

AUTHOR'S RESPONSE

Dear Editor:

We have attended successfully the comments from reviewers and revised the manuscript accordingly. All reviewer's comment (bold, red-colored), our answers (black), some modified parts (italic, blue colored) are included in the response to the reviewers:

Review 1, part 1 (Custodio)

General comments:

- 1. The paper presents an interesting point of view on groundwater hydrogeochemistry from the volcanic caldera toward the west to Guadalajara. Complementary hydrogeological details are scarce. They are needed to support what is presented and concluded.**

Answer:

We agree completely with the reviewer. We extended the Hydrogeological Settings (section 2.1), modified the Groundwater flow system (section 4.4) and replaced Figure 1 with two new figures (Fig. 2 Hydrogeological settings, Fig. 3 Cross sections) for a better visualization. The rest of the figures were renumbered.

- 2. Also water chemical data are treated with statistical tools of quite common nature. This is a good approach but the detail relative to groundwater flow are lost or poorly developed. So, the transfer of hydrochemical characteristics along the flow paths is not presented and exploited.**

Answer:

The reason that we did not include geochemical evolution along flow paths is that we are currently developing a paper that is dealing with geochemical transfers/reactions along selected flow paths using PHREEQC code. However, we agree with you that there should be a description in the current paper connecting the hydrochemical characterization with groundwater flow. Thus, we modified the section 4.1 and changed the title to "Groundwater Chemical Characterization".

- 3. Specific comments: geothermal conditions are no clearly shown as a 18O shift to heavier values, which are expectable when there is a mixing of recent recharge with thermally affected water containing evolved chemical characteristics.**

Answer:

We understand that there is a shift to heavier values, however it is relatively small. Recharge water from La Primavera (group 4) has a signature of (-68.5/-9.5 permil), while thermally affected water has a signature of (-66.7/-9.0 permil). The small difference may be explained by the effect that most waters have at least a small component of thermal affected waters, as also confirmed by the mixing model M3 (Table 4). On the other hand, Gutierrez et al. (1994) reports values of -8.7 to -9.2 permil for thermal waters in the study area with temperatures between 64 and 85 °C (Sanchez-Diaz, 2007).

4. The values of SiO₂ are not those expectable from a hot chemically active acid volcanic rock environment.

Table 1 should correctly say “Si” instead of “SiO₂”. The laboratory reported elemental concentrations. Otherwise the Si values must be converted to SiO₂ by dividing the Si values through 0.4674. We arrange the corresponding changes in Table 1.

5. 3H content is what is expectable from an unconfined system recharged from the surface taking into account the mixing produced by a spring or a long screened pumped well. This is not addressed. It seems that the groundwater equivalent water depth is relatively small. This is also not addressed.

Answer:

We agree that this issue is not addressed and propose to add the following paragraph which describes 3H results in the section “4.2 Isotope hydrology” (line 302 – 312):

Tritium results indicate that groundwater within the study area includes both pre-modern (pre-1950s) and modern recharge. The values range from 0.3 to 3.0 TU which suggests a contribution from modern water in every sampled site (Table 1). The majority of waters with ³H lower than 1.0 TU are in the southern portion of the aquifer system. Elevated ³H values (>1.5 TU) located mostly in the La Primavera volcanic system represent young waters or recent recharge with little mixing of path lines. Waters with ³H values <1.5 TU illustrates that these wells may represent mixing of flow paths with modern and pre-modern groundwater residence times. These waters are found mostly in Toluquilla, corresponding to elevated EC, Cl and DIC values. The mixing of water from different ages is expectable because the aquifer is under unconfined conditions, while wells penetrate the saturated zone to a considerable depth, at times up to 500 m, and are almost always completely screened.

6. Technical comments: in tables say that pH has no units. Make clear if what is given is SiO₂ or Si; both are used with close figures. TDS is as STD in the tables. The two cross sections of figure 8 are shown in figure 2 and not in figure 1; they seem too simplistic; some added hydrogeological information will be welcome. The two cross sections of figure 8 are shown in figure 2 and not in figure 1; they seem too simplistic; some added hydrogeological information will be welcome.

