Hydrogeochemistry of the Thermal Springs of Pojqpoquella and Phutina, Puno, Peru

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Abstract. This paper deals with the results of a hydrogeochemical study of two thermal springs that originate from in very high altitudes in southwestern Peru with outflow temperatures of maximal 38.4 °C and flow rates of 1.08 - 2.02 l/s. Water samples from the Pojqpoquella and Phutina geothermal wells, were collected during the period between September 2018 and January 2019 in the main area of Puno. Chemical types of the thermal spring are Na+, Ca2+, Cl– and CO3²⁻ in Ayaviri and Putina. According to the Piper and Schoeller diagrams for the Pojqpoquella thermal spring water is classified as Na+ K+ (75 %) and Cl– (60 %) type water while that of the Phutina thermal spring is classified as Na+ K+ (76 %) and Cl– (72 %) type water. The electrical conductivity (EC) values for the Pojqpoquella and Phutina thermal spring waters is 2160 - 3142 µS/cm and 3160 - 3184 µS/cm, respectively, the thermal spring waters have a high electrical conductivity which shows that it has interacted with the host rock for a long time. The reservoir rocks of the Pojqpoquella thermal system consist of a red sandstones and conglomerate rocks while the reservoir rocks of the Phutina thermal system consist of a thick sequence of cretaceous rocks.

1. Introduction
The purpose of this study is to examine the hydrogeochemistry of groundwater from the Pojqpoquella and Phutina hot springs in Puno, Peru. The Pojqpoquella bath is a hot water spring with a temperature of 36.5 °C and a flow rate of 2.02 l/s, at an altitude of 3907 meters above sea level, and the Phutina bath is similar with a temperature of 38.3 °C and a flow rate of 1.08 l/s, with an altitude of 3878 meters above sea level. These thermal springs have been used for bathing by the local population for a very long time [1]. The reservoir rock of the Pojqpoquella thermal system consists of red sandstones and conglomerate rocks while the reservoir rocks of the a Phutina thermal system consist of thick sequence of cretaceous rocks.

The thermal springs are a part of the geothermal energy manifestations that are observed in all continents [2]–[4]. The exploration for thermal water resources with medical applications has increased since the nineteenth century [5]–[7], however, biological research in thermal water began in the 1950's
The microbial community present on the thermal water consists of bacteria and archaea of a thermophilic and hyperthermophilic nature [9], [10]. Thermal springs have particular characteristics that depend on the composition of the internal and superficial rocks and the chemical reactions that can occur [11]. Therefore, the thermal water contains chemical constituents such as: Ca, Na, Mg, Cl, SiO$_2^4^-$ and SiO$_4^4^-$, which are generally present in geothermal water with medical applications [12], [13]. In addition, the thermal spring waters also contain Rn$^{222}$ and Ra$^{226}$ in concentrations of 0.48 - 1.54 Bq/L [14].

Thermal springs around the world have been properly studied and identified, such as in Chongqing, southeast China. The carbonate aquifers of these thermal springs predominate the chemical type of water as Ca-Mg-SO$_4$ and Ca-SO$_4$, high concentrations of Ca$^{2+}$ and SO$_4^{2-}$ are generated from the dissolution of carbonate rocks [15]. In Tehran, the Changal thermal spring water is Na, Cl and Ca-SO$_4$ type water, issuing from the limestone and carbonate rocks of Asmari [16], [17]. The high concentration of Na, Ca and Mg in the thermal spring is produced by the water-rock interaction and the cations exchange in the carbonate rocks [13], [17]. The hydrogeochemistry of the Birdsville thermal waters located in northeastern Australia, is that of a Na-HCO$_3$-Cl type water (Pirlo, 2004). The thermal waters of Pamukkale in Turkey, can be divided into two groups: group 1A: Ca-HCO$_3$ and group 1B: Ca-SO$_4$, the concentrations of these components are due to the water- basal metamorphic rocks interaction [18].

The positive effect on physical and mental health from the use thermal spring has been confirmed as the relief of the physical pain [19], [20], also relaxing and sedative effects [10], [21] and the relief of rheumatoid arthritis [22].

In this study, we focus on hydrogeochemistry characterization of two thermal springs located in the Ayaviri and Putina district of Puno, Peru. The thermal spring water contains trace elements such as Li, Rb, Cs and Sr, which predominantly originate sandstone, conglomerate and volcanic rocks [1].

