Hydrogeochemical Characterization as a Tool to Recognize “Masked Geothermal Waters” in Bahía Concepción, Mexico

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Abstract: Geo-thermalism has been widely recognized on the Baja California Peninsula, especially during the last decade. The current research, carried out on Bahia Concepcion, evidences the existence of geothermal springs, which get recharged mainly by groundwater and seawater. The groundwater can be characterized as Na⁺-Cl⁻ and Na⁺-HCO₃⁻ type, with a pH value close to neutrality. The slightly more acidic thermal sites presented temperatures between 32 °C and 59 °C at the surface. Based on the relationships of the Cl⁻ and Br⁻, as well as the B/Cl⁻, and Br⁻/Cl⁻ ratios, seawater was recognized as the main source of salinity. The spatial distribution is explained directly through marine intrusion, or via sprays and aerosols within the rainwater. Seawater ratios in thermal springs varied from 62% to 83%, corresponding mainly to shallow inflow, but seawater inputs into the deep thermal reservoir were also recognized. Temperatures in the geothermal deep reservoir were inferred from 114 to 209 °C, calculated through the SiO₂ and Na⁺-K⁺ geothermometers. In addition to previously reported thermal sites at Bahia Concepcion, and based on their elevated temperatures, two new sites were identified. Another five springs do not fulfill the commonly used definition, varied from 62% to 83%, corresponding mainly to shallow inflow, but seawater inputs into the deep thermal reservoir were also recognized. Temperatures in the geothermal deep reservoir were inferred from 114 to 209 °C, calculated through the SiO₂ and Na⁺-K⁺ geothermometers. In addition to previously reported thermal sites at Bahia Concepcion, and based on their elevated temperatures, two new sites were identified. Another five springs do not fulfill the commonly used definition, based on differential temperature, but show the typical hydrogeochemical signature of thermal water. A new approach to identify this low-temperature geothermal-influenced spring water by its hydrogeochemical composition is presented, for which the term “Masked Geothermal Waters” (MGW) is introduced. Our findings increase the area of the geothermal anomaly and, therefore, the potential of geothermal resources. The approach proposed in this research will also be useful to identify more MGW in other coastal areas.

Keywords: Br⁻/Cl⁻; California Peninsula; thermal springs; mix water; seawater signature

1. Introduction

Due to hydrocarbon deposit depletion, the need to reduce CO₂ release to the atmosphere, as well as international environmental agreements, renewable energies have largely escalated in importance in the world in becoming the future’s energy resources, [1,2]. The environmental importance of these alternative energy sources has been recognized [3,4]. Although geo-thermalism is a renewable resource with a significant global occurrence, its use is still incipient compared to other alternative energies. However, derived from scientific and technological advances, which allow the reduction of operating costs, its future promises to be interesting, competing with other sources of energy [5]. Based on their usefulness, the research on geothermal resources has focused mainly on the assessment of high-temperature geothermal fields, leaving those of medium and low temperature at a second level of importance. In recent years, interest has increased in medium and...
low-temperature geothermal sites, which can be used in small-scale power generation and other industrial activities that take direct advantage of the use of the geothermal fluid temperature [6].

Geothermal activity, manifested as low or high enthalpy thermal springs, is distributed throughout the world [7–9]. Due to its chemical characteristics, water from thermal springs has been used historically in balneology, balneotherapy, traditional medicine and more recently in the cosmetic or food industries [10–12]. However, several studies recognize the release of nutrients and potentially toxic elements from the discharge of thermal water into the environment [13–18].

The widely accepted definition for recognizing a water spring as thermal is based on its differential temperature values, compared with the average annual temperature in the respective area [19,20]. Groundwater chemical composition is an important aspect to understand the hydro-thermalism, as several springs do not show the mentioned differential, but their hydrogeochemical signature suggests a hydrothermal origin. Authors herein propose to define these kinds of waters as masked geothermal waters (MGW). In this context, the study of water mixtures of thermal fluids, groundwater and seawater [13,21–25] allows us to recognize origin of fluids, groundwater discharges, marine intrusion, movement of the saline interface, and coastal ecosystem relationship and vulnerability. Knowing these mechanisms allows for better resource management [22,25–27].

In Mexico, geothermal resources have been used as a source of energy production since the middle of the 20th century. In 2018, an estimated 5375 GWh were produced from high-enthalpy geothermal fields such as Los Azufres, Los Humeros, Cerro Prieto, and Las Tres Virgenes (LTV), which represents 1.7% of electrical national production [28,29]. The last two of these fields are located on the Baja California Peninsula (BCP). As a result of recognizing the high potential and heat flow prevailing in this area, including in the Gulf of California [6,30,31], several low and medium-temperature geothermal manifestations have been located and related to volcanic activity or/and fractured areas (regional faults), but not fully characterized from a hydrogeochemical point of view. In particular, on the southern portion of the peninsula, corresponding to the Baja California Sur State, geothermal sites have been described [6,32–38]. These manifestations are located mainly on the eastern margin of the BCP, discharging into the Gulf, and Bahía Concepción is one of the most important [6,36,39–41].

The aim of this study was to describe geothermal manifestations in Bahía Concepción and to identify their effects on groundwater geochemistry. Additionally, a new methodology based on hydrogeochemical signatures is proposed to recognize MGW. A hydrogeochemical characterization of the groundwater that discharges into the bay was performed to clarify the exchange and mixing of the fluid endmembers in the MGW. The information generated in this research contributes to an increase in knowledge on geothermal resources for their future use and management in a sustainable framework.