Answer:

- We attend these technical comments correspondingly in the manuscript as well as all other modification as result of the required changes.
- The two cross sections have been re-elaborated considerably addressing hydrogeological information and can be seen in new Figures 2 and 3.
- Original Figure 8 was cancelled.

Review 1, part 2 (Custodio)

7. 3H analyses are not inexpensive when electrolytic concentration is needed.

Answer:

3H analysis (including enrichment) cost typically 200 USD per sample at a commercial basis and with a turnaround time of more or less 2 months. We think that radioactive tracers like ^{14}C and ^3H are now relatively accessible in comparison to earlier times because the methods are now standard and there is an availability of a large number of competitive labs worldwide. We propose to use in the text “accessible” instead of “inexpensive” (line 53).

8. The accuracy of data is not given and this is important.

Answer:

The average accuracy of tritium analyses was ~ 0.3 TU (consider that groundwater values varied between 0.4 and 2.1 TU). We added this information in section 3.1 (Field and Laboratory, line 169).

9. Since ^{18}O and ^2H are highly correlated, one of them can be excluded from the statistical analysis or better ^2H can be substituted by excess deuterium to enhance the small differences in Fig 6 caption how and altitude has been given to the samples should be given to be able to understand properly the plot; it seems that some altitude effect is present but looks too high.

Answer:

- This information is complemented in section 4.2 (line 271-301).
- The graphical ^{18}O and deuterium excess was added in new Figure 7.

10. The calcedonia geothermometer does not point to the type of rock (basalt, andesite) as said in pp13 If possible fig 8 will improve introducing some more geological data instead of only rock classification

Answer:

This observation was also addressed in the comment 1 referring to the hydrogeological section. Fig. 8 was replaced with a new Fig. 3 as mentioned in the previous comments. In addition, pp.13 in Section 4.4 was changed.

Review 2 (anonymous)

- 1. GENERAL COMMENTS** The manuscript appears not well finalized to the scope of the research due to the scarce integration of geochemical analyses with a consistent conceptual hydrogeological model of the area. This scarce connection limits the significance of the research just to the geochemical aspect. Following, some specific comments are reported that would finalize the manuscript more clearly to the scope of the research (title).

Answer:

We agree that the hydrochemical work has to be connected with the hydrogeological framework. Thus we have revised the section 2.1 that describes the Hydrogeological Settings and included the evolution of hydrochemical facies in the Results section (see below).

- 2. SPECIFIC COMMENTS.**

Section 2:

- a) a classification of the climate type, by means of known system (e.g. Köppen-Geiger), would improve the description of the area;**
- b) the estimate of the mean annual actual evapotranspiration (e.g. by the Turc or Coutagne formulas) could give, together the mean annual rainfall, a general assessment of the groundwater recharge of the area.**

Answer:

The classification of climate has been considered in section 2 (line 79-84), as follows:

2. Study area:

The study area is situated in the central portion of the state of Jalisco (Fig. 1). It belongs to the Lerma-Santiago river system, which drains into the Pacific Ocean. The climate in the study area according Köppen is a warm temperate with dry winter "Cwa" (Peel et al., 2007; Kottek, 2006). The National Water Commission reports an average annual temperature of 20.9°C and an average annual precipitation of 904 mm, occurring mostly between May and October. The mean annual evapotranspiration is 712 mm according to Turc formula (CONAGUA, 2010).

