

## Use of Arsenic as a Complementary tool in Geothermal System Exploration

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### ABSTRACT

In the present work arsenic has been used in among with conservative elements Cl, B and Li, as a complementary exploration tool in geothermal systems. Ternary diagrams have been used, plotting Cl-HCO<sub>3</sub>-SO<sub>4</sub>, Cl-B-Li, Cl-SiO<sub>2</sub>-As y Cl-As(T)-As(III), in order to identify possible mixtures trends that could be occur in a geothermal exploration area. Diagrams log-log have been used to plot Cl vs B, Cl vs As(T) and Cl vs As(III) in order to identify through trend line the possible up flow zones in a geothermal system; which is evidenced by the linear correlation of these elements. Thus, additionally have been graphed As(T) /As(III) ratio contours that shows areal geochemical anomalies and could suggest the presence of geothermal up flow zone areas. Published data from Miravalles Geothermal Field, Costa Rica has been used in the present work.

### 1. INTRODUCTION

In environmental impact studies, the determination of arsenic (As) baseline has been usually considered in order to monitor the damage to the environment could occur during geothermal system exploitation, it was not yet considered their potential use as an exploration tool. Studies carried out in several geothermal fields prior to their exploitation have identified the mixture of arsenic rich groundwater with surface cold aquifers, producing pollution problems, the presence of As in spring for human consumption as well as for use in irrigation and agriculture soils around thermal manifestations exceed permissible limits for WHO, involving a high health risk conditions for the population close to the areas of development geothermal areas (Esetlili M. T. et al, 2014). In geothermal operation systems has been put special attention to geothermal discharges by the possible As increases in the natural manifestations due to the fast path discharges from the deep depth at the surface during the geothermal reservoir exploitation.

The present study has considered the use of arsenic as a complementary geochemical exploration tool in conjunction with the conservative elements Cl, B and Li.

### 2. BACKGROUND

The presence of arsenic has been commonly associated with fluid thermal manifestations discharges from areas of active volcanism in different studies around the world, highest concentrations of arsenic have been found in waters Na-Cl, determining arsenic content in hot springs, is depending on nature of the host rock, interaction water rock and reservoir temperature (Birkle et al., 2010), (Giggenbach 1988).

Hot springs analyses in Taupo volcanic area in New Zealand performed by Richie J. (1961), revealed a positive correlation between As and Cl which has been confirmed in many geothermal fields. Stauffer R. and Thompson J. (1984) noted the relationship between arsenic and salinity in geothermal waters in Yellowstone. Additional comparisons between relations As/Cl and Cl/B were useful, due to boron acts conservatively in solutions, if the As, Cl and Li were all derived from a common reservoir and conservative behavior during the migration of the fluid. Cl/As relationship can be used as a tool to trace the effects of dilution in geothermal water.

Arehart G. et al (2003) used the concentrations of arsenic and relations Li/Cl, B/Cl, and Ce/Cl, as a tool to differentiate a magmatic system of an extensional system; the slopes of the arsenic - temperature between extensional and magmatic systems relations differed clearly, concluding that the magmatic systems have considerably more content of arsenic than the extensional systems.

Arehart and Donelick, (2006) used elements traces conservatives like geothermal exploration tools, since water-rock geochemical reaction reacts at temperatures higher than 100°C releasing Li, As and (B); Besides knowing the correlation with Cl on Cl type water within the Basin and Range of Nevada and New Mexico Rio Grande rift geothermal waters, it is assumed that elements traces are retained in the phase liquid relative high concentrations as well as they ascend from a geothermal reservoir to cold surface aquifers.

Lopez et al, 2012, have described in detail four possible paths of geothermal fluids can ascend to the surface, changing its chemical composition due to physical-chemical processes:

- 1) If the upflow (for example along a fault zone to the surface) is fast, with a minimal lost of conductive heat to the wall rock, the composition of the discharging water is similar to the reservoir water producing a Na-Cl rich water, with near neutral pH, high silica content due to the long rock-fluid interaction, sulfate concentrations lower than Cl concentrations, and enrichment in CO<sub>2</sub>

and H<sub>2</sub>S gases. These are the mature Na-Cl waters described by Giggenbach (1988). Consequently, these waters should present As concentrations close to reservoir concentrations.

