Hydrogeochemistry Characterization of Hot Springs Located in The Andes of Ecuador

David Vinicio Carrera-Villacrés 1, Alexander Hidalgo-Hidalgo 1, Paulina Guevara-García 1, María Vivero-Balarezo1, Vicente Delgado-Rodríguez 1

1 Universidad de las Fuerzas Armadas-ESPE, Departamento de Ciencias de la Tierra y la Construcción, Grupo de Investigación en Contaminación ambiental (GICA), Av. Gral. Rumiñahui S/N, Sangolquí, Ecuador

E-mail address: dvcarrera@espe.edu.ec

Abstract. The formation of several sources of hot springs in the Andes from Ecuador is the result of an intense volcanic activity due to the subduction of the Nazca oceanic plate under the South American continental plate. The aim of this study was to describe the hydrogeochemistry water geothermal origin, its chemical classification and relationship with the complex geology of Ecuador, using different hydro chemical diagrams (Stiff, Piper and Schoeller-Berkaloff). Geothermal waters can be divided into two groups. The first group, associated with an extinct volcanic activity produced in the Cenozoic, represents the Na+-Cl-type. The second group is associated with a young Quaternary volcanic activity and its types of water are Mg2+-HCO3-, Na+-HCO3-, Na+-SO42-, Mg2+-SO42-.

1. Introduction
Ecuador has various sources of geothermal water originating from a strong magmatic activity produced in the Quaternary Period due to the subduction of the Nazca oceanic plate under the South American continental plate [1] These sources are located in the called zone of volcanic arc of Ecuador. The aim of this study is to describe the hydrogeochemistry of the hot springs used in the spas located in the Andes of Ecuador and also their behaviour, predominant ions, chemical classification and relationship with the complex geology of Ecuador, using different hydrochemical diagrams, such as Stiff, Piper and Schoeller-Berkaloff.

2. Materials and Methods
The samplings were taken in 34 places located along the Andes of Ecuador. The distance in sampling was about 3215 kilometres. The Sampling points can be observed in the Figure 1.

2.1. Determination of physico-chemical parameters
Physico-chemical parameters were taken in situ for these samples. These samples were measured for water temperature with a mercury thermometer. In the laboratory of the Universidad de las Fuerzas Armadas ESPE, the pH was analysed with the usage of the pH meter model Thermo Scientific Orion 3-Star and the electrical conductivity (EC) was measured using a conductivity meter model HACH.
Finally, Total Dissolved Solids (TDS) and Waste dry calcined (RSC) were measured with the support of APHA [2].

Anions and Cations of the first 24 samples were sent to Havoc, which is a laboratory in Ecuador, and they are by the Ecuadorian Accreditation Service. In the laboratory of environmental work from ESPE, 10 leftover samples were analysed. The concentrations of Ca$^{2+}$ and Mg$^{2+}$ were obtained by colorimeter methods, the values of the concentrations of Na$^+$ and K$^+$ were measured with an Ion Meter inoLab® pH / ION 7320, Cl$^-$ by colorimetry according to NTE INEN 0976 (1984), HCO$_3^-$ by the volumetric method and SO$_4^{2-}$, NO$_3^-$ and PO$_4^{3-}$ spectrophotometrically according to EPA [3].

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

After obtaining the results of the analysis, a control was performed to check the error in the results by calculating the percentage of error [1] existing in the sum of anions and cations, established by APHA [2].

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\% \text{Error} = \frac{\sum_{\text{cationes}} - \sum_{\text{aniones}}}{\sum_{\text{cationes}} + \sum_{\text{aniones}}} \times 100
\] (1)

Table 1 shows the percentages admissible for each range of sum of anions and cations. It is necessary to check the results with the information in the table 1 to review if the parameters measured in laboratory are right.

| Sum of cations (meq/L) | % Acceptable difference |
|------------------------|-------------------------|
| 0.0 – 3.0              | ± 0.2 %                 |
| 3.0 – 10.0             | ± 2 %                   |
| 10 – 800               | ± 2.5 %                 |
2.3. Development of hydrochemical diagrams
The hydrochemical diagrams were made with the software Diagrammes versión 6.5 and developed by the laboratory of the Hydrogeology of the Université d’Avignon. Piper diagrams triangular, polygonal and Stiff logarithmic diagrams Berkaloff Schoeller vertical columns in order to chemically classify water samples are plotted.

2.4. Mapping
The maps were produced using a software Arc GIS with the shape files of the Instituto Geográfico Militar in Ecuador (IGM) and the geological mapping of the Instituto Nacional de Investigación Geológico Minero Metalúrgico in Ecuador (INIGEMM). In these maps the polygonal diagrams of Stiff were added to appreciate the variation between cations and anions of the samples and the spatial arrangement of the Hydrogeochemical families.

3. Results and Discussions
For a better analysis and interpretation of hydrogeochemical data was divided in three zones: the north zone (Carchi, Imbabura and Pichincha), the centre zone (Cotopaxi, Napo, Tungurahua and Chimbacoro) and the south zone (Cañar, Azuay and El Oro).