- 3. Section 2.1:**

- c) This chapter reveals some discrepancies respect the declared scope of the research (title):**
 - a. regional geological setting and local hydrogeological setting should be described separately; in detail, the first aspect should be reduced respect to the present form, while the second one should be expanded.**
 - b. hydrogeological description of the area is very scarce and limited to surficial aquifers only; moreover it does not correspond to what is shown in Figs 2 and 8;**
 - c. hydrostratigraphic units should be described and characterized in terms of hydrogeological properties (e.g. type and degree of porosity and permeability, transmissivity, etc.);**
 - d. data regarding groundwater levels and altitude of springs should be illustrated and interpreted in order to support a conceptual model of groundwater flow of the area.**

Answer:

We agree completely with your suggestion. We revised the local hydrogeological settings (2.1) in the manuscript: In the Description of the Study area we propose to extend the description of the hydrogeology of the study area as follows, and replaced Figures 2 and 8 with two new figures (Fig. 2 Hydrogeological settings, Fig. 3 Cross sections) for a better visualization.

4. Section 3.2:

- d) “Techniques of analysis” seems describe better the contents of this paragraph instead of “Interpretation”.**

Answer:

Usually we use “Interpretation” in our papers but we have no problem with the suggestion and attend it correspondingly in the manuscript (line 170).

5. Section 4.4:

- A. Spatial distribution of groundwater types should be discussed consistently with the conceptual hydrogeological model and vice versa.**

Answer:

We agree with you and modified Section 4.4.

6. Figures 2 and 8:

- B. Fig. 2 seems to be not an ordinary hydrogeological map because it does not represent hydrostratigraphic units with a description of the related hydrogeological characteristics;**
- C. Fig. 2 should be associated to a hydrostratigraphic column provided with information about their hydrogeological characteristics, etc.;**
- D. groundwater flow paths are too approximate, not supported by explanations of a related conceptual groundwater flow model and not indicating to which aquifer they are related (e.g. surficial or deep);**
- E. topographic contour lines are not well visible.**

Answer:

We agree with the comments. Fig 2 was modified, hydrostratigraphic characteristics were described in the text (section 2.1, see above), groundwater flow paths are added to new Fig. 3, the text indicates that they relate to the upper aquifer; topographic contour lines were eliminated and water table contour lines added.

7. Figures 3 and 5:

- F. results reported in these geochemical graphical analyses should be reported in Fig. 2 or in other figures showing geographical distribution of groundwater types.**

Answer:

New Fig 3. shows water types of selected, representative wells along cross section.

Review 3 (anonymous)

- 1. The manuscript describes a very interesting study on a hydrothermal volcanic system with the aim to assess the hydrological processes occurring within the Atemajac–Toluquilla aquifer unit by means of a combination of different techniques. In particular, the combination of geochemical and statistical methodologies based on a huge dataset is a valuable approach to understand the complex dynamics taking place in the volcanic aquifer. The overall manuscript is well written, structured and referenced. Nevertheless, the paper has two main weak points: 1) the definition of the reference values for the different groundwater typologies; 2) the missing estimate of the overall uncertainty associated to the mixing proportions. From the reported data, the authors estimations of mixing proportions cannot be considered accurate, since, as they write in the text, they do not use “real” end-members. Nevertheless, if they wanted to use the most representative groundwaters (as supposed end-members), the estimations of the mixing proportions should be reported with amplified uncertainties, which are not even mentioned in the text. Moreover, since they are using data from one single campaign, the temporal variability of their reference values, which is another term contributing to the overall uncertainty, cannot be estimated.**

Answer:

- We agree that the endmembers are not “real”, especially the geothermal endmember. However, we found data from former studies (Mahood et al., 1991; Maciel-Flores and Rosas-Elguera, 1992; y Prol-Ledezma et al., 1995) about the La Primavera geothermal field which are considered as hydrothermal reference waters in the revised version. Concretely, data from 3 deep wells were used to estimate the mixing proportions with M3. These wells showed by far higher temperatures and Cl, B, Li and Na concentrations in relation to the sampled wells from our study. The results from these estimations were quite different from the first version. They were validated with the mixing proportions based on a Cl mass balance calculation. The methods and new results were included in section 3.2 (Techniques of analysis, line 186-202) and section 4.3 (Mixing patterns with M3). The abstract and conclusions were also revised accordingly.
- We are aware that the temporal variation of reference values undoubtedly plays an important role in estimation of groundwater mixing. However for various reasons it is not always possible to carry out a periodically sampling as in our case. There are also other studies applying M3 as a tool for evaluating mixing proportions using data from only one field campaign (e.g. Chae et al., 2006; Forrest et al., 2013). In our case, the resulting mixing proportions are only a first approximation (consider that this is the first paper at all describing groundwater flow and chemistry in Guadalajara area). This proportions may vary with time. However, our objective in this paper was to comprehend the groundwater flow and factors that control groundwater chemistry, among these the mixture of different fluids. An accurate quantification of mixing proportions is beyond the scope of this paper (see section 1 Introduction). In this paper we demonstrated the applicability of M3 program using groundwater that is affected by polluted and thermal waters, and its validation with an independent method, the Cl mass balance. It is however advisable to continue with this effort to perform more field campaigns addressing the seasonal variations (line 381-386).

