



# Hydrogeochemical Characterization and Subsurface Flow Analysis of Volcanic Hot Springs

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**Abstract.** Understanding of the hydrogeochemical system of volcanic hot springs in Tompasso, Minahasa, is still limited, especially regarding the origin of water and subsurface flow patterns. This study aims to classify geothermal water types and analyze groundwater flow systems in volcanic environments. A total of 15 hot spring samples were analyzed using field measurements (temperature, pH, electrical conductivity), ion chromatography, titration, and spectrophotometry. Data validation was done with ion balance, and water classification using Piper diagrams. The results showed four main types of water, namely Mg-SO<sub>4</sub>, H-SO<sub>4</sub>, Na-Cl, and Na-SO<sub>4</sub>. Most of the samples are from meteoric water directly heated by the geothermal system, while two samples (HT-11A and HT-11B) were heated by steam. These findings provide a scientific basis for sustainable geothermal exploration and groundwater conservation in volcanic areas with variable geothermal systems at the study site.

**Keywords:** Geothermal system, Hydrogeochemistry, Subsurface flow, Volcanic hot springs.

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## 1. Introduction

Hot springs that emerge in volcanic areas are a tangible manifestation of geothermal activity on the surface [1-3]. This phenomenon is formed through the interaction between groundwater, heat from magma, and rocks that serve as a medium for flow [4-6]. The existence of hot springs in areas still experiencing volcanic activity points to geothermal processes beneath the surface and carries significant data regarding the chemical and physical transformations happening in the ground, specifically the movement of warm water and the chemical interactions it has with rocks [7-10].

Many factors heavily influence the chemical composition of hot water, such as its point of origin, the type of rock it flows through on its subterranean path, and how it gets heated, be it by directly touching extremely hot rock or by rising hot steam from geothermal reservoirs deep below the surface [11-12]. Understanding the chemical composition, as well as the direction and patterns of subsurface flow of these hot springs, is crucial, particularly in efforts to explore the potential for sustainable geothermal energy [13-15]. This knowledge aids in identifying locations of geothermal reservoirs, estimating the magnitude of

stored energy potential, and designing appropriate strategies to ensure the sustainability of groundwater resources to prevent overexploitation [16, 17].

However, to date, there are still many areas in Indonesia that have not received adequate research attention, including active volcanic areas such as Tompaso in North Sulawesi [18]. This area has not been fully explored in terms of its hot water chemistry and subsurface flow dynamics, even though this information is crucial for the development of responsible and sustainable geothermal energy.

The Tompaso region has geological conditions characterized by the presence of faults and fractures with various dominant directions, namely northeast–southwest (NE–SW), northwest–southeast (NW–SE), east–west (E–W), and one north–south (N–S) direction. NE–SW-oriented fractures appear to cross rock units such as Young Volcanic Rocks, Tondano Tuff, and lake and river deposits. These fractures can be observed in several villages such as “Pulutan, Tolok Satu, Liba, Kamanga Dua, Tonsewer Selatan, Toure Dua, and Toure Satu”. In addition, faults with a similar orientation (NE–SW) cut through volcanic rock and tuff formations and pass through many village areas, including Kanonang Dua, Pinabetengan Selatan, Tompaso Dua, and others.

East–west (E–W) oriented fractures were also identified cutting through the Young Volcanic Rocks, Tondano Tuff, and lake and river deposits, with distribution in villages such as South Tonsewer, Toure Dua, Tumaratas Satu, and Taraitak. Meanwhile, a single north–south (N–S) fault zone was found in the Kanonang Satu and Kanonang Dua areas, particularly in the Young Volcanic Rock formation.

Lithologically, the Tompaso region consists of rocks from the Tertiary and Quaternary periods. The Tertiary sedimentary formation is composed of a combination of shale, sandstone, limestone, and siltstone, which were later covered by volcanic rocks from both periods. Tertiary volcanic rocks include breccia, tuff, and lava, which are the result of ancient volcanic activity. Meanwhile, Quaternary rocks in this area consist of “Young Volcanic Rocks (Qv), Tondano Tuff (Qtv), and lake–river deposits (Qs) that overlie the Tertiary volcanic formation (TMV)”. The composition of Tertiary volcanic rocks is dominated by breccia, lava, and tuff, with lava generally characterized as andesitic to basaltic.

