

Use of Arsenic as a Complementary Tool in Geothermal System Exploration

Hermas Alberto Dávila José
Nagarote, parque central ½ cuadra al Oeste, Nicaragua
hermasdavila@enel.gob.ni

Keywords: As(T)/As(III) ratio, speciation arsenic, geochemical exploration tool

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-HCO₃-SO₄, Cl-B-Li, Cl-SiO₂-As y Cl-As(T)-As(III), in order to identify possible mixtures trends that could 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 upflow 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 show areal geochemical anomalies and could suggest the presence of geothermal upflow 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 field 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 cold surface 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 geothermal development 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 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 these waters with 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 of 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 keep 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 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 occurs 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.

López 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 loss 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 CO₂ and H₂S 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 H₂S 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_2S is oxidized to sulfate (and different species of sulfate in solution such as 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).

Investigation of geothermal waters in deep wells and hot springs collected from western Anatoly, Turkey; carried out by Bundschuh et al. (2013) shows the dominance of reduced As species, i.e., As(III).

Pearson 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 referring to As use 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, where sampling procedures and analysis methods have been described in details.

3. MIRAVALLS GEOTHERMAL FIELD, COSTA RICA (HAMMARLUND L. AND PIÑONES J.)

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 stratovolcano 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 typically 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.

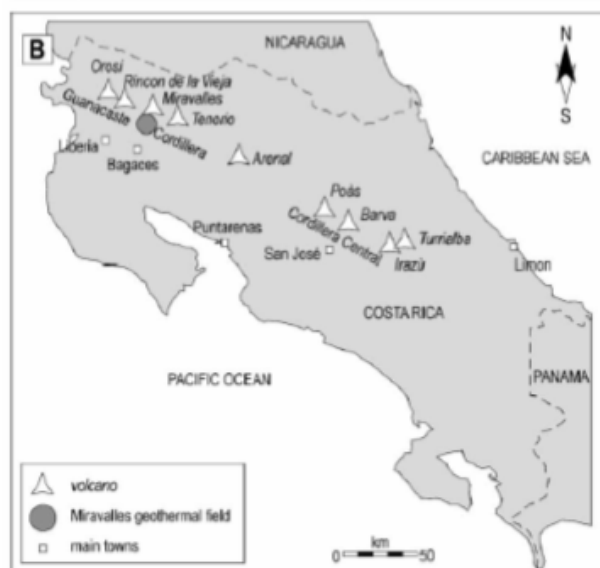


Figure 1: Geographical map of Costa Rica showing the location of the main volcanoes and Miravalles geothermal field (From Hammarlund L. and Piñones J. 2009).

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. 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, solfataras, mud volcanoes and hot springs (e.g., Las Hornillas at Hornillas fault) (Gherardi et al. 2002; Vega et al. 2005).

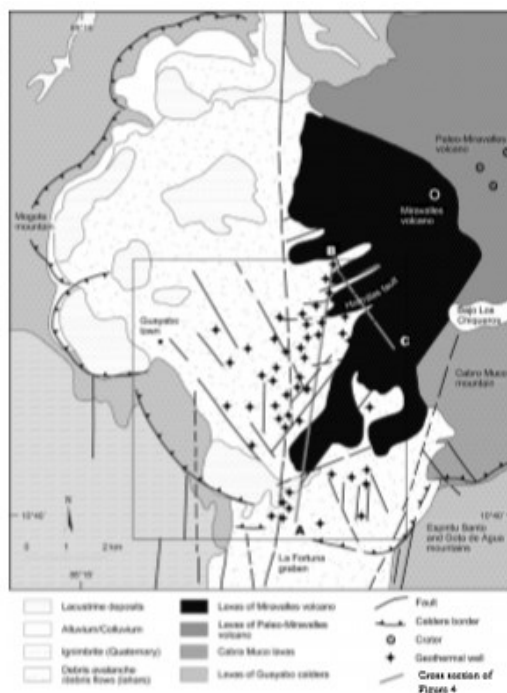


Figure 2: Geological-structural map of Miravalles geothermal reservoir and well field located in Guayabo caldera. The Map section of La Fortuna graben is enclosed by a black frame (Birkle and Bundschuh 2007).