- 2. The output numbers of the model M3 in the Table 4 should be reported with the overall associated uncertainties. In summary, the overall associated uncertainty should include, besides the sampling and analytical uncertainty, the variability associated to the supposed “end-members” considering also their seasonal variability. Only in the case of the uncertainty assessment, it would be possible to give accurate estimation of the mixing proportions. I would suggest to include in the Abstract at least the isotopic techniques used and the relative purpose. Regarding the study area, I couldn’t find a reference in text about its extension.**

Answer:

It would be difficult to calculate the overall associated uncertainty because some of the components are not available as mentioned above. Instead, we propose the following:

- The average and standard deviation of the estimation of mixing proportion with both methods (M3 and CI mass balance) are included in Table 4.
 - Table 1 includes the ion balance error of the analytical results.
 - M3 results are validated using a chloride mass balance (line 314-333).
 - The explanation was modified and expanded in Section 4.3: Mixing patterns with M3
 - In the abstract we included techniques used and respective purpose: Stable water isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$) were used to trace hydrological processes and tritium (^3H) to evaluate the relative contribution of modern water in samples (line 13-14).
 - The study area is 1368 km². We feel sorry for this omission It is added in the revised section 2: Study area (line 79).
- 3. Due to the number of wells monitored (about 40) it would be desirable to have a water table reconstruction at the time of the sampling, since from the text it is not pointed out this kind of survey has been realized in the study area. Moreover, I would suggest to write a sentence about the goodness of chemical analyses (e.g. reporting the range of the ion balance values for the acceptance of chemical analyses). Summarizing, the manuscript can be accepted only if major revisions will be done by the authors, regarding the main points previously illustrated and remarked.**
- The water table configuration was included in new Figure 2. We extended the Hydrogeological Settings (2.1), modified the description of the Groundwater flow system (4.4) and replaced Figure 2 with two new figures (Fig. 2 Hydrogeological settings, Fig. 3 Cross sections) for a better visualization.
 - The ion balance error was included in Table 1.

Groundwater flow processes and mixing in active volcanic systems: The case of Guadalajara (Mexico)

A. Hernández-Antonio¹, J. Mahlkecht^{1,*}, C. Tamez-Meléndez¹, J. Ramos-Leal², A. Ramírez-Orozco¹, R. Parra¹, N. Ornelas-Soto¹, C.J. Eastoe³

¹Centro del Agua para América Latina y el Caribe, Tecnológico de Monterrey

²División de Geociencias Aplicadas, Instituto Potosino de Investigación Científica y Tecnológica

³ Department of Geosciences, University of Arizona

Abstract:

Groundwater chemistry and isotopic data from 40 production wells in the Atemajac and Toluquilla Valleys, located in and around the Guadalajara metropolitan area, were determined to develop a conceptual model of groundwater flow processes and mixing.

Stable water isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$) were used to trace hydrological processes and tritium (^3H) to evaluate the relative contribution of modern water in samples. Multivariate analysis including cluster analysis and principal component analysis were used to

elucidate distribution patterns of constituents and factors controlling groundwater chemistry. Based on this analysis, groundwater was classified into four groups: cold groundwater, hydrothermal water, polluted groundwater and mixed groundwater. Cold groundwater is characterized by low temperature, salinity, and Cl and Na concentrations and is predominantly of Na-HCO₃ type. It originates as recharge at Primavera caldera and is found predominantly in wells in the upper Atemajac Valley.

