Hydrogeochemical analysis of volcanic and geothermal fluids in the Andes from Ecuador using hydrochemical plots (Stiff, Piper and Schoeller-Berkaloff diagrams)

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Abstract. The formation of several sources of hot springs in the Andes from Ecuador was the result of intense volcanic activity due to the subduction of the Nazca oceanic plate under the South American continental plate. The aims of this study include the presentation of chemical analysis in graphical form in order to describe the hydrogeochemistry water geothermal origins, their chemical classification and their relationship to the complex geology of Ecuador using different hydro chemical plots such as Stiff’s polygonal diagram, Piper’s trilinear diagram and Schoeller-Berkaloff’s logarithmic vertical columns diagram. Geothermal waters can be divided into two groups. The first group was associated with an extinct volcanic activity produced in the Cenozoic and were qualified based on the type of water Na+-Cl-, while the second group was associated with young Quaternary volcanic activity, and the types of water were Mg²⁺-HCO₃⁻, Na⁺-HCO₃⁻, Na⁺-SO₄²⁻,Mg²⁺-SO₄²⁻.

1. Introduction
Ecuador has various sources of geothermal water as a result of the strong magmatic activity produced in the Quaternary by the subduction of the Nazca oceanic plate under the South American continental plate [1]. These sources are located in the volcanic arc in Ecuador. The aims of this study include the presentation of chemical analysis in graphical form in order to describe the hydro geochemistry from hot springs used in spas located in the Andes of Ecuador, including their behavior and their predominant ions, their chemical classifications and their relationship to the complex geology of Ecuador according to different hydrochemical diagrams such Stiff’s polygonal diagram, Piper’s trilinear diagram and Schoeller-Berkaloff’s logarithmic vertical columns diagram.
2. Materials and methods
The samplings were taken from 34 locations along the Andes in Ecuador. The distance between sampling sites was approximately 3215 kilometers. The sampling points are shown in figure 1.

2.1. Determination of physico-chemical parameters
Any physico-chemical parameters were measured for all water samples. The first parameter was water temperature as measured in-situ by a mercury thermometer. Sample pH values were analyzed at the laboratory of the Universidad de las Fuerzas Armadas ESPE with a pH meter, Thermo Scientific Orion 3-Star model, and the electrical conductivity (EC) was measured with a conductivity meter, model HACH HQ14d. Finally, Total Dissolved Solids (TDS) and Waste Dry Calcined (WDC) were measured with APHA support [2]. Anions and cations of the first 24 samples were sent Havoc laboratory in Ecuador, accredited by the Accreditation Service Ecuadorian. The concentrations of Ca$^{2+}$ and Mg$^{2+}$ were obtained by colorimeter methods, the concentrations of Na$^+$ and K$^+$ were measured with an Ion Meter inoLab® pH / ION 7320, Cl$^-$ content was determined by colorimetry according to NTE INEN 0976 [3], HCO$_3^-$ was measured according to the volumetric method and SO$_4^{2-}$, NO$_3^-$ and PO$_4^{3-}$ content were determined spectrophotometrically according to EPA guidelines [4].

Determination of the error rate in the variables was measured in the laboratory.

After obtaining the results of the analysis, a control is necessary to check any result discrepancies according to the APHA [2] equation 1.

$$\% \text{ Mistake} = \left(\frac{\sum \text{meq L cation} - \sum \text{meq L anion}}{\sum \text{meq L cation} + \sum \text{meq L anion}}\right) \times 100$$

(1)

Table 1 shows the percentages of anions and cations admissible for each range.
Table 1. Percentage of allowable difference in analytical results.

| Sum of cations (meq/L) | % Acceptable difference |
|------------------------|-------------------------|
| 0.0 – 3.0              | ± 0.2 %                 |
| 3.0 – 10.0             | ± 2 %                   |
| 10 – 800               | ± 2.5 %                 |

Source:[2]

It is necessary to check the results with the information the Table 1 to review the accuracy of parameters.

2.2. Development of hydrochemical diagrams

The hydrochemical diagrams were developed with Diagrammes software versión 6.5, developed by the laboratory of hydrogeology at the Université d’Avignon.