2. Study Area

Bahía Concepción, located in the central-eastern portion of B. C. S. (Figure 1), is an area with a low population density. Its natural landscape’s beauty has made it a tourist destination, with future development projections, which implies the need for energy and water resources. The area has good accessibility and the most important settlements are: Santispac, El Burro, Rancho El Molino, Punta Arenas, El Coyote, La Posada, all on the west coast of the Bay (Figure 1).
2.1. Geological Units

The oldest unit outcropping on the Bahia Concepción region corresponds to cretaceous granitic rocks (Figure 2), with inclusions and pendants of schists, intruded by mafic, aplitic, and pegmatitic stocks and dikes [42,43]. The El Salto Formation (28.1 ± 0.9 Ma), discordant to that granitic basement, was formed by very fine to medium grain sandstones with cross-bedding stratification and tuffaceous intercalations [43].
Figure 2. Geological and structural generalized map of Bahía Concepción area. Modified from McFall [43], SGM [44], Ledesma-Vázquez and Johnson [45].

It is transitionally overlaid by rocks of the Comondú Group [43,46,47] volcano-sedimentary sequence (Figure 2). Umhoefer et al. [47] proposed three divisions: (1) a lower clastic unit with sandstones and tuffaceous intercalations, (2) a middle unit with volcanic breccias and dacitic-andesitic lava flows and (3) an upper unit of lava flows. The Comondú Group was deposited ca. 30 Ma–12 Ma [46–48]. In a transitional to discordant contact with the Comondú Group, the Infierno Formation, is overlaid composed of andesitic conglomerates, sandstones, siltstones, mudstones, and coquina intercalations, with a characteristic chert layer [49,50]. The Infierno Formation from the Upper Pliocene is deposited in a beach environment with marine transgression [43,49]. Lava flows and volcanic deposits overlay the previous units, identified as andesitic-basaltic alkaline to rhyolitic-dacitic calco-alkaline post-Comondú [51–53]. Alluvial deposits fill the dry stream, sands and heterogeneous conglomerates compose terraces at different levels associated with the structural system, as well as dune deposits, which currently make up the geomorphology of the coastal zone in the area.

2.2. Structural Setting

The structural genesis of Bahía Concepción is closely related to the events that occurred at the initial spreading of the Gulf of California in the late Miocene [45,48,52,54].
During the Cenozoic, the processes of a convergent margin ceased, originating an arc, whose volcanism (sensu lato) produced the Comondú Group deposits [42,55]. After the subduction, a trans-tensional process began, which would merge the Baja California peninsula as part of the Pacific plate [48,56]. The current boundary between the Pacific Plate and the North American plate, along with the GC, corresponds to an oblique (20° NW) transform fault [54].

The major structures in Bahía Concepción correspond to normal faults with associated listric structures (Figure 2) with a preferential direction 25–30° NW–SE, while secondary alignments are perpendicular NE–SW (Figure 2). The Concepción Fault is the main structure on the Conception peninsula which exhibits a general dip of 45° to the west [43,52]. A second structure (NW–SE) is the El Requesón Fault (Figure 2), which delimits the western margin of the bay where intertidal and submarine hydrothermal springs occur [57]. These two structures formed a graben, which corresponds to Bahía Concepción bay. Faulting is considered to completely affect the volcano-sedimentary sequence, probably as well as the intrusive igneous basement which can be considered almost impermeable. As the structural system of the area is related to the opening of the California Gulf, the main faults and their associated structures allow a relatively high permeability. The intensive faulting can explain the existence of deep circulation in the aquifers, which has been described as the main source of the geothermal system.

2.3. Climate and Hydrogeology

The climate in Bahía Concepción is semi-arid. Based on data from three meteorological stations [12], the time series of monthly records for 25 years indicates that the average annual precipitation is 145 mm, less than the average precipitation of the State (222 mm) [58]. The annual average temperature is approximately 23 °C (Table 1).

Table 1. Annual averages of precipitation (mm) and temperature (°C) in Bahía Concepcion [59].

| Parameter                        | San Nicolás | Mulegé | Ojo de Agua | Local Average in Bahía Concepción |
|----------------------------------|-------------|--------|-------------|----------------------------------|
| Annual precipitation average     | 142.3       | 153.6  | 141.8       | 145.9                            |
| (1980–2015)                      |             |        |             |                                  |
| Annual temperature average       | 23.73       | 22.31  | 22.37       | 22.80                            |
| (1980–2015)                      |             |        |             |                                  |

The drainage pattern in the area is dendritic and subparallel. The main creeks at the western side of the bay are Cadeje, Armenta, El Frijol, La Enramada, and El Tordillo; while Los Pelones, El León, Cardoncito, Los Pintados, and El Mono-Santa Rosalilíta creeks drain to the east coast of the bay.

For Bahía Concepcion watershed, including the aquifer, the Mexican National Water Commission (CONAGUA) calculated an average annual recharge of 5.7 Mm³; in contrast, the average annual discharge reaches approximately 4.9 Mm³ [60]. These numbers include the San Nicolás watershed, which discharges directly towards the Gulf of California and not towards the bay, thus the discharge into the bay is assumed to be lower than calculated. CONAGUA indicated that the aquifer is formed by the volcano-sedimentary rocks in the area [60]. These rocks, mostly, belong to the Comondú Group, according to the geology of the area (Figure 2). In the aquifer, a transmissivity of 0.5 to 3.5 × 10⁻³ m²/s was estimated. The depth of the water table varies between 1 to 20 m, obtained from wells in dry streams and near to the coastline, which is defined as the discharge area of the aquifer. Regarding to elevation of the water table, this was measured up to 230 m a.s.l., towards the mountainous area [60].