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 the 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).

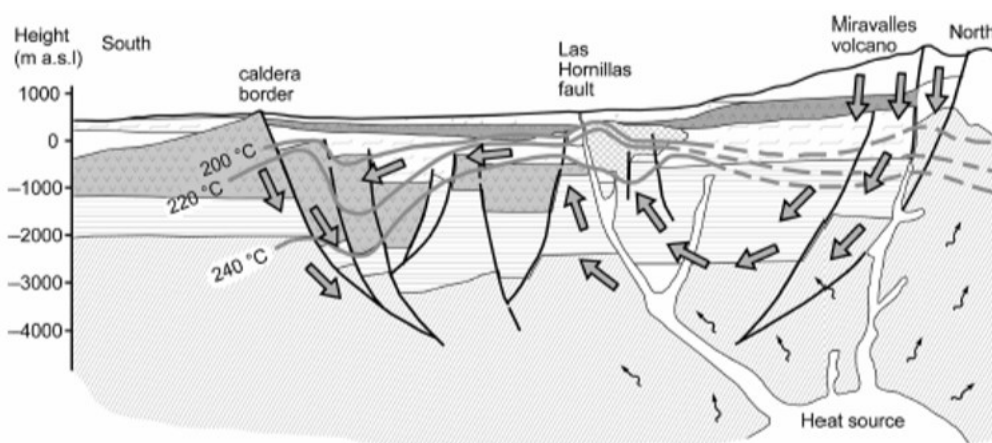


Figure 3: Conceptual model of Miravalles geothermal reservoir, with a heat source related to Miravalles volcano. Also shown are main aquifer systems of the geothermal reservoir with flow directions, which are influenced by major faults (e.g., Las Hornillas fault) (Birkle and Bundschuh 2007).

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

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

Dávila.

The neutral pH waters emerge from the inside of the caldera, following an N–S trending belt that coincides with La Fortuna graben, 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)