**Figure 1.** Pojpoquella and Phutina thermal water springs map of Puno, Peru.
2. Methodology

The "Pojqpoquella" thermal spring is located northeast of the Ayaviri district of the Melgar province in Puno, Peru, with the geographic coordinates: -14.886505 N, -70.579934 E, an average altitude of 3907 meters above sea level (masl), a relative humidity of 78 %. The "Pojqpoquella" thermal spring applied for curing rheumatism, arthritis, and infections like other thermal springs (Rodriguez, 1996), also applications to recreational use [3].

The stratigraphic and structural setting of the Pojqpoquella thermal spring is formed by red sandstones and conglomerate rocks [23]. Six samples were collected from the pool and the swimming pool (Figure 2).

![Figure 2. Pool and swimming pool sampling points from Pojqpoquella, Ayaviri, Peru.](image)

The "Phutina" thermal spring is located east of the Putina district of the “San Antonio de Putina” province in Puno department, Peru, with the geographic coordinates: -14.912995 N, -69.866926 E, an average altitude of 3878 meters above sea level (masl), a relative humidity of 79%. The thermal spring of "Phutina" is a geothermal reservoir with medical applications to which is attributed the cure of rheumatism and arthritis, also applications to recreational use, like many others (Quintana, 2011; Rodriguez, 1996). The stratigraphic and structural setting of the “Phutina” thermal spring is formed by a thick sequence of cretaceous sinters [23]. Six samples were collected from the pool and the swimming pool (Figure 3).

![Figure 3. Pool and swimming pool sampling points from Pojqpoquella, Ayaviri, Peru.](image)

Six samples from the "Pojqpoquella" thermal spring, Ayaviri, Peru (Figure 2) and six samples from the "Phutina" thermal spring, San Antonio de Putina, Peru (Figure 3) the samples were collected in polyethylene bottles during the period between September 2018 and January 2019 in the main area of Puno. The determination of the concentrations of Ca^{2+}, Mg^{2+}, and SO_{4}^{2-} was using the EDTA titration method. The determination of K and Na concentrations was by flame atomic absorption
spectrophotometry with an accuracy of 0.1 mg/L in the Quality Control Laboratory of the Faculty of Chemical Engineering of the National University of Altiplano Puno and Analytical Laboratories of South, calibrated by OSHAS 18000, SA 8000, ISO 14000 and ISO / IEC 17025 by the National Quality Institute-INACAL. And were determined by ICP-OES (Inductively coupled plasma - optical emission spectrometry).

Piper [25] plots of the major cation and anion concentrations (Figure 4 and 5) were used to map the hydrogeochemical facies of the Pojqpoquella and Phutina thermal spring samples. Schoeller [26] semi-logarithmic plots were used to represent major ion analysis in milliequivalents per liter (Figure 6 and 7) and to demonstrate different hydrochemical spring types [27]. SPSS software was used to find the Pearson correlation. Possible correlations between various physical and chemical parameters were examined by Pearson's r correlation analysis.

3. Results and discussions
The physical and chemical indices for the six samples: A1, A2, A3, B1, B2 y B3 (Fig. 2), from the “Pojqpoquella” thermal waters, located in Ayaviri district, Peru, are presented in Table 1, for the two study areas. The main cations and anions present in the Pojqpoquella thermal spring waters are: (K+, Mg++, Ca++, Na+) and (HCO₃⁻, CO₃²⁻, SO₄²⁻, Cl⁻) respectively, in the study areas (Table 1), the main concentrations of the cations are the Na⁺ and Ca²⁺ are 1875.92 - 1949.42 mg/L and 404.51 - 416.98 mg/L respectively and the main anions present in the Pojqpoquella water samples are: Cl⁻ and CO₃²⁻ with minimum and maximum values 3436.53 - 3798.82 mg/L and 1132,82 - 1143.92 mg/L respectively, The pH ranges from 6.76 to 7.25 indicating a weak alkalinity [10]. The high concentration of ions SO₄²⁻ and Ca²⁺ ions it is characteristic of thermal waters generally brackish [12], [15], [23], [28].