2.4. Geothermal Research in the Area

Former investigations, related to the geothermal system in Bahía Concepción, are mainly focused on the submarine discharges of thermal water and intertidal thermal...
springs, located near Santispac and Mapachitos [36]. Water composition of two intertidal thermal springs (Santispac and La Posada), as well as a submarine hot spring (Mapachitos), was described as a mixture of seawater and thermal fresh groundwater. These thermal springs are enriched in several elements, but depleted in Mg, with respect to seawater [32,36]. The temperature in the deep reservoir was calculated at about 200 °C [36]. A high heat flux (up to 200 mW/m²) is concentrated in this region [53]. The geothermal system was defined as controlled by deep normal faults, associated with the oblique extensional system of the Gulf of California [36,39,61].

Villanueva-Estrada et al. [41] used data from Prol-Ledesma et al. [36] and proposed a mixing model that explains the final fluid discharge. They concluded that the water source of the thermal system is meteoric water (80%) and the remaining 20% represents high saline fluids. Elements such as Mn, Ba, Hg, and Si occur in the areas of submarine thermal discharges, as well as at the intertidal springs. The elevated concentrations of As and Hg, among other potentially toxic elements, were related to the discharges of the intertidal hydrothermal spring of Santispac and Mapachitos; these elements are found to be assimilated by macroalgae [40,62]. Estradas-Romero et al. [63] and Melwani and Kim [64] related species richness of phytoplankton and benthic fauna to higher water temperature and the hydrogeochemical composition of thermal discharges.

3. Methods

In February 2018, seven groundwater (hand-dug shallow wells, called norias) and 13 spring water samples were collected from the coastal margins of Bahía Concepción, following the recommendations of Arnórsson and D’Amore [65]. The samples from wells were taken with a bailer, avoiding shaking and contamination. In the case of springs, the sample was taken directly from the emanation point. All samples were filtered with a 0.45 µm cellulose Millipore® filter (Merkmillipore, Burlington, MA, USA) and stored in new polyethylene bottles previously rinsed with distilled water, and again with water from the source to be sampled. Finally, the samples for cation analyses were acidified with HNO₃ (pH < 2) (J.T. Baker®-Avantor, Center Valley, PA, USA), and all samples were stored at 4 °C until analysis.

At each site, three physicochemical parameters were measured: firstly, the temperature, using a pH/temperature meter (Hanna Instruments® HI9124; Woonsocket, RI, USA) with a resolution of 0.1 °C and an accuracy of 0.4 °C. The electrical conductivity (EC), as well as the total dissolved solid (TDS) were measured by a CE/TDS/temperature DiST® 6 m (Hanna Instruments® HI98312; Woonsocket, RI, USA) with temperature compensation, and detection ranges of up to 20,000 µS/cm and up to 10 ppt, respectively. The resolution and accuracy of this device are 10 µS/cm and ±2% for EC and 0.01 ppt and ±2% for TDS. For sites with high salinity, a portable refractometer was used to measure the percentage content of salts in UPS. The pH was also measured, using the Hanna Instruments® meter, HI9124 (Woonsocket, RI, USA), with resolution of 0.01 and an accuracy of ±0.01. It was previously calibrated, using Buffer solutions (4.01, 7.01, 10.01 Hanna®; Woonsocket, RI, USA). The main cations (Ca²⁺, Na⁺, K⁺, Mg²⁺) were determined with a Perkin Elmer® (Waltham, MA, USA) PinAAcle 900F Flame Atomic Absorption Spectrophotometer (recovery 101%, 102%, 96%, 102% and limits of detection -LOD- 0.02, 0.03, 0.12, 0.02 mg/L, respectively). The major anions (Cl⁻, SO₄²⁻, Br⁻) were analyzed in a Metrohm® (Herisau, Switzerland) Ion Chromatograph model 861 Advanced Compact IC (recovery of 95%, 107%, 104% and LOD 0.01, 0.03, 0.02 mg/L, respectively). These analyses were validated (±5%), calculating the charge balance of the major cations and anions for each sample. The elemental concentration of B (recovery 94%, LOD 0.07 µg/L) was determined by mass spectrometry using a Thermo Scientific® (Waltham, MA, USA) ICP-MS iCAP Q equipment. The concentration of HCO₃⁻ was determined by automatic titration with a Hanna® HI-902C (Woonsocket, RI, USA) equipment. SiO₂ was analyzed by a Hanna® photometer (±0.03 mg/L) (Woonsocket, RI, USA). All the analyses were validated using control reference solutions and NIST-1643f as certified reference material. For quality control, laboratory
and field blanks were also analyzed and no chemical interferences (sample contamination) were found.

According to Vengosh [66], the Br⁻/Cl⁻ and B/Cl⁻ relationships allow the recognition of the mixing effects of thermal water with seawater, evaporated seawater, fresh groundwater, or agricultural return flow. Hernandez-Morales and Wurl [34] used the diagram proposed by Vengosh [66], to define typical positions of thermal water at the southern tip of the peninsula of Baja California Sur. The origin of the salinity in the study area is discussed based on Cl⁻, Br, and B relationships.

The temperature in the deep thermal reservoir was inferred using the silica geothermometer [67] with the SOLGeo software [68], which allows estimation of the uncertainties for the incorporated geothermometric equations.

### 4. Results

The physicochemical results measured in the field indicated that the water from the sampling sites had temperatures ranging from 22 °C (CB12) to almost 60 °C in the coastal thermal springs (CB14, CB15, and CB16, Figure 1). The sites CB2 (Cadejé) and CB3 (El Tordillo) showed a temperature above 32 °C and therefore fall into the definition of thermal water, considering the average temperature of the area (22.8 °C). The temperature was higher on the slope that discharges into the west of the bay. Temperature, electrical conductivity and pH had a greater variability on the western margin of the bay, due to the occurrence of geo-thermalism and a stronger seawater influence. The eastern margin (CB17, CB18, CB19, and CB20) showed electrical conductivities from 1082 to 2130 µS/cm, with a pH average of 6.9. The sampling sites on the western portion (Figure 1) showed high values of electrical conductivity for the sites near the coast, in contrast to the sites upstream of the hydrological watershed; a variation was found from 430 µS/cm (CB11) to greater than 20,000 µS/cm in coastal thermal springs (CB14, CB15, CB16). Regarding the pH of the coastal thermal springs, slightly more acidic values (pH 6.5) were found than the values registered in the samples of the other analyzed sites, which varied from a neutral pH to 8.7 (CB10). Detailed information is presented in Tables 2 and 3.