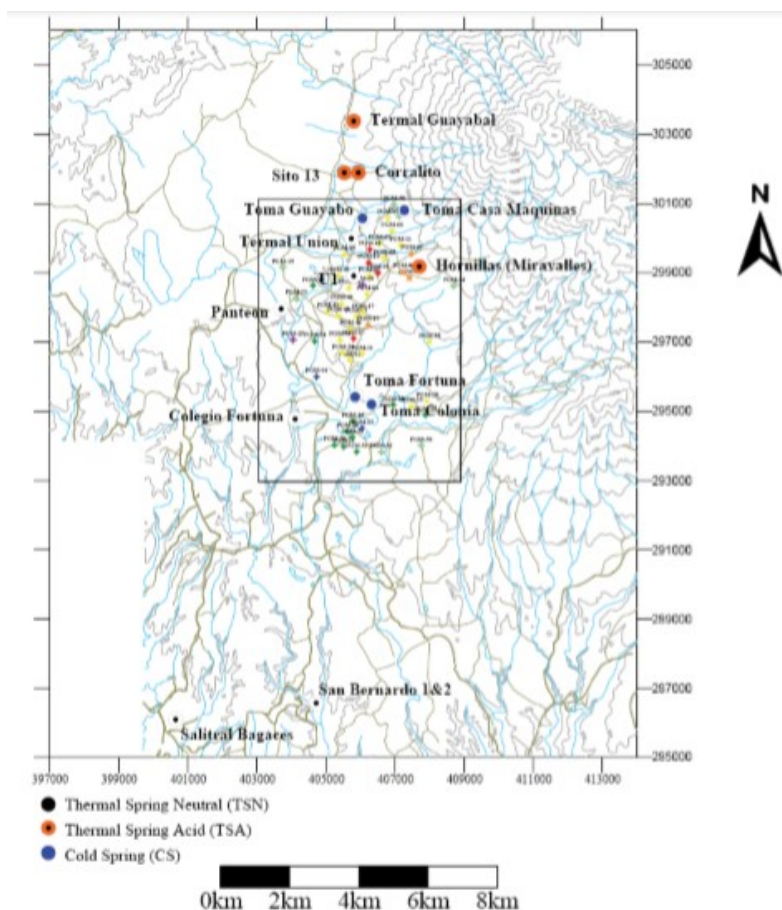


Figure 4: Map of spring locations around Miravalles. (From Hammarlund L. and Piñones J. 2009)

4. METHODOLOGY

It has been proposed the use of As as an exploration tool in geothermal areas, using ternary diagrams $\text{Cl-HCO}_3\text{-SO}_4$, Cl-B-Li , $\text{Cl-12SiO}_2\text{-635As}$ (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 up flow of geothermal fluids in according with the highest values of elements in analysis.

According to López et al., 2012, the upflow discharge is abundant 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 $\text{As(T)}/\text{As(III)}$ indicates the process of mixing with surface water. The values contours diagram on surface of the relationship $\text{As(T)}/\text{As(III)}$ surface water could be identified as an anomalous geochemical zone in the area of research associated with an upflow considering that As(III) species as the representative parent As from the reservoir.

5. RESULTS

Ternary diagram $\text{Cl-SO}_4\text{-HCO}_3$ (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).

Ternary diagram $\text{Cl}/100\text{-B}/4\text{-Li}$ (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.