- 2) If a vapor phase rich in H<sub>2</sub>S separates from the reservoir due to pressure changes, and the vapor condenses at shallower levels, acid sulfate waters low in Cl are formed (Giggenbach, 1988). According to Birkle et al (2010), these condensed waters are low in As because As is partitioned preferentially into the reservoir water instead of the vapor phase, leaving water enriched in As in the lower evaporated aquifer.
- 3) If the upflow of Na-Cl waters occurs in such a way that the waters have time to oxidize, H<sub>2</sub>S is oxidized to sulfate (and different species of sulfate in solution such as  $\text{HSO}_4^-$ ) and pH of water decreases. These are the acid sulfate-Cl waters described by Giggenbach (1988) in volcanic settings. As the As-rich waters ascend and get close to the atmosphere, oxygen-rich waters can mix with the geothermal waters, or soil air in the unsaturated zone, promoting the conversion of As(III) to As(V) and precipitation of As minerals if the concentrations are high enough.
- 4) Mixing of Na-Cl waters with shallower meteoric waters can produce the bicarbonate rich waters described by Giggenbach (1988).

Pearson M et al (2015), combined geochemistry trace elements and analysis of hydrological tracers to identify upflow zones areas of geothermal systems in southwestern New Mexico, USA.

At date it has full knowledge of correlations of Cl with elements B, Li, Br and As, but the literature concerning to the use of the As as a geothermal exploration tool is scarce. This paper tries to give steps in this direction using published data from Miravalles geothermal field Costa Rica carried out by Hammarlund and Piñones (2009) for their thesis degree work, where sampling procedures and analysis methods have been described in details.

### 3. STUDY CASE MIRAVALLES GEOTHERMAL FIELD, COSTARICA (HAMMARLUND AND PIÑONES, (2009))

Miravalles geothermal area is located in the northwestern part of Costa Rica in the Guanacaste Mountain range of Guanacaste Province (Figure 1). Miravalles volcano is a Quaternary strato-volcano rising to 2028 masl and is currently inactive. The geothermal reservoir is high-temperature and liquid-dominated. Miravalles field area is characterized by the Guayabo caldera which is an active hydrothermal system of a caldera-type collapse structure of about 15 km diameter (Bundschuh et al. 2002; Vega et al. 2005). The highest reservoir temperature measured was 255 °C with typical measured temperatures ranging between 230-240°C. The north-eastern part of the Guanacaste Cordillera seems to be the main recharge zone. In order to study the hydrologic relations between the reservoir and the surface water bodies samples were taken from zones surrounding Miravalles geothermal field and geothermal well fluids. Here 53 wells were drilled; 32 of them are used for production while 14 wells are used for gravity injection of residual waters.



Figure 1. Geographical map of Costa Rica showing location of main volcanoes and Miravalles geothermal field.

Miravalles geothermal field is located inside the Guayabo caldera (Figure 2), which formed during the Pleistocene after three separate phases of volcanic activity. Within the Guayabo caldera the volcanic activity gradually shifted in a northwest direction and then south-westwards during these phases. Revealing the existence of strong tectonic activity, four main fault systems have been identified in the

area (Gherardi et al. 2002) all of which contribute to the hydraulic permeability of the geothermal reservoir (Vega et al. 2005). In order of decreasing age, they are oriented:

- 1) NW-SE direction sub-parallel to that of the main Central-American mountain chain, and, in particular, to the axis of the Guanacaste volcanic belt.
- 2) N-S, formed during the Holocene, has produced a graven-like structure about 3 km in width known as La Fortuna Graven (Figure 2). La Fortuna graven has displaced part of the Guayabo caldera and forms the eastern and western margin of the geothermal field.
- 3) NE-SW, sub-parallel to the migrating eruptive centers of the Miravalles volcano
- 4) E-W, intersects the graven surface, and has been encountered in several productive wells. This is the youngest fault system and is expressed at the surface as hydrothermal alterations, sulfataras, mud volcanoes and hot springs (e.g., Las Hornillas at Hornillas fault) (Gherardi et al. 2002; Vega et al. 2005).