#### Table 2. Sampling sites code and physicochemical parameters.

| Sample  | Locality         | Electric Conductivity (µS/cm) | TDS (mg/L) | Salinity (UPS) | Temperature (°C) | pH  |
|---------|------------------|-------------------------------|------------|----------------|------------------|-----|
| Western margin |
| CB1     | Casa de Piedra   | 981                           | 698        | –              | 27.4             | 7.7 |
| CB2     | Cadejé           | 1160                          | 506        | –              | 36.4             | 8.2 |
| CB3     | El Tordillo      | 8300                          | 4069       | –              | 32.7             | 7.7 |
| CB4     | El Llanito       | 15,720                        | 9133       | –              | 28.8             | 6.5 |
| CB5     | Arminta          | 737                           | 384        | –              | 25.8             | 7.2 |
| CB6     | Pocitos 2        | 4446                          | 3231       | –              | 23.6             | 7.5 |
| CB7     | Pocitos 3        | 8160                          | 6440       | –              | 30.3             | 7.3 |
| CB8     | Predio Adelaida  | 6070                          | 3014       | –              | 29.4             | 7.3 |
| CB9     | Arroyo Cadejé    | 4020                          | 2571       | –              | 27               | 7.3 |
| CB10    | Las Cruces       | 1779                          | 1143       | –              | 22.8             | 8.7 |
| CB11    | Las Cuevitas     | 490                           | 338        | –              | 30.7             | 7.9 |
| CB12    | La Enramada      | 949                           | 741        | –              | 22.2             | 8.1 |
| CB13    | El Coyote        | 4660                          | 3442       | –              | 31.6             | 7.2 |
| CB14    | La Posada        | >20,000                       | 25,942     | 22             | 53.4             | 6.9 |
| CB15    | Santispac        | >20,000                       | 29,320     | 25             | 42.1             | 7.8 |
| CB16    | Agua Caliente    | >20,000                       | 24,214     | 21             | 58.6             | 6.5 |
| CB21    | Santa Barbara    | 4960                          | 3167       | –              | 30.4             | 7.2 |
| Eastern margin |
| CB17    | El Mezquite      | 2130                          | 1338       | –              | 29.8             | 6.7 |
| CB18    | El Salto         | 1135                          | 675        | –              | 24.3             | 6.9 |
| CB19    | McFall           | 1082                          | 653        | –              | 24.7             | 6.9 |
| CB20    | La Pintada       | 1161                          | 735        | –              | 23.2             | 6.9 |

Most of the analyzed samples indicate Cl⁻ and HCO₃⁻ as dominant anions. Only for CB19 was the dominant anion SO₄²⁻. Regarding cations, a higher concentration of Na⁺
prevails in all samples. In addition, the results indicated high concentrations of Na\(^+\) and Cl\(^-\), with values up to 17,629 and 8150 mg/L, respectively, for the CB15 sample. On the contrary, the lowest concentration in Na\(^+\) and Cl\(^-\) (53.6 and 44.5 mg/L) corresponded to the CB11 sample.

Table 3. Hydrogeochemical composition of the samples collected in the Bahía Concepción area. Units are in mg/L.

| Sample | Na\(^+\) | K\(^+\) | Ca\(^{2+}\) | Mg\(^{2+}\) | Cl\(^-\) | SO\(_{4}^{2-}\) | HCO\(_{3}^{-}\) | Br\(^-\) | B | SiO\(_{2}\) | Electrical Balance Error (%) |
|--------|--------|--------|----------|--------|--------|-----------|------------|------|---|--------|-----------------------------|
| CB1    | 148.0  | 3.6    | 26.2     | 26.1   | 164.7  | 24.8      | 285.0      | 0.5   | 0.6| 42.3   | −1.2                        |
| CB2    | 112.0  | 4.5    | 26.4     | 14.8   | 130.9  | 27.6      | 162.8      | 0.5   | 0.5| 78.8   | 0.6                         |
| CB3    | 615.0  | 32.4   | 434.0    | 235.5  | 2391.9 | 166.2     | 152.0      | 8.4   | 0.7| 121.6  | −3.8                        |
| CB4    | 1590.0 | 74.2   | 807.0    | 494.0  | 5472.6 | 414.5     | 231.0      | 18.4  | 1.4| 129.5  | −4.9                        |
| CB5    | 67.0   | 9.4    | 23.5     | 10.4   | 64.9   | 10.0      | 197.8      | 0.2   | 0.1| 43.0   | −1.1                        |
| CB6    | 900.0  | 26.0   | 54.8     | 108.0  | 1635.5 | 237.6     | 234.0      | 5.4   | 0.7| 77.8   | −4.0                        |
| CB7    | 1900.0 | 68.9   | 112.0    | 204.6  | 3397.0 | 460.4     | 278.7      | 11.2  | 1.0| 103.0  | −1.6                        |
| CB8    | 600.0  | 33.4   | 180.4    | 167.0  | 1659.6 | 212.3     | 122.9      | 5.6   | 0.8| 53.0   | −4.0                        |
| CB9    | 845.0  | 22.2   | 7.1      | 20.8   | 977.1  | 167.9     | 482.9      | 3.2   | 1.3| 64.6   | −1.5                        |
| CB10   | 320.0  | 6.3    | 20.6     | 23.0   | 338.9  | 103.3     | 312.7      | 8.4   | 0.8| 83.1   | −0.9                        |
| CB11   | 44.5   | 4.0    | 21.8     | 22.6   | 53.6   | 11.1      | 170.9      | 0.3   | 0.1| 80.0   | −1.2                        |
| CB12   | 120.2  | 36.1   | 26.1     | 30.7   | 142.3  | 15.1      | 356.1      | 0.7   | 0.3| 63.2   | −3.2                        |
| CB13   | 735.0  | 30.3   | 158.0    | 200.8  | 1943.1 | 216.6     | 127.3      | 6.5   | 0.5| 72.7   | −4.0                        |
| CB14   | 7225.0 | 446.3  | 1229.5   | 404.0  | 15,620.4 | 946.8 | 70.4 | 52.6 | 8.7 | 75.1 | −4.7 |
| CB15   | 8150.0 | 455.4  | 1271.0   | 519.0  | 17,629.5 | 1213.4 | 81.6 | 59.9 | 7.6 | 78.8 | −5.2 |
| CB16   | 7100.0 | 521.1  | 1092.5   | 276.0  | 14,585.9 | 495.0 | 143.3 | 51.1 | 15.4 | 211.7 | −3.0 |
| CB17   | 717.5  | 28.3   | 110.0    | 174.0  | 1757.3 | 197.0 | 150.9 | 5.9  | 0.4 | 72.0 | −4.6 |