2.3. Mapping

The maps were produced using Arc GIS software with shape files obtained by the Instituto Geográfico Militar of Ecuador (IGM) and geological mapping accomplished by the Instituto Nacional de Investigación Geológico Minero Metalúrgico in Ecuador (INIGEMM). The maps were added to the polygonal Stiff diagrams to analyze the variation between the cations and anions of the samples and the spatial arrangement of the hydrogeochemical families.

3. Results and discussions

To achieve better analysis and interpretation, the hydrogeochemical data was divided into three zones: the northern zone (Carchi, Imbabura and Pichincha), central zone (Cotopaxi, Napo, Tungurahua and Chimborazo) and the southern zone (Cañar, Azuay and El Oro).

In the northern zone, the greatest numbers of samples (20) were obtained due to the presence of volcanoes with their bases in the Cordillera Occidental and the Andes Valley. The recorded temperature values ranged from 18 to 60 °C, with pH values between 4.96 to 7.65 and electrical conductivity values ranging from 166 to 6795 μS / cm. Relative pH values <6 (Lloa and Aguas Hediondas) indicated a possible interaction with acidic gases [5]. Table 2 shows the parameters measured in Ecuador.
Table 2. Temperature, pH, EC, WDC, cation and anion in water samples in the Andes of Ecuador.

| No. | Location                          | T°C  | pH  | EC (dS/m) | TDS (ppm) | WDC (ppm) | CATION (mg/l) | ANION (mg/l) |
|-----|-----------------------------------|------|-----|-----------|-----------|-----------|---------------|--------------|
|     |                                    |      |     |           |           |           | K⁺ Na⁺ Ca⁺² Mg⁺² | SO₄⁻² Cl⁻ HCO₃⁻ CO₃⁻² |
| 1   | Guachalá                          | 39.6 | 6.4 | 2.6       | 1424.0    | 260.0     | 43.5          | 335.4        |
| 2   | Oyacachi                          | 50.6 | 6.6 | 5.5       | 3184.0    | 2056.0    | 32.1          | 389.3        |
| 3   | Cunayacu                         | 26.7 | 7.0 | 1.2       | 660.0     | 172.0     | 12.2          | 105.2        |
| 4   | El Tingo                          | 40.7 | 7.0 | 3.5       | 3848.0    | 972.0     | 22.7          | 445.0        |
| 5   | La Merced                         | 35.6 | 6.5 | 1.2       | 1912.0    | 172.0     | 11.0          | 103.1        |
| 6   | Lloa                              | 29.0 | 6.9 | 3.9       | 1076.0    | 152.0     | 10.8          | 200.0        |
| 7   | Guapán                            | 60.7 | 7.1 | 20.2      | 11308.0   | 10124.0   | 91.3          | 4462.0       |
| 8   | Agua Caliente - Portovelo         | 52.1 | 8.1 | 3.4       | 4012.0    | 1840.0    | 34.0          | 459.5        |
| 9   | Baños de Cuenca                   | 62.7 | 7.2 | 4.6       | 4512.0    | 2028.0    | 54.3          | 637.5        |
| 10  | Los Eléntres                      | 21.6 | 6.9 | 2.3       | 1576.0    | 952.0     | 7.0           | 158.8        |
| 11  | Cununyacu (Tungurahua)            | 47.5 | 8.3 | 5.1       | 3408.0    | 1816.0    | 4.7           | 690.0        |
| 12  | La Virgen (Baños)                 | 53.6 | 6.5 | 5.9       | 660.0     | 172.0     | 12.2          | 105.2        |
| 13  | El Salado VT (Baños)              | 40.6 | 7.2 | 7.2       | 3184.0    | 2056.0    | 32.1          | 389.3        |
| 14  | El Salado Pucima (Baños)          | 45.6 | 9.0 | 7.9       | 7932.0    | 5476.0    | 47.2          | 481.9        |
| 15  | Guapán                            | 52.1 | 8.2 | 1.2       | 1088.0    | 540.0     | 10.1          | 84.0         |
| 16  | Nachehe                          | 27.8 | 7.6 | 4.0       | 2616.0    | 1480.0    | 38.4          | 338.0        |
| 17  | Abacán                            | 43.0 | 7.0 | 1.5       | 1088.0    | 540.0     | 10.1          | 84.0         |
| 18  | Jumanco                           | 61.7 | 6.7 | 7.7       | 4772.0    | 4060.0    | 56.0          | 256.0        |
| 19  | Santa Catalina (Papallacta)       | 56.7 | 7.1 | 2.1       | 1376.0    | 980.0     | 5.7           | 235.3        |
| 20  | Nangulvi                          | 50.7 | 7.4 | 4.9       | 3016.0    | 1840.0    | 34.0          | 459.5        |
| 21  | Lagartijas                        | 18.6 | 6.1 | 0.5       | 284.0     | 116.0     | 4.5           | 22.0         |
| 22  | Peguche (Piscina Incaica)         | 23.6 | 6.5 | 1.9       | 1132.0    | 512.0     | 13.0          | 67.4         |
| 23  | Peguche (Vertiente Sagradillo)    | 23.6 | 6.6 | 2.2       | 1332.0    | 900.0     | 23.3          | 165.0        |
| 24  | Chachimbro 1                      | 52.6 | 7.6 | 6.6       | 4128.0    | 3528.0    | 210.7         | 968.2        |
| 25  | Chachimbro 2                      | 60.6 | 6.4 | 6.8       | 4076.0    | 3432.0    | 182.3         | 964.0        |
| 26  | La Calera                         | 34.3 | 6.3 | 1.3       | 852.0     | 552.0     | 29.1          | 73.4         |
| 27  | Guata de la Paz                   | 40.0 | 6.9 | 2.6       | 1748.0    | 1232.0    | 74.6          | 156.1        |
| 28  | Pukar                            | 21.6 | 6.2 | 3.1       | 764.0     | 508.0     | 4.7           | 32.9         |
| 29  | Ruminchaca                       | 34.3 | 7.1 | 3.1       | 2023.0    | 1444.0    | 96.3          | 267.5        |
| 30  | Los 3 Chorros (Neptuno)           | 25.0 | 6.0 | 0.8       | 588.0     | 456.0     | 27.4          | 57.3         |
| 31  | Complejo Turístico Tufiño          | 25.6 | 6.6 | 0.9       | 640.0     | 484.0     | 24.4          | 69.6         |
| 32  | Aguas Hediondas                   | 58.0 | 5.0 | 1.8       | 1572.0    | 1288.0    | 56.6          | 149.5        |
| 33  | Sin Miguel de Car                 | 23.6 | 6.2 | 0.4       | 764.0     | 240.0     | 10.0          | 26.5         |
| 34  | El Puetate                        | 18.5 | 6.7 | 0.2       | 208.0     | 128.0     | 1.3           | 7.1          |