Figure 2: Geological-structural map of Miravalles geothermal reservoir and well field located in Guayabo caldera. The Map section of La Fortuna graben is enclosed by a black frame (Birkle and Bundchuh 2007).

The highest temperatures are found in the north of the production zone indicating that,

- 1) the heat source is related to the Paleo-Miravalles and Miravalles volcanoes, and
- 2) The fluid movement is generally north to south.

This provides the conceptual model of Miravalles geothermal reservoir shown in Figure 3. From this figure can be observed that the temperature of the production zone decreases to the south, east and west (Vega et al. 2005).

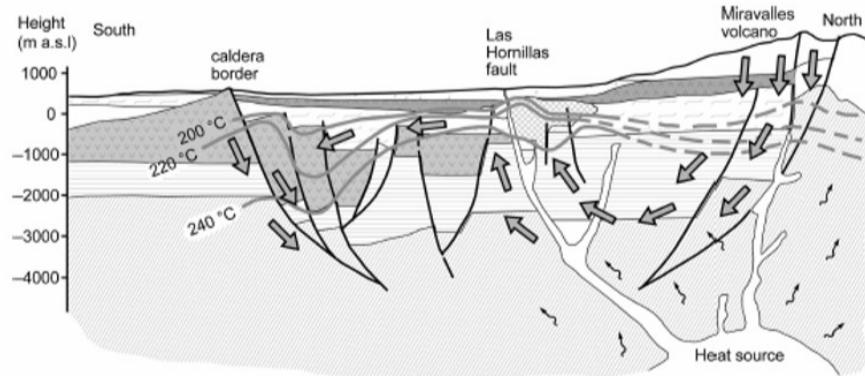


Figure 3: Conceptual model of Miravalles geothermal reservoir, with a heat source related to Miravalles volcano. Also shown are main aquifer systems of the geothermal reservoir with flow directions, which are influenced by major faults (e.g. Las Hornillas fault) (Birkle and Bundchuh 2007).

There are three types of water associated with natural manifestations in the Miravalles area, other than of geothermal reservoir water:

- 1) Cold water from streams, shallow aquifers and rivers,
- 2) Neutral pH thermal waters
- 3) Sulphate-rich acid thermal waters.

The neutral pH waters emerge from the inside of the caldera, following a N–S trending belt that coincides with La Fortuna graven, while the manifestations of sulphate-rich acid waters are found along the slopes of the volcano at relatively high elevation (> 500 m a.s.l.). The surface waters are present over the whole area and form a dense hydrographic network of streams of relatively low flow-rate. The largest thermal manifestations in Miravalles volcano are located in Las Hornillas zone (Figure 4). Thermal manifestations contain lakes and acid-sulphate springs, steaming ground, fumaroles emissions, small craters and mud volcanoes (Gherardi et al 2002)