Based on the concentration of the major ions, hydrogeochemical facies can be generalized according to Piper’s diagram [69,70]. The hydrogeochemical classification of the analyzed sites in this work resulted in Na\(^+\)-HCO\(_{3}^{-}\) type waters in the area with contribution mostly of fresh groundwater (CB1, CB2, CB5, CB10, CB11, CB12, CB17, CB20); while, in the sites near the coastal zone the type of water is Na\(^+\)-Cl\(^-\) (CB3, CB4, CB6, CB7, CB8, CB9, CB13, CB14, CB15, CB16, CB21). Sites CB18 and CB19, located on the central portion of the Concepción Peninsula, belong to a Na\(^+\)-SO\(_{4}^{2-}\) water type. The Piper diagram (Figure 3) exhibits two main groups of waters, group 1 that enclose samples related to seawater reference and group 2, in the central part of the rhomboid, with less mineralization and bicarbonate-sodium type. The average concentration of anions and cations for both groups, from highest to lowest, is as follows: (1) Cl\(^-\) > SO\(_{4}^{2-}\) > HCO\(_{3}^{-}\) > Br\(^-\); Na\(^+\) > Ca\(^{2+}\) > Mg\(^{2+}\) > K\(^+\). (2) HCO\(_{3}^{-}\) > Cl\(^-\) > SO\(_{4}^{2-}\) > Br\(^-\); Na\(^+\) > Ca\(^{2+}\) > Mg\(^{2+}\) > K\(^+\).
Hydrogeochemical Characterization

The Santispac, La Posada, and Agua Caliente (CB14, CB15, CB16) localities, with a salinity greater than 21 PSU and temperature up to 50 °C, correspond to intertidal thermal springs and have been described as mixtures of thermal water and seawater \cite{36,41}. This is in agreement with our results (Table 1). The samples CB1, CB5, CB11, CB12, and those located on the Concepcion Peninsula, presented lower mineralization. The site CB11 (Cuevitas) has a similar hydrogeochemical signature as that described by Birkle et al. \cite{71}, as meteoric recharge water for the Las Tres Vírgenes geothermal field (ca. 100 km northwest). A slight SO$_4^{2-}$ enrichment was found in samples CB18 and CB19 respecting their other anions; this is probably added from a mineral alteration of a tertiary igneous intrusion \cite{48} occurring in that area (Figure 2).

Most of the sites fall into the region of alkali dominance in the Piper diagram (Figure 3). This is in accordance with the occurrence of alkaline to calco-alkaline volcanic and volcanioclastic rocks from the Comondú Group (Figure 2) in the area \cite{46,55}, indicating a probable water–rock interaction process. Two groups of samples are recognized from the Piper diagram. Group (1) on the upper right, with high contents of chloride, is formed by sites located near the west coastline (Figure 4); they show a trend in the direction of the decrease or exchange of Na$^+$ and this is associated with a mixture of seawater (SWR) and fresh groundwater. The second group on the central portion represents fresh groundwater and includes the site CB11, which shows an ionic composition commonly considered as recharge water. The sites belonging to this group are further from the coastline than those from group 1 (Figure 4), which could indicate a spatial evolution, as suggested Tomaszkiewicz et al. \cite{72}, based on the water mineralization from the recharge zone towards the coastline, where it acquires higher mineralization.
Figure 4. Spatial distribution of ionic concentration ratios.

The \( \text{Br}^- \text{--Cl}^- \) relationship maintained as constant, and similar to the relation from the seawater reference; although, for some sites, the \( \text{Cl}^- \) concentration is as low as that for meteoric water, following a common mixing pattern (Figure 5). Similarly, most of the samples maintain the seawater \( \text{B--Cl}^- \) ratio, except the sites CB10, CB14, CB15, CB16, with elevated boron concentration (Figure 5). In addition, the last three sites also showed lower \( \text{Mg}^{2+} \) ratios than seawater.
Figure 5. Relationships between Cl$^-$ vs. Br$^-$, B and Mg$^{2+}$ in groundwater from Bahía Concepcion watershed. Seawater data after Nozaki [73].