| Sample | T     | CE (µS/cm) | pH   | HCO₃⁻ | CO₃²⁻ | SO₄²⁻ | Cl⁻ | Na⁺ | Ca²⁺ | Mg²⁺ | K⁺ | % salinity |
|--------|-------|------------|------|-------|-------|-------|-----|-----|------|------|----|------------|
| A1     | 36.4  | 2160.00    | 7.21 | 925.52| 1144.29| 865.00| 3798.82| 1945.31| 404.64| 97.44| 73.45| 1.96       |
| A2     | 36.7  | 2162.00    | 7.22 | 921.23| 1143.92| 864.08| 3791.59| 1949.42| 405.10| 97.31| 73.49| 1.96       |
| A3     | 36.3  | 2161.00    | 7.25 | 932.20| 1143.90| 865.07| 3796.00| 1947.12| 404.51| 97.50| 73.48| 1.96       |
| B1     | 33.8  | 3140.00    | 6.77 | 946.68| 1132.95| 905.00| 3438.93| 1875.92| 416.00| 92.53| 72.48| 1.98       |
| B2     | 32.5  | 3141.00    | 6.78 | 952.20| 1133.45| 904.54| 3436.53| 1879.96| 416.84| 92.61| 72.34| 1.98       |
| B3     | 32.4  | 3142.00    | 6.6  | 949.40| 1132.82| 906.79| 3439.65| 1881.98| 416.98| 92.57| 72.33| 1.98       |

| Sample | T     | CE (µS/cm) | pH   | HCO₃⁻ | CO₃²⁻ | SO₄²⁻ | Cl⁻ | Na⁺ | Ca²⁺ | Mg²⁺ | K⁺ | % salinity |
|--------|-------|------------|------|-------|-------|-------|-----|-----|------|------|----|------------|
| C1     | 38.4  | 3160.00    | 6.88 | 256.20| 232.64| 792.00| 2499.00| 1158.56| 257.76| 47.81| 53.93| 3.10       |
| C2     | 38.3  | 3161.00    | 6.89 | 222.91| 231.80| 791.92| 2498.49| 1152.58| 258.39| 48.41| 53.92| 3.12       |
| C3     | 38.2  | 3162.00    | 6.01 | 223.00| 232.70| 792.13| 2491.28| 1162.57| 275.25| 47.93| 53.94| 3.14       |
| D1     | 37.2  | 3180.00    | 7.02 | 245.10| 241.25| 752.00| 2519.22| 1215.67| 277.92| 41.57| 50.98| 3.40       |
| D2     | 37.1  | 3184.00    | 7.01 | 245.20| 242.01| 751.54| 2520.08| 1223.71| 278.15| 42.11| 51.29| 3.41       |
| D3     | 37.3  | 3182.00    | 7.02 | 245.10| 241.20| 752.18| 2519.12| 1218.68| 277.81| 41.83| 51.19| 3.42       |
The physical and chemical parameters of the six samples: C1, C2, C3, D1, D2 and D3 (Figure 3), from the “Phutina” thermal spring, located in Putina district, Peru, are presented in Table 2. The main cations and anions are: $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Na^+$ and $HCO_3^-$, $CO_3^{2-}$, $SO_4^{2-}$, $Cl^-$ respectively, (Table 2). The main concentrations of the cations are the $Na^+$ and $Ca^{2+}$ are 1152.58 - 1223.71 mg/L and 257.76 - 278.15 mg/L respectively and the main anions present in the “Phutina” spring samples are: $Cl^-$ and $SO_4^{2-}$ with minimum and maximum values 2491.28 - 2520.08 mg/L and 751.54 - 792.13 mg/L respectively. The pH ranges from 6.01 to 7.02 indicating a weak acidic. The high concentration of $SO_4^{2-}$ and $Ca^{2+}$ ions, it is characteristic of thermal waters that are generally brackish (Benitez et al, 2015; Yang et al., 2017)

The Piper, [25] diagrams were used to show the hydrogeochemical facies of the main cations and anions of the thermal springs. The six samples from the “Pojqpoquella” thermal spring are of the Na-K-Cl type, the cation concentration average percentages are 18% of $Ca^{2+}$, 7% of $Mg^{2+}$ and 75% of $Na^+$. and the anion concentration average percentages are 10.0% of $SO_4^-$, 60.0% of $Cl^-$ and 30.0% of $HCO_3^-$. (Figure 4). The six samples of “Phutina” thermal spring are of the Na, K-Cl type, the cations concentration percentages are 19.0% of $Ca^{2+}$, 5.0% of $Mg^{2+}$ and 76.0% of $Na^+$ and $K^+$ and the anions concentration percentages are 15.0% of $SO_4^-$, 72.0% of $Cl^-$ and 13.0% of $HCO_3^-$. (Figure 5). Bicarbonate-rich waters originate through the dissociation of $H_2CO_3$ which converts feldspars to clays. This natural aqueous solution is typically rich in sodium and bicarbonate [29].