In the north zone the largest number of samples (20) was taken due to the presence of the volcanoes that have their base in the Cordillera Occidental and the valley of the Andes. The temperature values were recorded between 18 - 60 °C, having the pH values between 4.96 and 7.65 and the electrical conductivity from 166 to 6795 µS / cm. Relatively pH values <6 (Lloa and Aguas Hediondas) indicated a possible interaction with the acid gases [4].

The total dissolved solids (TDS) ranged from 208 to 4128 mg l⁻¹. In the Figure 2A the Piper Diagram is represented and Figure 3 shows the Stiff Diagram. Four water families were determined in the Piper and Stiff diagrams: sodium bicarbonate, (Guachalá and El Tingo), sodium Chloride (Chachimbiro y Nanguí), sulphated sodium (Aguas Hediondas) and bicarbonate magnesium, the rest samples were characterized by their low salinity. The hot springs from Province of Pichincha are associated with the Chacana caldera located in the volcanic centre of the largest rhyolite quaternary volcanic complex of Ecuador [5]. In the province of Carchi is associated with volcanoes called Chiles (Aguas Hediondas) and the pyroclastic deposits of extinct volcanoes that exist in the Province, in Imbabura to volcanic deposits Yanahurco volcanoes (Chachimbiro) and Imbabura (Peguche).

Figure 2. (A)Piper diagram of samples points in North Zone. (B) Schoeller – Berkaloff diagram of samples points in North Zone
In the Central Zone, the recorded temperature values ranged from 21 to 61 °C, with the pH values between 6.2 and 8.3 and EC between 1150 and 8970 µS / cm.

**Figure 3.** Hydro-geochemical Map of north zone with Stiff diagrams
The values from 1008 to 7932 mg l\(^{-1}\) were measured in TDS (El Salado). As shown in the diagram Piper (Figure 4a) and in the Stiff diagrams (Figure 5), there are four family types. The first family is bicarbonate magnesium (Guapante and Nagsiche), probably because of the shallow water areas with a sediment accumulation [6] and a low mineralization and temperature.

The second family is magnesium sulphate (El Salado, La Virgen and Los Elenes). The third one is sodium chloride (Papallacta, Cununyaku and Jamanco).

The fourth one is bicarbonate sodium (Aluchán and Oyacachi). The hot springs in this area are located within the Cordillera Real and they are associated with the Quaternary volcanic activity of the existing stratovolcanoes characterized by their lava flows and pyroclastic basaltic to rhyolitic composition [7]. In the case of SPAS called La Virgen and El Salado (Volcano Tungurahua), Cununyaku (Chimborazo Volcano), Jamanco, Papallacta and Oyacachi (Volcanic Formation Pisayambo).

![Figure 4. (A) Piper diagram of samples points in Centre Zone. (B) Schoeller – Berkaloff diagram of samples points](image)

In the South Zone the highest temperature and EC values were measured: Baños de Cuenca (62°C) and Guapán (20,220 μS cm\(^{-1}\)). The pH values were neutral except for Portovelo, (8.09) showing a slightly basic value and therefore also high values of TDS> 4000 mg l\(^{-1}\), and the special case of Guapán (11308 mg l\(^{-1}\)), whose high salinity is a result of the prolonged rock-water interaction and the evaporation processes, [4]. As shown in the Stiff diagrams (Figure 7) and the Scholler Berkaloff graph (Figure 6B), the most abundant ions in these samples are Na\(^+\) and Cl\(^-\).

The Piper diagram (Figure 6A) identified a family type of water: chloride sodium. This type of water is characterized by ancient deep aquifers and the remaining geology of the extinct volcanic activity of this area of Ecuador during the Miocene [8]. These waters are probably near or passing through the salt diapers [9, 10].
**Figure 5.** Hydro-geochemical Map of centre zone with Stiff diagrams
Figure 6. (A) Piper diagram of samples points in South Zone. (B) Schoeller – Berkaloff diagram of samples points in South Zone.

Figure 7. Hydro geochemical Map of south zone with Stiff diagrams

4. Conclusions
The hot springs in Ecuador can be divided into two groups. The first group is associated with the extinct volcanic activity produced in the Cenozoic (Oligocene, Miocene and Pliocene) and the second
group is associated with the young Quaternary volcanic activity. The first group is characterized as sodium chloride water (Guapán, Los Elenes, Baños de Cuenca, Cutunyaku and Nagulvi), which recorded higher temperatures and higher mineralization than the other groups, and the Stiff diagrams were in "T" form. The water samples from the Quaternary Era are: bicarbonate magnesium and bicarbonate sodium, sulphate sodium and sulphate magnesium. These kinds of waters are related to the complex geology of the characteristic volcano clastic deposits of igneous rocks (basalts and rhyolites) and metamorphic rocks (schists) of the Cordillera Real and Inter-Andes Valley where they emerge. Stiff diagrams are shaped as arrowhead (Mg²⁺ - HCO₃⁻-Na⁺-HCO₃⁻) and irregular polygons (Mg²⁺-SO₄²⁻, Na⁺-SO₄²⁻).

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