5. Discussion

Based on the Br$^-$–Cl$^-$ relationship (Figure 5), a theoretical dilution line (Figure 6) was modeled between the two end-members (recharge freshwater represented by CB11 and seawater SWR), using the PHREEQC software [74]. According to the percentage of SWR, three groups are well distinguished:

1. The samples CB14, CB15, and CB16, with more than 75% of seawater, correspond to the intertidal hydrothermal springs in La Posada, Santispac, and Agua Caliente (Figure 1).

2. Three sites, located within the intertidal area (CB6, CB7, CB13), and five sites, located within a distance of less than 3 km to the coastline (CB3, CB4, CB8, CB9, and CB21), presented a fraction of seawater ranging between 5% and 30%. This proportion of seawater results from either tidal pump or groundwater extraction.

3. The remaining sites, with less than 2% seawater, are located at distances of more than 3 km to the coastline.
The probable addition of the seawater signature respecting its \( \text{Br}^- / \text{Cl}^- \) relationship would be explained by aerosols and spray particles added in the recharge from meteoric rainwater as explained for thermal springs at the southern tip of BCP [34]. The low percentage of seawater fraction in those sites could be an indicator of this process (Figure 6). With no storms or hurricanes occurring, marine aerosols can be recognized up to 20 km inland. Conversely a higher transport of marine spray and aerosols is expected in the rainy season which are mixed with the recharge meteoric water [75–77]. At Bahía Concepcion, the rains are associated with hurricanes and storms and represent the main source of recharge [78].

5.1. Origin of Water Salinity and Mixing of End Members

The hydrogeochemical compositions of four end-members were defined as follows: (a) seawater [73], (b) meteoric recharged groundwater (CB11), (c) thermal water with meteoric water recharge [34], and (d) thermal water from the geothermal field LTV (LV4) [79]. The proportion of each end-member in the water samples was evaluated, based on the elements \( \text{Cl}^- \), \( \text{Br}^- \), and \( \text{B} \), which represent conservative ions [67,80]. According to Vengosh [66], the relationship between \( \text{Br}^- / \text{Cl}^- \) and \( \text{B} / \text{Cl}^- \) ratios allows the recognition of mixtures of water. This relationship has been widely used in former studies on hydrothermalism in several countries [9,34,81–83].

All data from samples from Bahia Concepcion, as well as those from the known end-members, were plotted in the modified Vengosh diagram (Figure 7). The sites, including the thermal intertidal ones, maintained a \( \text{Br}^- / \text{Cl}^- \) ratio similar to that from the seawater reference; however, the \( \text{B} / \text{Cl}^- \) ratio remarkable varied among samples, oscillating from 0.0008 up to 0.08 (Figure 7). This can be explained by thermal water-rock interaction processes, providing a considerable increase in boron concentrations [84,85]. In the case of seawater evaporation, both ratios (\( \text{Br}^- / \text{Cl}^- \) and \( \text{B} / \text{Cl}^- \)) vary systematically, indicated in Figure 7 by a blue arrow. This effect is notable in the Mapachitos site from Bahía Concepcion (BC1) described by Prol-Ledesma et al. [36]; however, in this study this was not observed.

The black diagonal arrows, parallel to the blue arrow, correspond to the trend of the \( \text{Br}^- / \text{Cl}^- \) and \( \text{B} / \text{Cl}^- \) ratios that has been described for hydrothermal manifestations of the Los Cabos Block [34], a mountain range in the center of the southern tip of the peninsula of Baja California. The thermal springs at El Chorro and Buenavista [34] are taken here as references (Figure 7).

Figure 6. \( \text{Cl}^- \) and \( \text{Br}^- \) relationship with the samples analyzed, respecting the theoretical dilution line of seawater (SWR).
According to the Br\(^{-}/\text{Cl}^{-}\) and B/Cl\(^{-}\) relationship (Figure 7), trend lines are projected in the same direction for evaporated seawater, as defined by Vengosh [66]. There is a contribution of marine waters from recharge, subsequently mixed either with a geothermal member or/and seawater. In the case of mixing with thermal water with meteoric recharge, samples tend to shift from the seawater Br\(^{-}/\text{Cl}^{-}\) ratio (dashed line, Figure 7), towards an increase of the Br\(^{-}/\text{Cl}^{-}\) and B/Cl\(^{-}\) ratios as in the case of the LV4, El Chorro and BC1. The relationship between the conservative Br\(^{-}\), and Cl\(^{-}\) in the geothermal system of Bahía Concepción maintains the common seawater molar ratio of 0.0015 [75,84,86], which rejects that the water in the aquifer has interaction with brines or strata with relict seawater, as has been indicated for sedimentary basins in China, U.S. and Poland [82,83,87,88].

B/Cl\(^{-}\) ratio varies with respect to seawater. Elevated boron concentrations are common in thermal studies [66,87], since this element is adsorbed by oxides or clay minerals and can be released into the water due to changes in temperature. Stefánsson et al. [84] indicate that low temperature thermal waters increase their B/Cl\(^{-}\) ratios, almost reaching the common ratio for basalts (0.017), upon progressive leaching processes during water-host rock interaction.

Birkle et al. [71] used a logarithmic scale to represent the Br\(^{-}\) and Cl\(^{-}\) relationship between the mixture of meteoric water and seawater (Figure 8). It is observed that the Las Tres Virgenes thermal fluids are close to the relationship of seawater, inferring a direct mixture of marine water with groundwater recharge. In contrast, on the Br\(^{-}/\text{Cl}^{-}\) vs. B/Cl\(^{-}\) diagram [66], the sample LV4 is located close to the field defined as thermal water. Birkle et al. [71] described meteoric recharge as the main source. For LV4, the Br\(^{-}/\text{Cl}^{-}\) ratio similar to that of seawater also probably results from meteoric recharge, as indicated for the Bahía Concepción thermal sites, and would not correspond to a mixture with seawater in-depth (Figure 8). All samples maintain the Br\(^{-}/\text{Cl}^{-}\) ratio of seawater (Figures 7 and 8), however, the B/Cl\(^{-}\) ratio above 0.007 is a strong indicator to recognize MGW, considering anthropogenic inputs of boron in the area are negligible.
Figure 8. Diagram of log Cl$^-$ and log Br$^-$ showing samples from Bahía Concepción. LV-11 and LV-4 corresponding to the Las Tres Virgenes (LTV) geothermal water in depth [71,79].