Hydrothermal water is characterized by high salinity, temperature, Cl, Na, HCO₃, and the presence of minor elements such as Li, Mn and F. It is a mixed HCO₃ type found in wells from Toluquilla Valley and represents regional flow circulation through basaltic and andesitic rocks. Polluted groundwater is characterized by elevated nitrate and sulfate concentrations and is usually derived

from urban water cycling and subordinately from agricultural return flow. Mixed groundwaters between cold and hydrothermal components are predominantly found in the lower Atemajac Valley. Most groundwater contains at least a small fraction of

modern water. The application of a multivariate mixing model allowed to evaluate the mixing proportions of hydrothermal fluids,

polluted waters and cold groundwater in sampled water. This study may help local water authorities to identify and dimension

groundwater contamination, and act accordingly.

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* Corresponding author: Jürgen Mahlkecht, Centro del Agua para América Latina y el Caribe, Tecnológico de Monterrey, Ave. Eugenio Garza Sada No. 2501, C.P. 64849 Monterrey, Nuevo León, México. E-mail: jurgen@itesm.mx

30 1 Introduction

31 Active volcanic systems are frequently accompanied by an intense hydrothermal circulation, which is
32 controlled by the exchange of mass and energy between groundwater systems, magmatic fluids and hot
33 rock (Goff and Janik, 2000; Di Napoli et al., 2009). The characterization of such hydrothermal systems
34 helps on the one hand to quantify its geothermal energy potential and, on the other hand, to assess
35 volcanic-related risks (Di Napoli et al., 2011). Hot springs, mud deposits, fumaroles, vaporization and
36 degassing soils give initial clues about subsurface hydrothermal conditions (Hockstein and Browne, 2000;
37 Navarro et al., 2011). The chemical characterization of fluids and groundwater has been used as an
38 indicator of the subsurface structure and the origin of released fluids when hydrogeological information
39 is scarce (Henley and Ellis, 1983; Appelo and Postma, 2005). Hydrochemical data, such as high electrical
40 conductivity (EC), high temperatures and elevated concentrations of As, B, Br, Cl, Cs, F, Fe, Ge, I, Li, Mn,
41 Mo, Na, Rb, Sb, Ta, U and W denote the presence of hydrothermal fluids in groundwater (Reimann et al.
42 2003; Dogdu and Bayari, 2005; Aksoy et al. 2009). However, hydrothermal volcanic systems are
43 sometimes difficult to analyse due to the fact that groundwater is a mixture of fluids from various sources,
44 sometimes consisting of shallow meteoric waters from recent infiltration, seawater and hot water rising
45 from deep hydrothermal reservoirs (Chiodini et al., 2001; Evans et al, 2002; Di Napoli et al., 2009).

46 The combination of different environmental tracer techniques helps elucidate the groundwater's origin,
47 recharge, flow velocity and direction, residence or travel times, connections between aquifers, and
48 surface and groundwater interrelations (Edmunds and Smedley 2000; De Vries and Simmers 2002; Appello
49 and Postma, 2005; Ako et al., 2013; Stumpp et al., 2014). These techniques have been applied in large
50 semiarid to arid rift systems (Bretzler et al., 2011; Furi et al. 2011; Ghiglieri et al, 2012; Siebert et al., 2012;
51 Panno et al., 2013; Forrest et al., 2013; Williams et al., 2013). Stable isotopes (^2H , ^{18}O) provide information
52 regarding origins, recharge processes, flow paths and residence times, especially in fractured rock

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53 aquifers. Radioactive tracers like tritium (^3H) are relatively [accessible](#) methods to estimate groundwater
54 ages and characterize groundwater flow systems. Relatively few studies attempt to quantify mixing
55 between different hydrothermal and cold fluids (Forrest et al., 2013).