![Figure 4. Piper plot for the Pojqpoquella thermal spring samples, All the samples are of the Na$^+$+K$^+$ type.](image)
Figure 5. Piper plot for the Phutina thermal spring samples. All the samples are of the Na, K–Cl type.

The thermal spring waters have an initial composition caused by physical-chemical interaction between water and rocks [15], [30], [31]. The high SO₄²⁻ concentration is associated with carbonate aquifers [31]–[33] the main ions of the Pojqpoquella and Phutina thermal spring waters are SO₄²⁻ and Ca²+. The SO₄²⁻ concentrations are associated with thermal spring waters of volcanic origin, whose formation is given by: H₂S + 2O₂ + 2CaCO₃ = 2Ca²⁺ + SO₄²⁻ + 2HCO₃⁻ [34].

In the Pojqpoquella thermal spring the correlation coefficient of the SO₄²⁻ concentration and Ca²⁺ concentration is 0.98, SO₄²⁻ and Ca²⁺ are generated from the dissolution of evaporates such as gypsum and anhydrite while in the Phutina thermal spring water the correlation coefficient between SO₄²⁻ and Ca²⁺ is -0.78 this means SO₄²⁻ and Ca²⁺ ions, are not derived from the dissolution of evaporites such as gypsum and anhydrite [15], [30]. In the Pojqpoquella thermal spring the positive correlation coefficient between Na⁺ and Cl⁻ concentrations is 0.98 while in the Phutina thermal spring the correlation coefficient between Na⁺ and Cl⁻ concentrations is 0.96 which involves the salt dissolution from the rocks [16], [23], [35].

The concentration of Mg²⁺ in the Pojqpoquella and Phutina thermal spring waters are similar to that of Obuki Spring, [36] and Kärstica thermal waters in Chongqing (Yang et al., 2013). In the Pojqpoquella thermal spring water the correlation coefficient of the Mg²⁺ concentrations and HCO₃⁻ concentrations is -0.94 while in the Phutina thermal spring the correlation coefficient between Mg²⁺ and HCO₃⁻ concentrations is -0.48 which implies that the Mg²⁺ concentration is not derived from dolomite, this suggests that Mg²⁺ concentration is derived from rocks that contain magnesium sulfate [31]. The low concentration of the anion HCO₃⁻, in the Pojqpoquella thermal spring water (Table 1), suggests that the production of Ca²⁺ are derived through the dissolution of gypsum and anhydrite [31], [38].

The Pojqpoquella and Phutina thermal springs plot in one group in the Schoeller [26] diagrams (Figure 6 and Figure 7): the thermal spring water involve important concentration of Na, Cl and CO₃ (meq/L) it is characteristic of thermal water that is generally brackish [1], [39].
Figure 6. Major element concentration plots (Schoeller Plots) for Pojqpoquella thermal spring waters from six samples, located in Ayaviri, Peru.

Figure 7. Major element concentration plots (Schoeller Plots) for Phutina thermal waters from six samples, located in San Antonio de Putina, Peru.

In the Piper and Schoeller diagrams, it is seen that Pojqpoquella and Phutina thermal spring waters are enriched with Na, Cl and CO$_3^{2-}$ (Figure 4 - 7), and the electrical conductivity (EC) values for the Pojqpoquella thermal spring waters are 2160 - 3142 $\mu$S/cm (Table 1) and the values for the Phutina thermal spring waters are 3160 - 3184 $\mu$S/cm (Table 2). The thermal waters have a high electrical conductivity which showing that they have interacted with the host rock for a long time [40]–[42]. In other words, the production of thermal waters can lead to excellent groundwater quality for domestic purposes.
4. Conclusions
The Pojqpoquella and Phutina thermal springs in Puno in southwestern Peru, are formed in red sandstone and conglomerates and thick sequence of Cretaceous sinter [23]. The main ions are Na\(^+\), Ca\(^{2+}\), Cl\(^–\) and CO\(_3^{2–}\) in Ayaviri and San Antonio de Putina districts in Puno, Peru. According to Piper [25] and Schoeller [26] diagrams the chemical types of the Pojqpoquella thermal spring samples are Na\(^+\)+ K (75.0%) and Cl\(^–\) (60.0%) and the Phutina thermal spring samples are Na\(^+\)+ K (76.0%) and Cl\(^–\) (72.0%) these are characteristic of thermal waters that are generally brackish. The electrical conductivity (EC) values for the Pojqpoquella and Phutina thermal spring waters that are 2160–3142 µS/cm and 3160–3184 µS/cm respectively, the thermal waters have a high electrical conductivity which shows that it has interacted with the host rock for a long time [30].

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