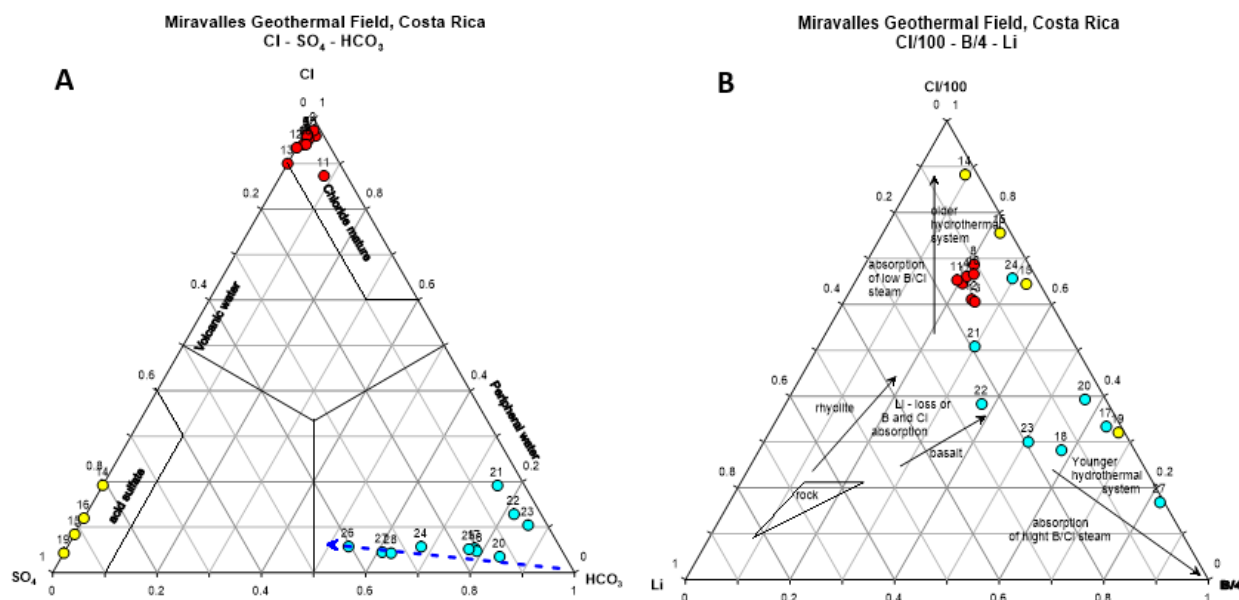


Figure 5: A) Ternary diagram Cl-HCO₃-SO₄ B) Ternary diagram Cl/100-B/4-Li

Ternary diagram Cl-SiO₂-635As (Figure 6A) shows that all geothermal wells in operation plot near the axis Cl-As(III), they have the highest values of chlorides and As(III) (red circles); from of surfaces water Termal Guayabal (point 14, yellow circle) has the highest content of As(III), meteoric waters (blue circles) have the lowest chlorides and arsenic content.

Ternary diagram Cl-226As(T)-635As(III) (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.

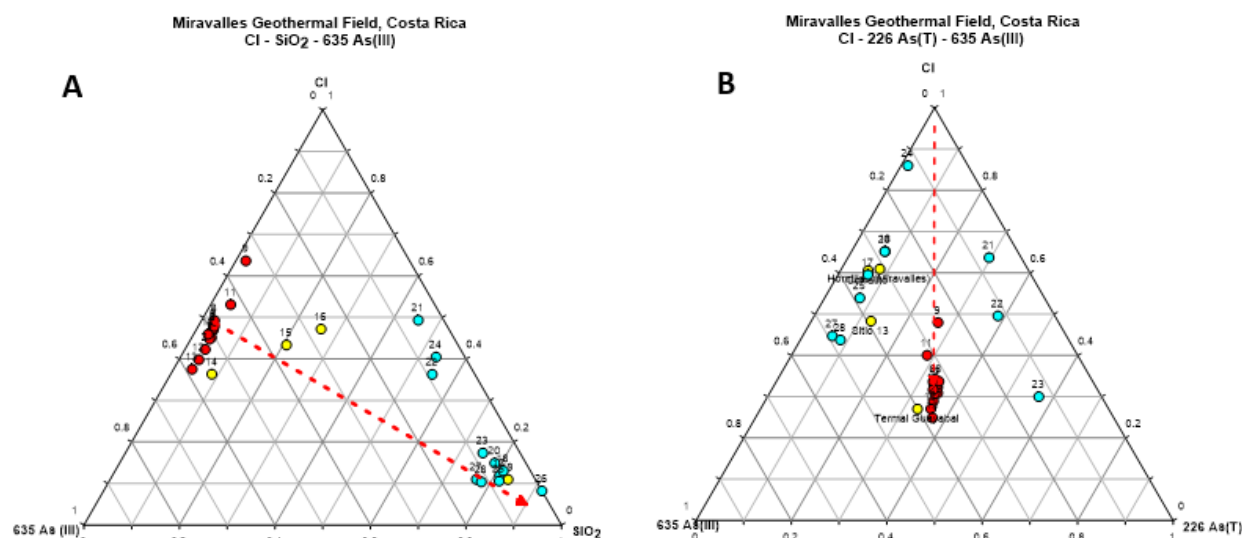


Figure 6: A) Ternary diagram Cl-SiO₂-635As (III) B) Ternary diagram Cl-226As (T)-635As (III)

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 according with Sanchez D. (1993), the yellow circles represent hot springs waters and the red circles geothermal wells waters, bicarbonate waters graphed on the bottom left with the smaller contents of chloride and arsenic (blue circles). 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.

Figure 7B, As(T) vs. Cl shows a trend line considering only surfaces water with some scattered points, the correlation value is 0.707, 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.