Young volcanic rock formations, which form young volcanoes such as Mount Soputan, consist of lava, volcanic bombs, lapilli, and ash. Tondano tuff is characterized by coarse volcanic material with an andesitic composition, consisting of subangular to slightly rounded components, pumice fragments, tuff, and lapilli tuff breccia. The dense ignimbrite structure and clear flow patterns are also distinctive features of this deposit. In addition, lacustrine and fluvial deposits in this area consist of sedimentary materials such as sand, silt, conglomerate, and clay, which were deposited in lake and river environments. Given this geological complexity, this study aims to identify the type of hot water based on its main chemical parameters and to understand how subsurface flow patterns influence the emergence of hot springs on the surface.

A number of international studies have extensively explored the hydrogeochemical characteristics and subsurface flow patterns in geothermal areas. For example, a study by Ngansom et al. examined the geological conditions and hydrogeothermal properties of the Kapong non-volcanic hot spring area in southern Thailand [19]. Another study by Zhou et al. analyzed the geochemistry of 19 hot springs distributed across the Litang Fault Zone (LFZ) during the period from 2010 to 2019 [8]. Meanwhile, Stavropoulou et al. conducted a comprehensive study in the Kyllini region, which included analysis of geological structure, water chemistry, and isotopes to trace the origin and recharge mechanisms of hot mineral water. The results showed that during a one-year hydrological cycle, the groundwater type in Kyllini remained stable (Na–Cl–HCO<sub>3</sub>), with only minor variations [20].

Meanwhile, research in Indonesia, which has enormous geothermal potential, is still limited. A study by Iswahyudi et al. examined the geochemical content of hot springs and local meteorite water scattered in the area between Mount Slamet, Paguyangan, and Cipari District [21]. Another study by Pinning et al. explored the hydrogeochemical and isotopic characteristics of hot springs in Wapsalit, one of the geothermal potential sites in Buru District, Maluku Province [22].

However, in areas such as Tompaso, North Sulawesi, in-depth studies combining water type analysis, water source analysis, and subsurface flow path analysis remain very limited. This situation creates a significant gap in data and scientific knowledge, particularly regarding the understanding of how hot water forms and flows in volcanic geothermal systems like Tompaso. Such research is crucial for the sustainable development of geothermal energy and for enriching scientific mapping of hydrogeothermal systems in

Indonesia as a whole.

To address this lack of information, this study combines a hydrogeochemical approach with spatial analysis to identify the types of hot water, their origins, and the patterns of subsurface water flow in the volcanic region of Tompaso. The novelty of this study lies in the combination of using a trilinear diagram for hot water classification and the conceptual application of a subsurface flow model.

The study area includes rice fields, horticultural land, and several villages scattered within a radius of approximately 20 kilometers from north to south and east to west in the Tompaso region, Minahasa, North Sulawesi. Water samples were collected from various points at varying elevations, ranging from 767 meters above sea level at the Tompaso-10 hot spring (HT-10) to 972 meters at HT-11B, located on the slope of the Soputan volcanic mountain.

The main objective of this study is to uncover the original source of hot springs and groundwater movement patterns in the Tompaso area. Effective management of groundwater quality and quantity, as well as protection of recharge areas (water absorption areas), is very important to ensure that groundwater supplies remain available on a sustainable basis and can be relied upon by the surrounding community. By maintaining and regulating recharge zones and utilizing groundwater wisely, this water resource can be preserved for the needs of both the present and future generations [23,24].

The findings of this research are expected to have a significant impact, not only as an addition to scientific knowledge regarding the characteristics and dynamics of geothermal systems but also as a strong foundation for more effective and sustainable groundwater resource management. With a deeper understanding of hot water types, origins, and subsurface flow patterns, resource managers and policymakers can design appropriate groundwater conservation and utilization strategies, particularly in volcanic areas prone to overexploitation. This contribution is important for maintaining ecosystem balance and ensuring the availability of clean water for current and future generations, while also supporting the development of geothermal energy as a renewable energy source in Indonesia.

## **2. Research methods**

### *2.1. Research Location*

This research was conducted in the Tompaso geothermal area, Minahasa, North Sulawesi, Indonesia, which is an active volcanic area with natural hot springs. Site selection was based on geological distribution, surface geothermal activity, and variations in water temperature and geochemistry. A total of 15 hot springs were strategically selected to represent the spatial distribution of the local hydrogeological system, covering both the central zone of activity and the transition area.

### *2.2. Sample Collection and Preparation*

Water samples were collected during the dry season to minimize the influence of rainfall runoff. All samples were collected in 1000 mL polypropylene bottles that had been washed and rinsed with deionized water and local samples. Filtration was done using 0.45  $\mu\text{m}$  membrane filters in the field. To avoid contamination, QA/QC procedures such as trip blanks and duplicates were applied to 10% of the total samples.