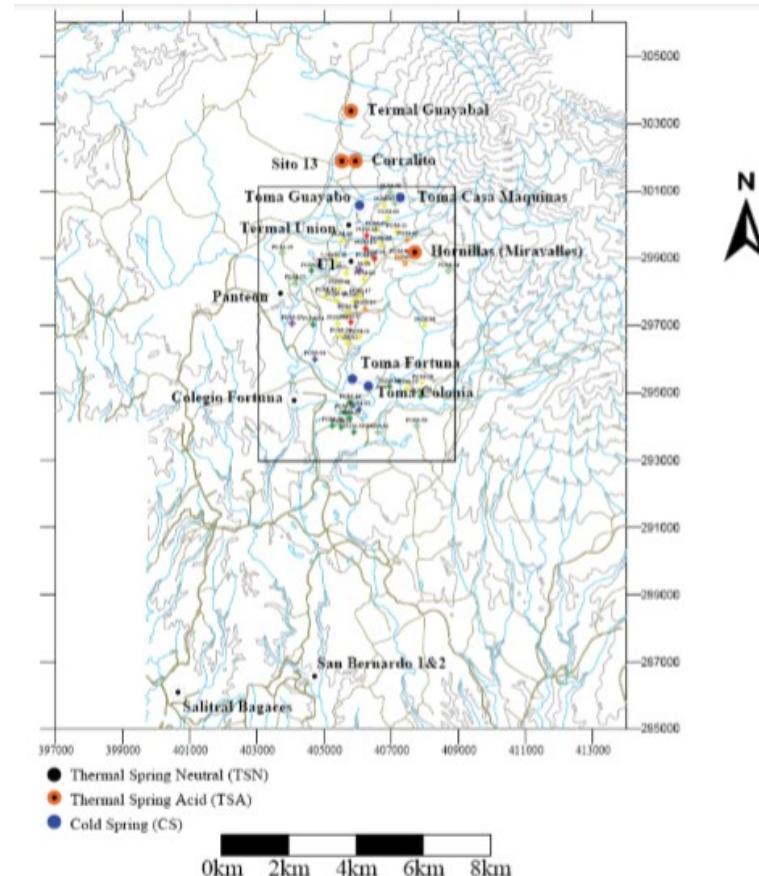


Figure 4. Map of spring locations around Miravalles. (From Hammarlund and Piñones, 2009)

#### 4. USING TRACERS ELEMENTS IN GEOTHERMAL EXPLORATION

It has been proposed the use of the As as a exploration tool in geothermal areas, using ternary diagrams Cl-HCO<sub>3</sub>-SO<sub>4</sub>, Cl-B-Li, Cl-12SiO<sub>2</sub>-635As (III) and Cl-226AS (T) - 635As (III), for the characterization of the sampled waters. The log-log graphs B vs Cl, As (T) vs. Cl and As(III) vs Cl, have been used for determining the linear correlation, identifying the possible upflow of geothermal fluids in according with the highest values of elements in analysis.

According to López et al, 2012, the up flow discharge is rich in As(III) when they are arising to the surface, this mix with surface waters rich in oxygen or by the presence of air in the non-saturated zones, promoting the conversion of As(III) to As(V), then the relationship As (T)/As (III) indicates the process of mixing with surface water. The values contours diagram on surface of the relationship As (T)/As (III) surface water could be identify anomalous geochemical zone in the area of research associated with an up flow considering that As(III) specie as the representative parent As from the reservoir.

## 4.1 Ternary Diagram Use

Cl-SO<sub>4</sub>-HCO<sub>3</sub> Ternary diagram (Figure 5A) was used to classify the waters in the study area, showing that most of the waters are Bicarbonate type (blue circles), hot springs are the Sulfated type (yellow circles) and the geothermal wells waters are located at the apex of the chloride waters (red circles).

Cl/100-B/4-Li Ternary diagram (Figure 5B) indicates that the hot springs sampled (yellow circles) and the waters wells in operation (red circles) of the study area correspond to a geothermal system old except the 19 sampling point. Peripheral waters plot in a younger geothermal system.