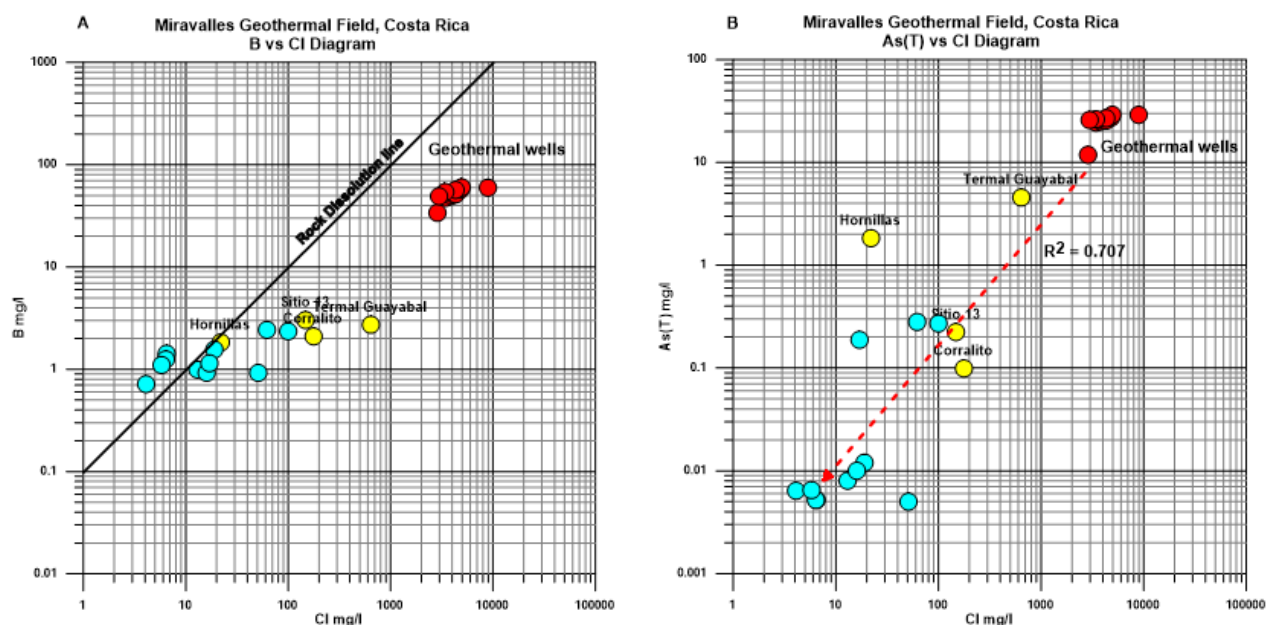


Figure 7 A) B vs Cl diagram B) As(T) vs Cl diagram

In Figure 8A, it has plotted values of As(III) vs Cl, the trend line considering only surface water has improved the correlation value to 0.7618, 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 Terral Guayabal is close to the area of upflow zone, (Figure 8B) shows the trend line considering just only hot springs, the correlation is 0.9637, the maximum As(III) concentration value is determined in Thermal Guayabal waters, Figure 5A shows that not mixing with surface water occurs (point 14).

