reservoirs. The Cl vs Na interpretation in **Figure 6** shows that the hot springs from Badaberena, Taptapani, and Boden have low Cl and Na concentration values. The Badaberena, Taptapani, and Boden hot spring plots have similar characteristics to meteoric water. This plot is also similar to the Cl vs $_{SO4}$ interpretation that describes the sulphate content. The Cl vs $SO_4$ plot tends to be more homogeneous than the Cl vs Na plot.

The plots for Attri, Tarabalo and Deulajhari springs have higher Cl and Na than Badaberena, Taptapani and Boden. The highest Cl and Na concentration values came from Attri hot spring at 283 - 289 mg/L and 210 - 219 mg/L respectively, while the highest $_{SO4}$ concentration values came from Deulajhari hot spring at 83.6 - 130 mg/L. Judging from the plot distribution, differences in the rainy season affect the concentration changes in Attri, Tarabalo, and Deulajhari hot springs. While hot springs with dominant meteoric water such as Badaberena, Taptapani, and Boden are not very influential. This proves that Attri, Tarabalo, and Deulajhari hot springs (group 1) have component origins that are derived and dominated by deep groundwater compared to Badaberena, Taptapani, and Boden hot springs (group 2).

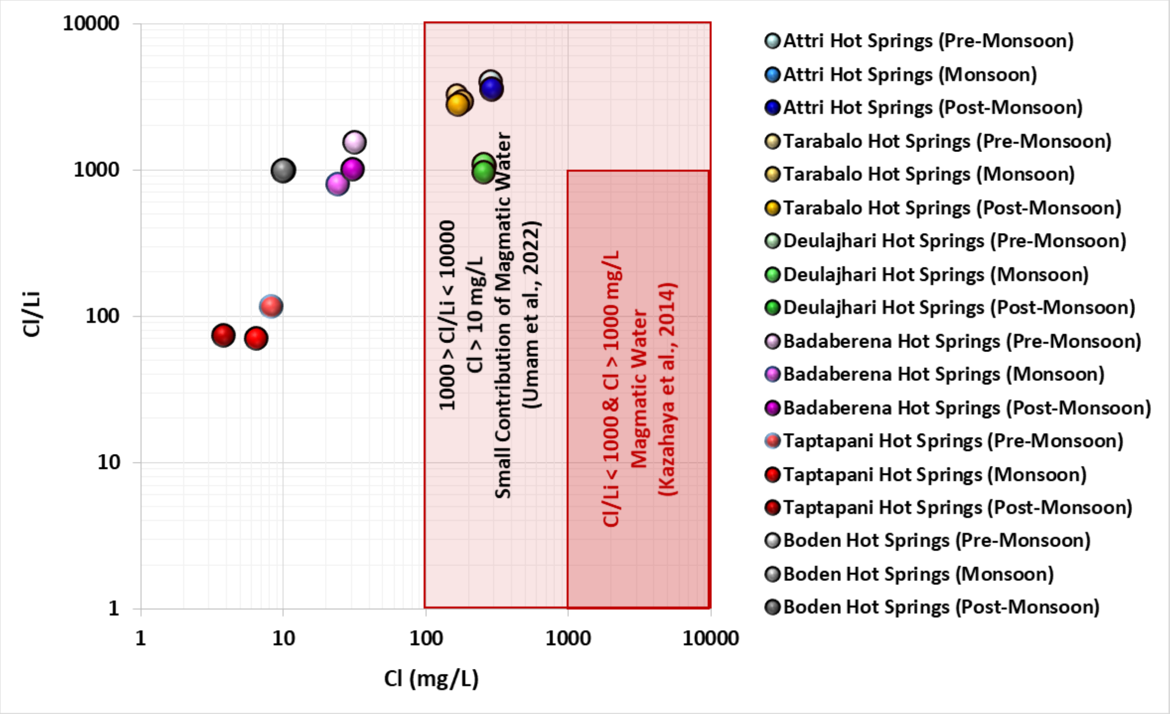

**Figure 5.** Interpretation of Cl/Li ratios vs concentration of chlorine (Cl). Chlorine (Cl) concentrations < 100 mg/L are more easily shifted due to the rainy season, while Cl concentrations > 100 mg/L are more homogeneous despite the influence of the rainy season (seasonal differences)