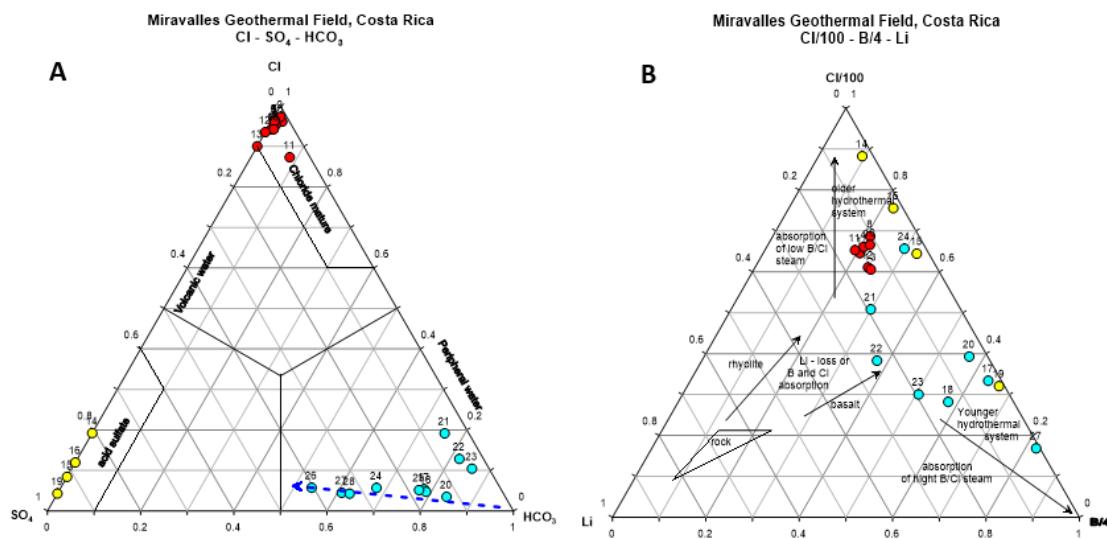
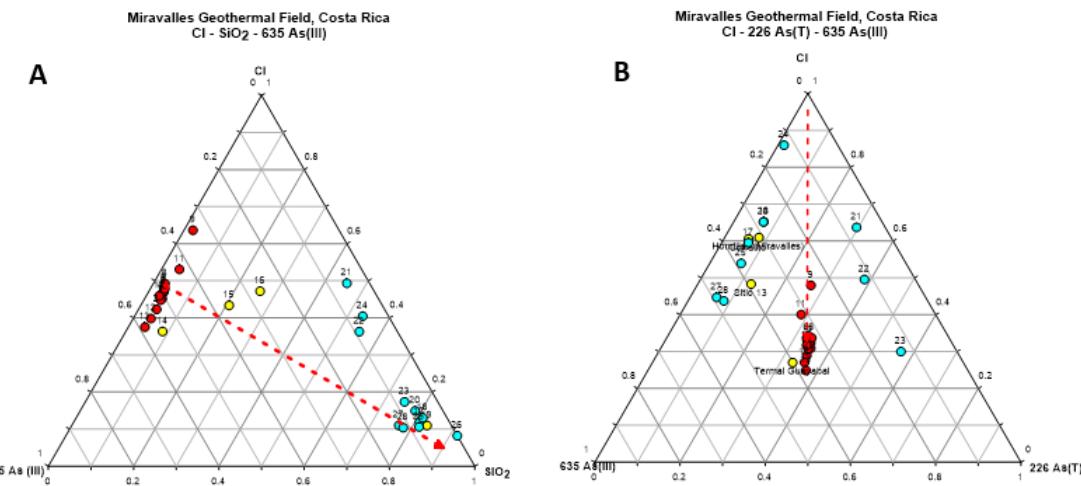


Figure 5 A) Cl-HCO<sub>3</sub>-SO<sub>4</sub> Ternary diagram B) Cl/100-B/4-Li Ternary diagram

Cl-SiO<sub>2</sub>-635As Ternary diagram (Figure 6A) shows that all geothermal wells in operation plot near the axis 635 As (III), they have the highest values of chlorides and As(III) (red circles); from surfaces water Termal Guayabal (point 14, yellow circle) have the highest content of As(III), and meteoric waters (blue circles) have the lowest content of chlorides and arsenic.

Cl-226As (T) - 635As(III) Ternary diagram (Figure 6B) shows a trend line of geothermal wells in exploitation and water sampled from Termal Guayabal plots next to the trend line, as an evidence of a possible common source.

Figure 6 A) Cl-SiO<sub>2</sub>-635As (III) Ternary diagram B) Cl-226As (T)-635As (III) Ternary diagram

#### 4.2 Log-log Diagram: B vs Cl and As(T) vs Cl, As(III) vs Cl.

Values of B vs Cl have been plotted (Figure 7A) and shows that geothermal wells and hot springs are plotted below the rock dissolution line (Sanchez D. 1993), the yellow circles represent hot springs waters and the circles red geothermal wells waters, bicarbonate waters graphed on the bottom left with the smaller contents of chloride and arsenic. The hot springs have B values from 1,833 to 3.03 mg/l; and geothermal wells waters B values vary from 33.9 to 60.1 mg/l.

As (T) vs Cl diagram (Figure 7B) shows a trend line with some scattered points, geothermal wells present the As (T) highest concentrations with values between 11.86 and 29.13 mg/l (red circles), values of As (T) in hot springs (yellow circles) vary between 0.017 and 4,564 mg/l and they are scattered from the trend line, cold springs have As (T) concentration values between 0.281 and 0.005 mg/l.