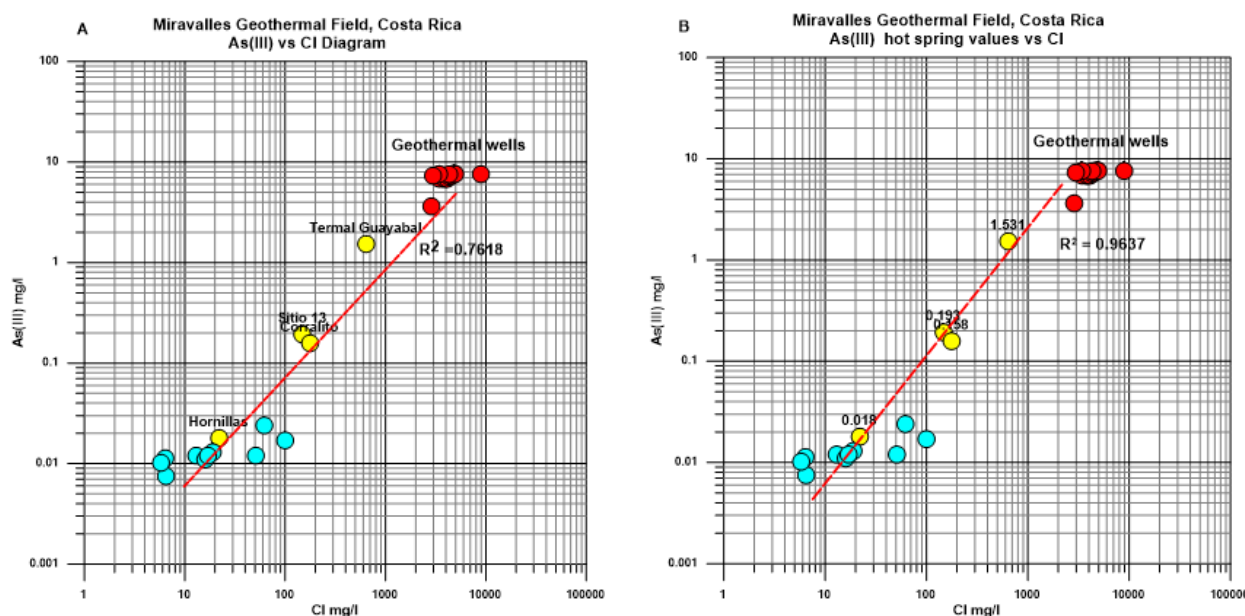


Figure 8 A) As(III) vs Cl diagram B) As(III) vs Cl (concentrations) diagram, Hot Springs.

Figure 9A shows the contours As(T)/As(III) relationship for surface water of the geothermal 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 by Toma Colonia and Colegio Fortuna. Toward the Southern As(T)/As(III) relationship 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 associated with the outflow zone of the geothermal area. Figure 9B shows the contours As(T)/As(III) considering geothermal wells in exploitation and surface waters, geothermal wells plot within the unity area determined initially considering only the surface waters values of As(T)/As(III).