5.2. Masked Geothermal Water (MGW)

The temperatures of the intertidal thermal springs (CB14, CB15, and CB16) were measured at around 58 °C in February 2018, and similar temperatures were reported previously [36,40,41], indicating only little temporal variations. The temperature at the sites CB2, CB3, CB7, CB8, CB11, CB13, CB17, and CB21 (Table 1) varied from 29.4 to 36 °C (6 to 12 °C above the annual average for the area), which corresponds to the common definition of geothermal sites (according to the annual average temperature), but their hydrogeochemical composition also supports this finding, particularly B, Mg$^{2+}$ and SiO$_2$ (Table 1).

The thermal springs CB14, CB15, and CB16 are closely related to seawater (more than 90%) and to the thermal end-member (Figure 8). The second group of samples (CB3, CB4, CB6, CB7, CB8, CB11, and CB21) are in the mixing zone between SWR and recharge, indicated by a depletion in Br$^-$ from freshwater. The sites for CB3, CB6, CB7, and CB8 represent a subgroup, where an increase in B/Cl$^-$ ratio indicates mixing with thermal water. Recharge of meteoric water explains most of the salinity for the rest of the sites (CB1, CB2, CB5, CB9, CB12, CB18, and CB19), mixed with a very low portion of other fluids (seawater fraction) (Table 4) and/or with the thermal end-member. As indicated by the Br$^-$/Cl$^-$-B/Cl$^-$ diagram (Figure 7) and B/Cl$^-$-Br$^-$ (Figure 9), recharge water is introduced to the aquifer with a proportion of seawater through aerosols. The sites CB2 and CB3 show a geothermal influence that has not been described before. These sites can be related to different mixing portions (Figures 6 and 9), where CB2 is very close to the recharge water (Figure 9) and the thermal end-member, and El Tordillo CB3 results from mixing with seawater due to seawater intrusion and thermal water-freshwater. At both sites, the water temperature was above 32 °C (Tables 1 and 2).
This type of water can be named Masked Geothermal Water MGW and would correspond to those located in the Concepcion Peninsula, which would also denote the water-rock interaction derived from the existence of a lower topographic slope from the upper part of the basin towards the discharge area, which delays the residence period of the water in the rock, as well as its distance between these. The foregoing allows the conclusion that the origin of the salinity is primarily of meteoric origin, with a signature of seawater in the aforementioned contexts, and the mixture of these with seawater intrusion and thermal water; therefore, it may be possible to determine that the analyzed samples present waters little altered by salinity from the thermal system, maintaining their signature of origin to a certain degree. This is in agreement with Villanueva-Estrada et al. [41] who defined a mixture of two-phase fluids, a primary mixture in the recharge and a secondary in the mixture with the thermal end member, for intertidal and submarine springs. Based on its relative temperatures, several sites would not fall into the category of thermal water, due to the arid climate of the Baja California Peninsula, although their hydro-chemical composition indicates clear influence through hydro-thermalism (the B/Cl− ratio was especially useful, as anthropogenic impact of boron in the study area can be negligible). This type of water can be named Masked Geothermal Water MGW and would correspond to the sites CB1, CB4, CB5, CB6, and CB19 with a B/Cl− ratio above 0.007.

5.3. Geothermal Water and Geothermometry

High salinity in thermal springs affects the calculation of reservoir temperatures through geothermometers [67,80]. Especially, the seawater fraction modifies not only the cation ratios, but also the SiO2 concentration; therefore, in this study, corrected reservoir temperatures were calculated without the seawater component (Table 4, Figure 10). For that purpose, a mixing model was constructed, based on four end-members (SWR [73], CB11, EMPL [34], and LV4 [79]), explaining the composition of the five thermal springs (CB2, CB3, CB14, CB15, CB16). As multiple combinations are possible, the chosen model seeks the simplest explanation, in agreement with the Br−/Cl− and B/Cl− diagram (Figure 7), which indicates the strong influence of seawater on CB14, CB15 and CB16. The model

![Figure 9. Br− and B/Cl− ratio for samples at Bahia Concepcion and their relationship with the end-members LV4 [79], seawater (SWR) [73], Recharge [34], theoretical end member (EMPL) [36].](image-url)
considers the concentration of Cl$^-$ as the main benchmark; furthermore, Na$^+$, Mg$^{2+}$, and SiO$_2$ were taken into account to find the proportions of each member, respectively.

**Table 4.** Results from the mixing model and seawater exclusion. Ionic concentration in mg/L.

| Sample | EMPL (%) | LV4 (%) | SWR (%) | CB11 (%) | Original Data | Seawater Excluded |
|--------|----------|---------|---------|----------|---------------|-------------------|
| | | | | | Na$^+$ | K$^+$ | Mg$^{2+}$ | SiO$_2$ | Na$^+$ | K$^+$ | Mg$^{2+}$ | SiO$_2$ |
| CB2    | 99.1     | 0.6     | 0       | 0.4      | 112           | 4     | 15     | 79      | 65     | 8     | 22     | 83     |
| CB3    | 84.4     | 0       | 4       | 11.6     | 615           | 32    | 236    | 122     | 717    | 65    | 20     | 128    |
| CB14   | 16.5     | 0       | 72      | 11.5     | 7225          | 446   | 404    | 75      | 2357   | 213   | 14     | 243    |
| CB15   | 6.5      | 0       | 83.5    | 10       | 8150          | 455   | 519    | 79      | 3455   | 313   | 9      | 319    |
| CB16   | 20.5     | 0       | 62.5    | 17       | 7100          | 521   | 276    | 212     | 2595   | 235   | 13     | 259    |

$^*$ Mg$^{2+}$ from Las Virgenes geothermal field. $^1$ Deep thermal seawater. $^2$ Deep thermal freshwater. $^3$ Seawater reference. $^4$ Local recharge water.