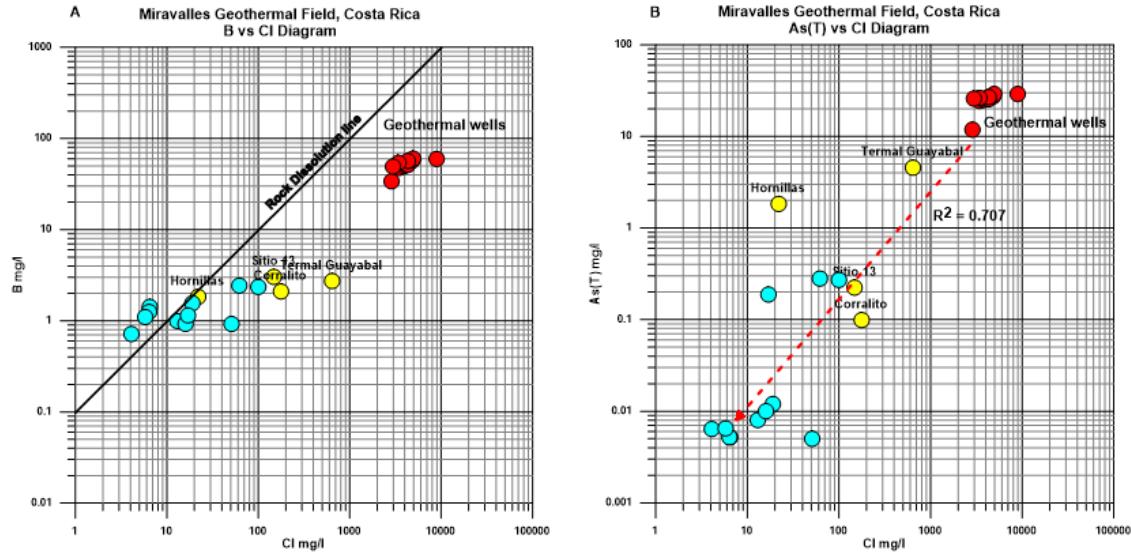


Figure 7 A) B vs Cl diagram B) As(T) vs Cl diagram

In Figure 8A, it has plotted values of As (III) vs Cl, the trend line is best defined, As (III) concentration of geothermal wells waters (red circles) vary from 3.63 to 7.69 mg/l, hot springs concentrations vary from 0. 018 to 1.531 mg/l and As (III) values for cold springs range from 0.024 to 0.0075 mg/l, so it can be deduced that Termal Guayabal is close to the area of upflow zone (Figure 8B) and presents a biggest As(III) concentration of surface waters and not mixing with surface water (Figure 5A).