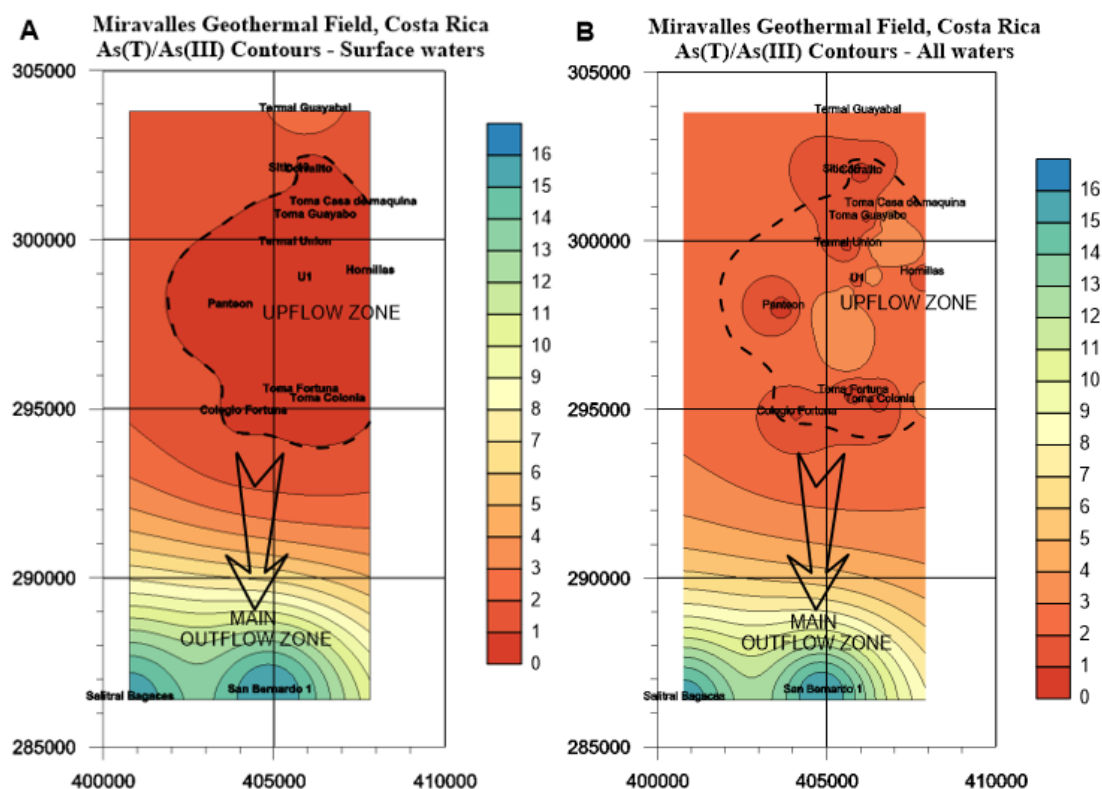


Figure 9: A) Contours diagram As(T)/As(III) Surface waters B) Contours diagram As(T)/As(III) All waters

Figures 10A and 10B have plotted As(T) and As(III) contours respectively considering all 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 initial relationship As(T) / As(III) unity anomaly boundary of surface waters indicated by the dashed black line; Figure 9B, 10A and 10B suggests that the relationship As(T)/As(III) could be used as a potential geochemical exploration tool that would help to identify the geothermal upflow zone.

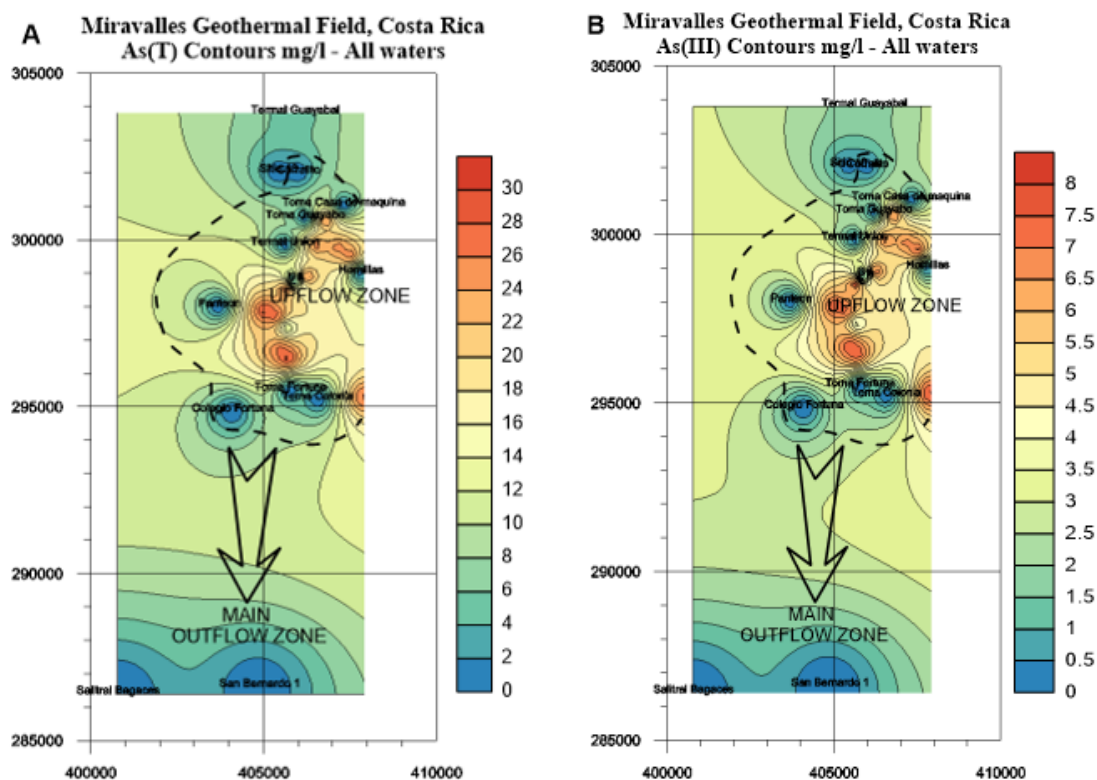


Figure 10: A) Contours diagram As(T) All waters B) Contours diagram As(III) All waters

6. CONCLUSION

In the present study has been determined that log-log plot As(III) vs. Cl presents a better linear correlation considering only the hot springs.