| No. | Location                          | T°C  | pH  | EC (dS/m) | TDS (ppm) | WDC (ppm) | CATION (mg/l) | ANION (mg/l) |
|-----|-----------------------------------|------|-----|-----------|-----------|-----------|---------------|--------------|
|     |                                    |      |     |           |           |           | K⁺ Na⁺ Ca⁺² Mg⁺² | SO₄⁻² Cl⁻ HCO₃⁻ CO₃⁻² |
| 18  | 4.96                             | 0.1669 | 208  | 116  | 1,329  | 7.13 | 8.6 | 9,0425 | 2 | 11,36 | 24,4 | 0 |
| Average | 38.7 | 6.7 | 3.7       | 2616.0    | 1716.1    | 43.5          | 457.2        |
| Maximum | 62.3 | 8.2 | 2.0       | 11308.0   | 10124.0   | 210.7         | 4462.0       |

Total dissolved solid (TDS) content ranged from 208 to 4128 mg l⁻¹. Figure 2a represents the associated Piper Diagram, and Map 1 depicts the related Stiff Diagram. Four water families were determined in the Piper and Stiff diagrams: sodium bicarbonate, (Guachalá and El Tingo), sodium Chloride (Chachimbro y Nangulvi), sulfated sodium (Aguas Hediondas) and bicarbonate magnesium, while the remaining samples were characterized by their low salinity. The hot springs from Pichincha Province are associated with the Caldera Chacana located in the volcanic center of the largest rhyolite volcanic quaternary in Ecuador [6]. Carchi Province is associated with the Chiles volcanoes (Aguas Hediondas) and the pyroclastic deposits of extinct volcanoes in Imbabura to the volcanic deposits of the Yanahurco volcanoes (Chachimbro) and Imbabura (Peguche).
Figure 2. (a) Piper diagram of sample points in the northern zone.  
(b) Schoeller – Berkaloff diagram of sample points in the northern zone.