56 This study was carried out in the Atemajac-Toluquilla aquifer system (ATAS) which underlies the
57 metropolitan area of Guadalajara, [second-most populated city in Mexico](#) (~4.6 million inhabitants), and is
58 located in a complex neotectonic active volcanic system in the Tepic-Zacoalco Rift. Adjacent to this aquifer
59 system is the “La Primavera” caldera. Several survey wells have been drilled up to 3 km deep at La
60 Primavera to explore the potential for geothermal energy (CFE, 2000). Temperatures between 80 and 300
61 °C have been registered in these wells (Verma et al., 2012), and temperatures higher than 40°C have been
62 measured in adjacent springs (Sánchez-Díaz, 2007). The hydrothermal fluids and springs are characterized
63 by high concentrations of Na, Cl, SiO_2 , HCO_3 , B, F, and TDS. A mixture of hydrothermal fluids and meteoric-
64 derived water has been identified in the springs of “La Primavera” (Sánchez-Díaz, 2007). While it is
65 assumed that this caldera influences the aquifer system [underneath](#) the metropolitan area, the
66 proportion of hydrothermal fluids and cold water is not clear. [Moreover, nitrate contamination has been](#)
67 [related to exogenic processes induced by anthropogenic activity \(GEOEX-SIAPA, 2003\).](#) The diversity of
68 the chemical results from previous studies has contributed to the difficulty in clearly evaluating the
69 relationship between the fluids (see Results and Discussion section).

70 This study aims to understand the flow dynamics of groundwater by using the combination of statistical
71 and geochemical methods. Water groups and factors that control the groundwater chemical processes
72 were identified using a cluster and principal component analysis. Environmental tracers were used to
73 assess chemical evolution. [Mixing proportions of selected fluids in public wells were estimated by means](#)
74 [of a multivariate mixing calculation and validated by a chloride mass balance.](#) This study is the first of its
75 kind to report a comprehensive understanding of groundwater flow processes below the Guadalajara

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76 metropolitan area. This information is strategic to decision makers from local water authorities regarding
77 water resources management.

78 **2 Study area**

79 The study area (1368 km²) is situated in the central portion of the state of Jalisco (Fig. 1). It belongs to the
80 Lerma-Santiago river system, which drains into the Pacific Ocean. The climate according to Köppen is a
81 warm temperate with dry winter “Cwa” (Peel et al., 2007). The National Water Commission reports an
82 average annual temperature of 20.9°C and an average annual precipitation of 904 mm, occurring mostly
83 between May and October. The mean annual evapotranspiration is 712 mm according to Turc formula
84 (CONAGUA, 2010).

85 **2.1 Hydrogeological Settings**

86 The study area is located in the western portion of the Mexican Volcanic Belt (MVB), a 1000 km-long
87 volcanic arc that crosses central Mexico in E–W direction from the Pacific to the Atlantic Ocean. The MVB
88 originated in the Late Miocene in response to the subduction of the Cocos and Rivera plates below the
89 North American plate along the Middle America Trench. The belt has a composition of intermediate to
90 silicic rocks (Alva-Valdivia et al., 2000). The western end of the MVB defines the fault bounded crustal
91 Jalisco Block (Ferrari et al., 2007; Valencia et al., 2013). The northern and eastern boundaries of this block
92 consist of asymmetric continental rifts formed by tilted blocks with escarpments between 800 and 1000m
93 (Zárate-del Valle and Simoneit, 2005); the Tepic–Zacoalco Rift to the north runs in an NW–SE direction,
94 and the Colima Rift to the east runs in an N–S direction; these rifts join the E–W oriented Citala or Chapala
95 Rift in what is known as the Jalisco Triple Junction located 60 km SSW of the city of Guadalajara (Fig. 1).
96 This area is a complex and active neotectonic structure that controls and regulates the development of
97 the rift-floor, limited by normal faults (Michaud et al., 2000; Zárate-del Valle and Simoneit, 2005). The
98 Atemajac and Toluquilla Valleys are located in the lower Tepic–Zacoalco Rift and are bordered by hills,

99 volcanic cones (El Cuatro, San Martín), plateaus (Tonalá) and volcanic calderas (La Primavera), among
100 other features (Sánchez-Díaz, 2007).