Original and corrected data were used to construct ternary Na$^+$-K$^+$-Mg$^{2+}$ diagrams and a Cl$^-$-SiO$_2$ plot, as well as to employ a SiO$_2$ geothermometer [67] to obtain the equilibrium reservoir temperatures in the Bahía Concepción region.

The ternary Na$^+$-K$^+$-Mg$^{2+}$ diagram [70,89], with the influence of seawater (Figure 10a), shows that intertidal thermal springs fall into the partial equilibria field indicating an equilibrium temperature between 190 and 210°C, while sites CB2 and CB3 correspond to immature water. In contrast, after the effect of seawater was removed (Figure 10b), intertidal thermal springs moved closer toward the equilibrium line, indicating a homogeneous temperature of 220°C, which is equal to that calculated for the EMPL. CB3 shift closed to the partial equilibria field.

On the other hand, when seawater is removed, a substantial increase (up to six times) of the SiO$_2$ concentration was observed (Figure 11). This fact led to a more reliable estimation of the equilibrium reservoir temperature, applying the SiO$_2$ geothermometer.

According to the data from the SiO$_2$ geothermometer (Table 5), two groups of geothermal sites can be distinguished. One group, formed by the intertidal thermal springs, showed a wider interval of temperature (108 to 175°C) without the correction for seawater. Conversely, removing the seawater effect led to an increase (and a narrower range) in the calculated temperature (186 to 209°C), which is close to the obtained temperature in the Na$^+$-K$^+$-Mg$^{2+}$ diagram. The second group (CB2 and CB3) is little affected by seawater correction. Slightly lower temperatures (151–188°C) were calculated by Prol-Ledesma et al. [36] for submarine thermal springs in Bahía Concepción. The obtained temperatures from SiO$_2$ geothermometers are also similar to the results from different geothermal sites, such as Aysen, Chile [9] Doña Juana, Colombia [90], Java Island [91], South Island, New Zealand [92], and Simao, China [93].

**Table 5.** Surface and equilibrium reservoir temperatures, based on a SiO$_2$ geothermometer. After Arnórsson [67].

| Site     | Surface Temperature (°C) | Equilibrium Reservoir Temperature | Original Data | Seawater Excluded |
|----------|--------------------------|----------------------------------|---------------|-------------------|
| CB2      | 36.4                     |                                  | 112           | 141.4             |
| CB3      | 32.7                     |                                  | 137           | 140.3             |
| CB14     | 53.4                     |                                  | 108           | 186.6             |
| CB15     | 42.1                     |                                  | 110           | 209.9             |
| CB16     | 58.6                     |                                  | 175           | 191.9             |
Due to the small extension of the hydrological watershed and its geological-structural characteristics, it is assumed that at least two levels of groundwater flow occur (Figure 12):
(a) a shallow flow system (Groundwater Shallow level (GWSL)) of rapid circulation in the porous aquifer, constituted by sedimentary deposits in streams and alluvial terraces, in which a short period of residence time between recharge and discharge towards the coastline is presumed [78]; (b) a deeper infiltrated flow system (Groundwater deep level (GWDL)), related to structural discontinuities that affect volcanic and volcanoclastic rocks, generating significant secondary permeability. The geothermal system in depth mainly receives seawater inflows [36]. This recharge occurs when the main faults cross the seabed, providing more seawater influence; Prol-Ledesma et al. [36] and Santos et al. [94] have evidenced a dilution of seawater in the submarine vents of the area. Heated seawater is considered a significant source of submarine groundwater discharges (SGD), involving relevant geochemical processes such as nutrients and pollutants transport [95,96]. Nevertheless, novel findings herein documented indicate the important role meteoric water plays in the recharge of the deep thermal reservoir.

The participation of a high saline thermal end-member in the geothermal system of Bahía Concepción was previously proposed by Villanueva-Estrada et al. [41]; however, the mixing relationships found in this study did not show any evidence for this. In contrast, the existence of a probable deep thermal freshwater end-member was inferred, in agreement with Prol-Ledesma et al. [36].

6. Conclusions

The results obtained explain important processes involved in the mixing of groundwater in contact with seawater, e.g., water–rock interaction, rainwater effects. The use of $\text{Br}/\text{Cl}$ and $\text{Br}/\text{Cl}$ relationships, coupled with hydro-geochemistry and geo-thermometry, allowed the recognition of five MGW in the coastal area of Bahía Concepción (sites CB1, CB4, CB5, CB6, and CB19). It is proposed to apply this methodology in other coastal areas with geo-thermalism of low enthalpy, in order to evaluate potential environmental impacts. Seawater represents the most common origin of salinity (up to 83%) in the coastal thermal spring of Bahía Concepción. Even, sites far from the coastline showed the common $\text{Br}/\text{Cl}$ ratio of seawater, due to local rainfalls that incorporate aerosols and spray water droplets from the sea. Thermal springs in the study area are associated with the El Requesón fault, which is the main tectonic structure on the western margin. Geothermal springs related to the Concepción fault were not found; however, the occurrence of MGW indicates the presence of hydro-thermalism. The temperature in the deep geothermal reservoir varies from 114 to 209 °C. This research contributes to an increase
in knowledge of geothermal resources, improving their future use and management in a sustainable framework.

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