Figure 3. Hydrogeochemical map of central zone via Stiff diagrams.
In the central zone, recorded temperature values ranged from 21 to 61 °C, with pH values between 6.2 to 8.3 and EC values between 1150 to 8970 µS / cm.

The values from 1008 to 7932 mg l\(^{-1}\) were measured in TDS (El Salado). As shown in the Piper diagram (figure 3a) and the Stiff diagrams (Map 2), four family types were determined. The first family was bicarbonate magnesium (Guapante and Nagsiche), likely the result of shallow water areas where sediment can accumulate [7] and matching its low mineralization and temperature. The second family was sulphate magnesium (El Salado, La Virgen and Los Elenes). The third family was sodium chloride (Papallacta, Cununyaku and Jamanco). The fourth family was sodium bicarbonate (Aluchán and Oyacachi). The hot springs in this area are located within the Cordillera Real and associated with volcanic activity produced in the Quaternary period by existing strata volcanoes as characterized by their lava flows and pyroclastic basaltic to rhyolitic composition [8]).

![Piper diagram and Schoeller–Berkaloff diagram](image-url)

**Figure 4.** (a) Piper diagram of samples points in central zone. (b) Schoeller – Berkaloff diagram of sample points.
Figure 5. Hydro geochemical map of central zone Stiff diagrams.
In the southern zone, the highest temperature and EC values were measured as follows: Baños de Cuenca (62 °C) and Guapán (20,220 μS cm⁻¹). The pH values were neutral except for Portovelo (8.09) which indicated a slightly basic value. Portovelo also indicated high TDS values greater than 4000 mg l⁻¹, except for Guapán (11308 mg l⁻¹). This high salinity is the result of prolonged interaction with rock-water and processes of evaporation [5]. As shown in the related Stiff diagrams (Map 3) and Scholler-Berkaloff graph (figure 4b), the most abundant ions in these samples are Na⁺ and Cl⁻.

The Piper diagram (figure 4a) identified a water family: sodium chloride characterized by deep ancient aquifers and remaining geology of the extinct volcanic activity in the Miocene [9] in this area of Ecuador. These waters are likely near or pass through salt diapirs [10].

![Piper diagram](image1.png)

**Figure 6.** (a) Piper diagram of sample points in the southern zone.

![Scholler-Berkaloff diagram](image2.png)

(b) Schoeller – Berkaloff diagram of sample points in the southern zone.

![Hydrogeochemical map](image3.png)

**Figure 7.** Hydrogeochemical map of south zone via Stiff diagrams.
4. Conclusions
The hot springs in Ecuador can be divided into two groups. The first group was associated with extinct volcanic activity produced in the Cenozoic (Oligocene, Miocene and Pliocene) and the second group was associated with young volcanic activity in the Quaternary. The first group was characterized by sodium chloride water (Guapán, Los Elenes, Baños de Cuenca, Cununyaku and Nagulví); these samples were associated with higher recorded temperatures and higher mineralization than other groups, and Stiff diagrams in “T” shapes. The water samples from the Quaternary were magnesium bicarbonate and sodium bicarbonate, sodium sulfate and magnesium sulfate. These types of waters are related to the complex geology of characteristic volcano deposits of igneous rocks (basalts and rhyolites) and metamorphic rocks (schists) of the Cordillera Real and Inter-Andes Valley where they were found, and characterized by Stiff diagrams shaped like arrowheads (Mg$^{2+}$- HCO$_3^-$, Na$^+$- SO$_4^{2-}$) and irregular polygons (Mg$^{2+}$-SO$_4^{2-}$, Na$^+$-SO$_4^{2-}$).

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