### *2.3. Field Measurements*

Temperature, pH, and electrical conductivity (EC) parameters were measured directly in the field using a multi-parameter portable instrument (Horiba U-52G) that had been calibrated daily with standard solutions. The measurement uncertainty of temperature was  $\pm 0.2^\circ\text{C}$ , pH  $\pm 0.05$ , and EC  $\pm 1\%$ . Sampling locations were mapped using GPS with an accuracy of  $< 5$  meters.

### *2.4. Laboratory Analysis*

Concentrations of major anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ) and cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) were determined by ion chromatography using a Dionex ICS-5000. Operational parameters were in accordance with EPA Method 300.0 procedures. The minimum limit of detection (LOD) for anions and cations ranged from 0.01-0.1 mg/L, with analytical uncertainty  $< 5\%$ .

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Bicarbonate ( $\text{HCO}_3^-$ ) concentration was determined by acid-base titration using methyl orange indicator (APHA 2320 B). Replication was done three times to ensure consistency. Silica ( $\text{SiO}_2$ ) and total iron (Fe) concentrations were analyzed using UV-Vis spectrophotometry (Hitachi U-1800), respectively by the yellow molybdate (silica) and 1,10-phenanthroline (iron) methods according to SNI 6989.75:2009. Analytical uncertainty for spectrophotometry was determined from the standard deviation of replicates ( $n = 3$ ), and was below 3%.

### 2.5. Validation and Data Quality

Validation of the results was carried out by calculating the ion balance (IB) using the following formula:

$$IB(\%) = \frac{\sum \text{Cations}(\text{meq./L}) - \sum \text{Anions}(\text{meq./L})}{\sum \text{Cations}(\text{meq./L}) + \sum \text{Anions}(\text{meq./L})} \times 100$$

Data with  $\pm 5\%$  ion balance values were considered analytically valid. Results beyond this threshold were rechecked or eliminated.

### 2.6. Water Type Classification

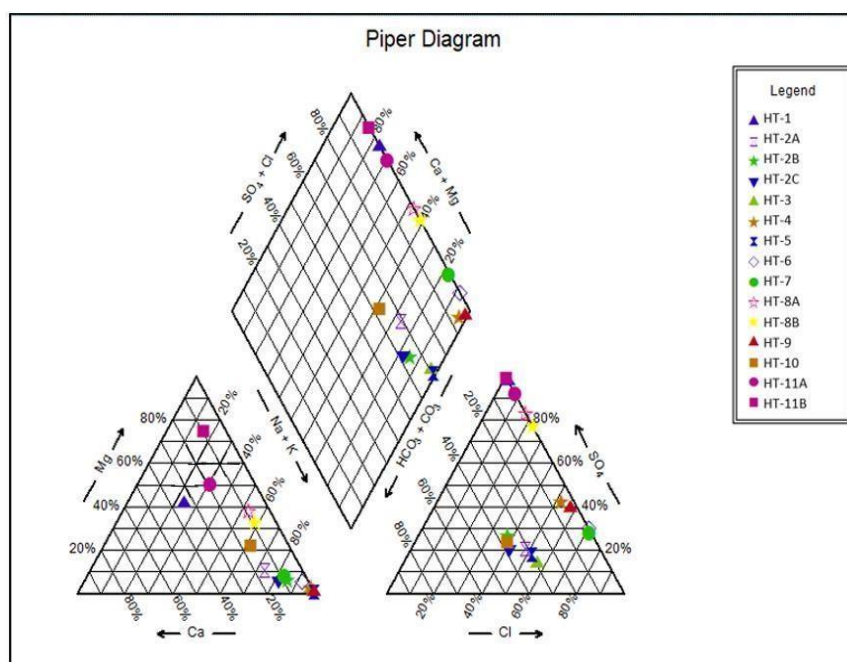
Water types are classified using Piper diagrams, which consist of two ternary triangles for cations and anions, and a center diamond plane for data integration. The proportions of cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+ + \text{K}^+$ , and anions  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  are plotted in milliekivalents per liter (meq/L). This ternary plot is then projected onto a diamond-shaped plane. The diamond is obtained through a matrix transformation that integrates the anion ratio (sulfate + chloride/total anions) and the cation ratio (sodium + potassium/total cations). This combined representation facilitates the interpretation of water chemistry and its classification.

### 2.7. Statistical Analysis

Descriptive statistical analysis was used to look at the distribution of geochemical data. In addition, correlations between key parameters were performed to identify the relationship between chemical components and the mechanism of hot water formation. Spatial mapping of parameters was performed using kriging interpolation to understand the geostatistical distribution patterns.