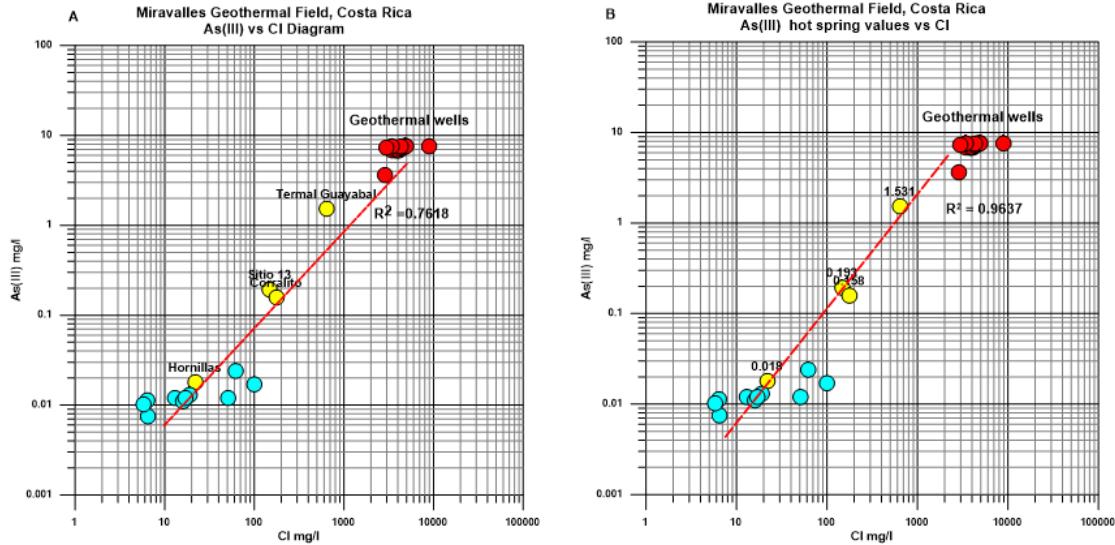


Figure 8 A) As(III) vs Cl diagram B) As(III) vs Cl (concentrations) diagram

#### 4.3 Arsenic Contours Diagram

Figure 9A shows the contours of relationship As (T)/As (III) for surface water of the exploration area, contour with value equal to the unity has been marked with a dashed black line, indicating the possible upflow of the system; that is bordering to the North with El Corralito and Sitio 13, South to Toma Colonia and Colegio Fortuna. Toward the Southern the relationship As (T)/As (III) in San Bernardo 1 and Salitral Bagaces have values close to 16, indicating that in this area the geothermal fluids have undergone a process of mixing with cold waters with high oxygen content reducing the content of As(III) and transforming to other As species, this feature is identified as the outflow zone of the geothermal system. Figure 9B shows the contours As (T)/As (III) considering geothermal wells in exploitation and surface waters, geothermal wells graphed within the unity area determined initially considering only the surface waters values of As (T)/As (III).

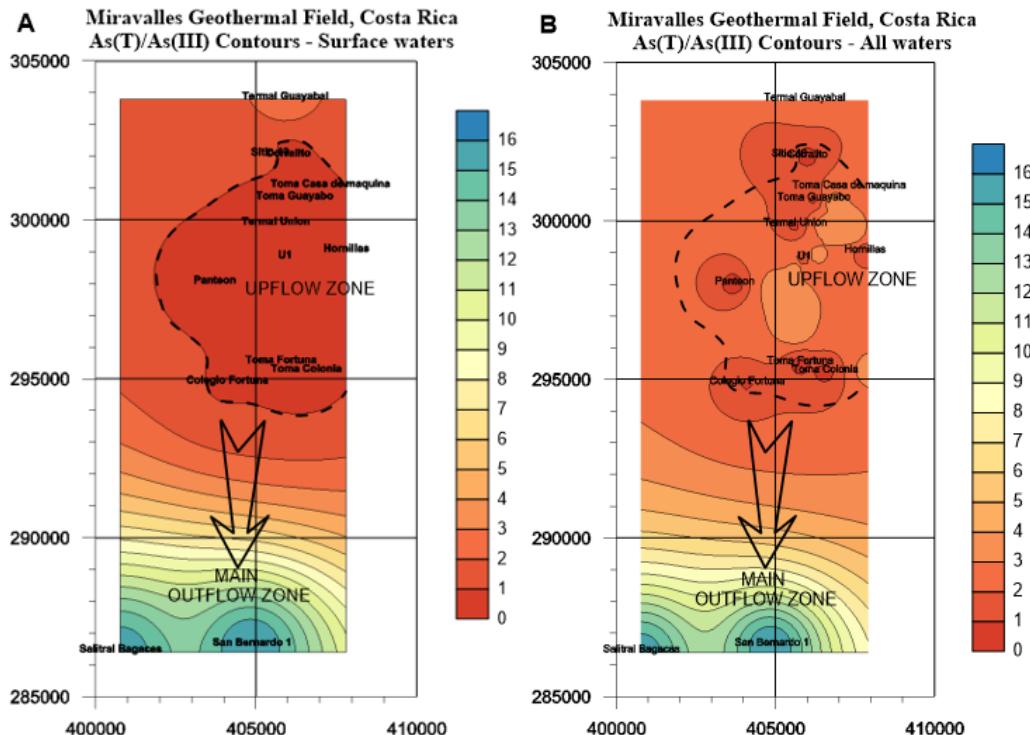


Figure 9 A) Contours diagram As(T)/As(III) Surfaces waters B) Contours diagram As(T)/As(III) all waters

Figures 10A and 10B have plotting As (T) and As (III) contours respectively considering all the values of the water sampled in the study area (surface and geothermal waters), these show that the greatest values As (T) and As (III) from geothermal wells plot inside the unity anomaly demarcated by the initial relationship As (T) / As (III) in surface waters indicated by the dashed black line; analysis from Figure 9B, 10A and 10B suggests that the relationship As (T)/As (III) could be a potential geochemical exploration tool that would help to identify the geothermal upflow zone.