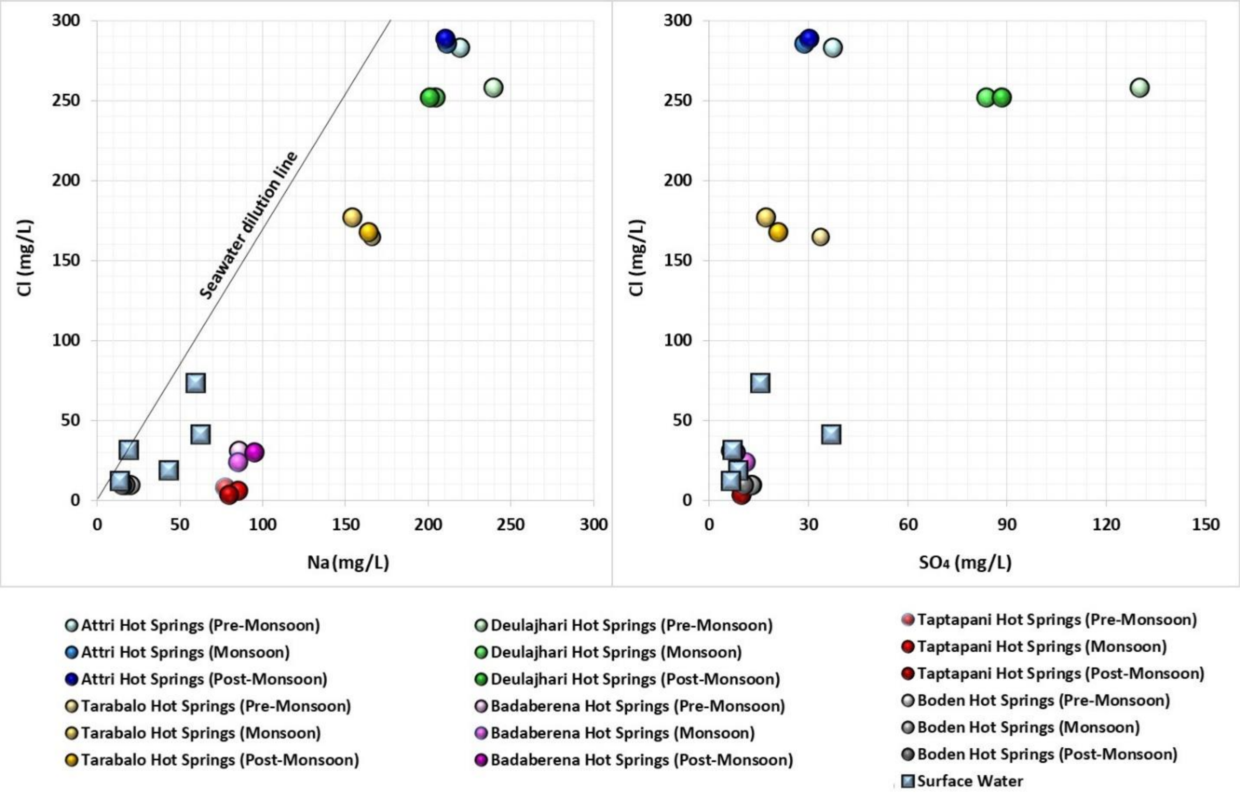

**Figure 6.** Interpretasi Cl vs Na and $SO_4$. The differences in the rainy season affect concentration changes in Attri, Tarabalo, and Deulajhari hot springs. Whereas hot springs with predominantly meteoric water such as Badaberena, Taptapani, and Boden are less affected. This proves that Attri, Tarabalo, and Deulajhari hot springs have water origin components that originate and are dominated by deep groundwater

## CONCLUSION

The effect of seasonal differences clearly affects the change in alkalinity concentration of each hot spring. However, hot springs with high alkalinity experienced greater changes. The Na+Ca interpretation results show that the hot springs with higher Na+Ca have little change in concentration due to seasonal differences. However, one of the hot springs originating from Deulajhari has high concentration changes before and during the rainy season. The results of the Cl/Li ratio vs water temperature analysis showed that the hot spring plots were divided into two distinct groups. The first group is hot springs taken from Attri, Tabarabalo, and Deuljahari which have water temperatures higher than 50 degrees centigrade with Cl/Li ratios between 1000 - 10000. The second group of hot springs taken from Badaberena, Taptapani, and Boden, have moderately cool to warm water temperatures. It is thought that the Badaberena, Taptapani and Boden hot springs are dominated by shallow groundwater/surface water to a large extent. The analytical results of chlorine (Cl) concentrations < 100 mg/L are more prone to shifts due to the rainy season, while Cl concentrations > 100 mg/L are more homogeneous despite the influence of the rainy season (seasonal differences). This interpretation suggests that there is a suspected contribution of deep magmatic water entering and mixing with Attri, Tarabalo and Deuljhari hot springs. The plots for Attri, Tarabalo and Deulajhari springs have higher Cl and Na values compared to Badaberena, Taptapani and Boden. Judging from the distribution of the plots, differences in the monsoon season affect the concentration changes in Attri, Tarabalo and Deulajhari hot springs. Meanwhile, hot springs that are dominated by meteoric water such as Badaberena, Taptapani, and Boden are less affected. This proves that Attri, Tarabalo, and Deulajhari hot springs originate and are dominated by deep groundwater.

## AUTHOR CONTRIBUTIONS

Conceptualization, MK and SVD; methodology, NS and PSB; software, NS; validation, AH, SBK, and MK; formal analysis, PSB; investigation, SVD and NS; resources, MK; data curation, AH; writing—original draft preparation, SVD and PSB; writing—review and editing, MK and SBK; visualization, NS; supervision, MK; project administration, MK; funding acquisition, MK.

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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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