## 3. Result and discussion

The results of the chemical analysis of hot water conducted in this study show that almost all samples have an Ion Balance (IB) value below the threshold of 12.5%, except for acidic samples. To further understand the chemical characteristics of the water, the analysis data was then plotted on a Piper diagram, which is an important tool for classifying water types based on their main ion composition. The results of this mapping revealed the diversity of hot water types in the Tompaso region, reflecting different geochemical processes and water sources.



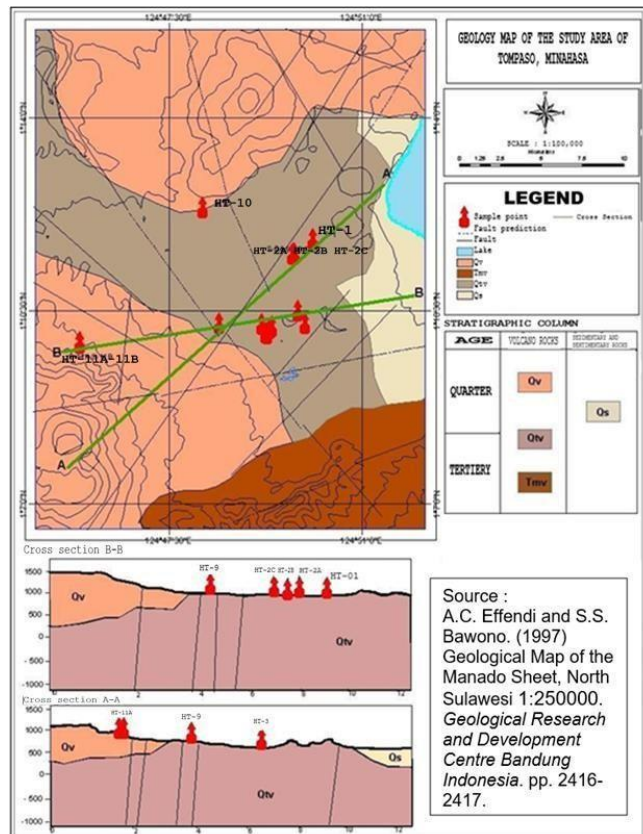
**Figure 1.** The water type of fifteen samples by diagram piper

The results of plotting the samples on the Piper diagram provide insights into the chemical properties and classifications of the water types. The details of these findings are outlined below.

**Table 1.** Classification of Hot Spring Types in the Tompaso Region

| Sample Code         | Water Type         | Origin/Source                                                                               |
|---------------------|--------------------|---------------------------------------------------------------------------------------------|
| HT-1                | Mg-SO <sub>4</sub> | Interaction of geothermal water with magnesium-rich rocks through mixing with surface water |
| HT-2A, HT-2B, HT-2C | Na-Cl              | Hot springs from geothermal sources                                                         |
| HT-3                | Na-Cl              | Hot springs from geothermal sources                                                         |
| HT-4                | Na-Cl              | Hot springs from geothermal sources                                                         |
| HT-5                | Na-Cl              | Hot springs from geothermal sources                                                         |
| HT-6                | Na-Cl              | Hot springs from geothermal sources                                                         |
| HT-7                | Na-Cl              | Hot springs from geothermal sources                                                         |
| HT-9                | Na-Cl              | Hot springs from geothermal sources                                                         |
| HT-10               | Na-Cl              | Hot springs from geothermal sources                                                         |
| HT-8A, HT-8B        | Na-SO <sub>4</sub> | Geothermal water containing sodium and sulfate                                              |
| HT-11A, HT-11B      | H-SO <sub>4</sub>  | Heated water; surface water that is heated, rises, and mixes back with other surface water  |

One sample, HT-1, was identified as SO<sub>4</sub>-type water formed through the interaction of hot water with magnesium-containing rocks, producing Mg-SO<sub>4</sub>-type water. This process indicates the mixing of geothermal water and surface water. Most of the other samples, such as HT-2A to HT-10, are classified as Na-Cl type, which is a common characteristic of hot springs from geothermal systems dominated by sodium and chloride. Meanwhile, samples HT-8A and HT-8B are classified as Na-SO<sub>4</sub> type, indicating the influence of sulfate ions from geothermal processes. On the other hand, samples HT-11A and HT-11B are categorized as H-SO<sub>4</sub> type, which is water heated by geothermal steam, typically originating from surface water that has been heated and mixed again with shallow groundwater.