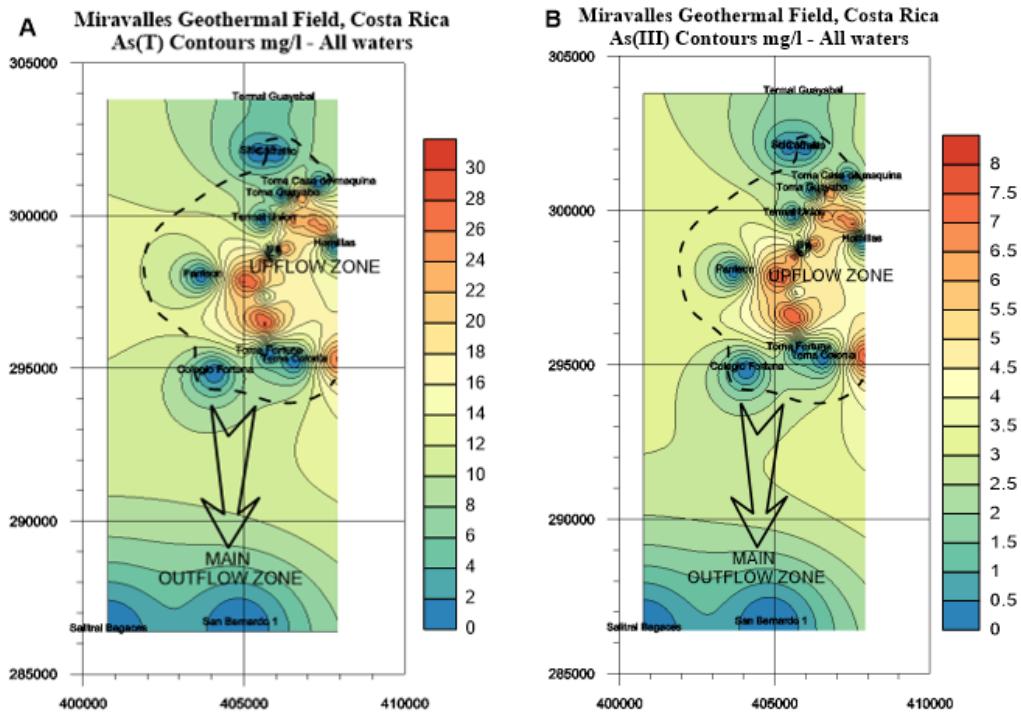


Figure 10 A) Contours diagram As(T) All waters B) Contours diagram As(III) all waters

## 5. CONCLUSION AND RECOMMENDATIONS

In the present study has been determined that log-log plot As (III) vs Cl presents a best linear correlation with respect to log-log plots B vs Cl and As (T) vs Cl.

It has been used log-log and triangular diagrams to identify the most representative sites of a geothermal system in exploration and by means of contours graphics of relationship As (T)/As (III) has been able to identify As geochemical anomaly area that could be interpreted as a possible geothermal system upflow zone in North area (Termal Guayabal, Hornillas) and the outflow zone in the South area (San Bernardo 1, Salitral Bagaces).

The relationship As (T)/As (III) unitary indicates geothermal upflow zone considering that As(III) is the dominant reservoir As specie, while high values indicate dilution with surface waters containing high oxygen, that promotes the As(III) conversion to other As species, reducing the As(III) content, this is associated to geothermal outflows.

It is necessary to point out that published As data is scarce specially for the initial geothermal exploration stages, and it is recommended to include As (T) and the As (III) analysis in the geochemistry exploration survey, in order to use them as an additional geochemical exploration tool.

It is recommended the use of the methodology proposed in new geothermal exploration fields that have available As (T) and As (III) data, in order to verify its application in liquid dominated geothermal systems.

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