It has been used log-log and triangular diagrams to identify the most reservoir representative manifestations of a geothermal system.

The relationship $As(T)/As(III)$ equal one indicates geothermal upflow zone, considering that As(III) is the dominant reservoir As species, 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 feature is associated to geothermal outflows.

Using $As(T)/As(III)$ relationship contours graphics has been able to identify As geochemical anomaly area that could be interpreted as a geothermal system upflow zone in the field (Termal Guayabal, Hornillas) and the outflow zone in the South area (San Bernardo 1, Salitral Bagaces), in agree with the known field information.

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

REFERENCES

- Archart GB, Coolbaugh MF, Poulson SR.: Evidence for a magmatic source of heat for the Steamboat Springs geothermal system using trace elements and gas geochemistry. *Geothermal. Resources Council Transactions*, 27, pp. 269–274.
- Birkle P., Bundschuh J., Sracek O.: Mechanisms of arsenic enrichment in geothermal and petroleum reservoirs fluids in Mexico. *Water Res* 2010. doi:10.1016/j.watres.2010.05.046.
- Bundschuh J., Prakash M. J., Nath B., Baba A., Gunduz O., Kulp T., J-S Jean J-S., Kar S., Yang H-J., Tseng Y-J., Bhattacharya P., Chen C-Y.: Naturally occurring arsenic in terrestrial geothermal systems of western Anatoly, Turkey: Potential role in contamination of freshwater resources. *Journal of hazardous materials* 262 (2013) 951-959.
- Esetlili M. T., Colak Esetlili B. *, Ozen F., Bolca M., Kurucu Y.: Determination of the arsenic pollution due to geothermal sources in the agricultural lands of Alangullu-Aydin region. *Journal of Environmental Protection and Ecology* 15, No 4, 1555–1563 (2014)
- Giggenbach W. F.: Geothermal solute equilibria. Derivation of Na–K–Mg–Ca geothermometers. *Geochim Cosmochim Acta* 1988; 52:2149–765.
- Hammarlund L. and Piñones J.: Arsenic in geothermal waters of Costa Rica. TRITA-LWR Master Thesis. Stockholm December, 2009.
- López Dina. L., Bundschuh J., Birkle P., Armienta M.A., Cumbal L., Sracek O., Cornejo L., Ormachea M.: Arsenic in volcanic geothermal fluids of Latin America. *Science of the total environment*, January 2012.
- Mark Person, Shari Kelley, Richard Kelley, Satish Karra, Dylan Harp, James Witcher, Jeffrey Bielicki, Glenn Sutula, Richard Middleton, and Jeff D. Pepin. Hydrogeologic Windows: Detection of Blind and Traditional Geothermal Play Fairways in Southwestern New Mexico Using Conservative Element Concentrations and Advective-Diffusive Solute Transport. *GRC Transactions*, Vol. 39, 2015.
- Richie J. A. Arsenic and Antimony in some New Zealand thermal water, *New Zealand Journal of Science*, 4, 218 – 229, 1961.
- Sánchez D.; Application of Cl, B tracers and geothermometers to delineate some production characteristics of Mt. Labo geothermal system, Philippines. UNU – Geothermal Training Program, Report 14, 1993.
- Stauffer Robert E., Thompson John M.: Arsenic and antimony in geothermal waters of Yellowstone National Park, Wyoming, USA, *Geochimica et Cosmochimica Acta* Vol. 48, pp. 2547-2561, 1984.