**Figure 2.** Hydrogeology system of Tompaso region

In terms of hydrogeological flow patterns, cross section A-A illustrates that groundwater receives recharge from the recharge zone upstream, then seeps through permeable layers. After being heated by the geothermal system, the water emerges to the surface as hot springs. Samples included in this cross-section, such as HT-1 and HT-2, are mostly Na-Cl type water, except for HT-1, which exhibits Mg-SO<sub>4</sub> characteristics. The location of this hot spring emergence has been identified in the villages of Tolok and Kamanga.

Section B-B shows a similar flow pattern, where groundwater from the recharge zone seeps through permeable rock layers toward the geothermal reservoir, then rises to the surface after being heated. Samples from this section include HT-3, HT-9, HT-11A, and HT-11B, which originate from the villages of Kanonang, Kamanga, and Toraget. The hot water in this area exhibits variations in water type, including H-SO<sub>4</sub> and Na-Cl types, reflecting the complexity of mixing and heating processes beneath the surface.

The change in water type from Na-Cl to Na-SO<sub>4</sub> and H-SO<sub>4</sub> indicates geochemical evolution influenced by heating mechanisms, rock-water reactions, and the effects of evaporation and shallow water mixing. The dominant Na-Cl type generally reflects meteoric water that has been in the reservoir for a long time and has undergone mineralization through ionic interaction with andesitic rocks. Conversely, the H-SO<sub>4</sub> type tends to form from steam rising through fracture zones, which then condenses and reacts with surface water in

shallow zones. This process produces more acidic water, as observed in HT-11A and HT-11B. The presence of acidic water reflects intense thermal conditions and active volcanic activity, which must be taken into account in terms of corrosion of infrastructure or local environmental pollution.

Thus, the hydrogeological system in the Tompaso area can be classified into three main flow patterns based on infiltration pathways and interaction with geothermal heat. First, meteoric water seeps into the surface through soil pores until it reaches an impermeable layer, then accumulates in shallow aquifers. During its journey, this water is heated by geothermal heat sources and then rises to the surface as hot springs in lower-lying areas. Second, meteoric water enters through permeable layers and descends deeper into underground aquifers, where heating processes cause steam to form. This steam then rises, mixes with surface water, and emerges as a manifestation of geothermal heat. Third, rainwater that seeps downward through soil pores continues its journey along fault lines until it reaches geothermal reservoirs. From there, hot water migrates back to the surface through fault lines and permeable layers, then emerges as hot springs. These three mechanisms reflect the complexity of interactions between water, rocks, geological structures, and geothermal energy in the Tompaso region.

The results of this study are consistent with the research by [8] in the Litang Fault Zone, where hot water patterns are controlled by fractures and water types vary due to chemical evolution within the geothermal system. The study by [20] in Kyllini shows that the stability of water composition within a single hydrological cycle can also occur, as seen in some samples from Tompaso. However, unlike non-volcanic areas such as Kapong in Thailand [19], Tompaso exhibits more complex geothermal activity due to contributions from volcanic heat, fault structures, and varying lithology.

The identification that most of the hot water in Tompaso comes from an active geothermal system indicates great potential for development as a geothermal energy source [25,26]. Na-Cl and Na-SO<sub>4</sub> water types are commonly found in reservoirs suitable for geothermal power plants (GPPs), provided that chemical parameters such as pH, silica, and scaling potential are controlled. Additionally, by understanding recharge zones and flow paths, conservation strategies can be designed to protect recharge areas from land degradation or contamination [27,28]. This management is crucial for maintaining the sustainability of groundwater resources [29,30], given the high dependence of communities on springs in mountainous regions like Tompaso.

#### **4. Conclusions**

This study successfully identified four main types of hot water in the Tompaso area namely Mg-SO<sub>4</sub>, H-SO<sub>4</sub>, Na-Cl, and Na-SO<sub>4</sub> that reflect the diversity of hydrogeochemical systems and subsurface heating mechanisms, and revealed three subsurface flow models involving the interaction of meteoritic water, aquifers, fault lines, and geothermal reservoirs. The scientific contribution of this research lies in the mapping of complex hydrogeochemical processes in active volcanic zones and the application of an integrated approach in the classification and analysis of geothermal groundwater flow. The practical implication of this research is to provide a scientific basis for geothermal energy exploration and sustainable conservation of groundwater resources. However, the limitations in spatial coverage and depth of observation due to the absence of geophysical or isotopic data are a challenge, so further research is needed with a multidisciplinary approach, such as the integration of geological, geophysical and stable isotope data, as well as three-dimensional hydrothermal modeling and long-term monitoring to strengthen the understanding of the Tompaso geothermal system and support adaptive management of geothermal potential.

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