101
102 Atemajac and Toluquilla valleys consist of a relatively thin cover of Quaternary lacustrine deposits
103 overlying a thick section of Neogene volcanic rocks including silicic domes, lava and cinder cones, lithic
104 tuffs, basalts, ignimbrites and other pyroclastic rocks, andesites and volcanic breccia, and a basement
105 consisting of Oligocene granite (Campos-Enríquez et al., 2005; Gutiérrez-Negrín, 1988; Urrutia et al., 2000)
106 (Fig. 2). Hydrogeologically, these valleys are underlain by two aquifers (Fig. 3). The upper aquifer consists
107 of alluvial and lacustrine sediments, Pleistocene pre-caldera pyroclastic materials (Tala tuff) such as
108 volcanic ash flows and lapilli, and rhyolitic domes. These sediments represent an unconfined aquifer of up
109 to 450 m thickness with hydraulic conductivities ranging from 1.6×10^{-7} to 2.0×10^{-4} m/s and porosities
110 from 20 to 40% (Sánchez-Díaz, 2007; CONAGUA, 2010). Groundwater recharge sources of this aquifer are
111 rainwater and ascending vertical fluids from the lower aquifer (Gutiérrez-Negrín, 1991). Groundwater
112 flows via faults and Toba tuffs in direction to the central and northern portion of the study area. The lower
113 aquifer consists of fractured andesites and basalts from Pliocene, with hydraulic conductivities and
114 porosities ranging from 10^{-8} to 10^{-4} m/s and from 5 to 50%, respectively. This semi-confined to confined
115 aquifer has been related to geothermal fluids (Venegas et al., 1991; GEOEX-SIAPA, 2003). Groundwater of
116 this aquifer flows preferentially in southeastern direction (Ramírez et al., 1982).

117 Pumping wells are drilled in the upper aquifer. Its water table distribution is shown in Fig. 2. In the
118 Atemajac valley, groundwater flow direction is oriented mainly from southwest to northeast, from the
119 topographically higher areas, towards the Santiago river, with possible recharge from normal faults west
120 from Guadalajara city (Fig. 3, section I and II); while in Toluquilla the flow of groundwater circulates from
121 northwest to southeast (Fig. 3, section III) (GEOEX-SIAPA, 2003; CONAGUA, 2009). However,

122 anthropogenic activity has been changing the flow paths, resulting in the formation of different cones of
123 depression. The major discharge is given by well pumping activities and springs in the escarpment of the
124 Santiago river (GEOEX-SIAPA, 2003; CONAGUA, 2009 and 2010). Due to the heavy extractions from the
125 aquifer system, water table levels are falling up to 2.2 m/year and 0.3 m/yr on average in Atemajac and
126 Toluquilla aquifers, respectively (GEOEX-SIAPA, 2003). The constructed well depth is up to 500 m and up
127 to 380 m in the valley of Atemajac and Toluquilla, respectively. Depth to water table reaches up to 150 m
128 below ground level in the Atemajac valley and 50 m in Toluquilla valley (GEOEX-SIAPA, 2003).

129 2.2 Hydrothermal System

130 The La Primavera caldera, with a diameter of ~10 km, borders the study area to the west. It is a very young
131 (Late Pleistocene) volcanic complex underlain by a magma chamber whose top reaches a depth of 4 km
132 (Verma et al., 2012). Drilling has revealed that the oldest units consist of granitic and granodioritic rocks
133 found mainly at a depth of approximately 3000 m. These rocks are mainly overlain by andesitic rocks
134 approximately 1150 m thick. The third lithologic unit, which is approximately 100 m thick, consists of
135 rhyolites. The uppermost unit is a sequence of lithic tuffs and minor andesite with an average thickness
136 of approximately 750 and 1000 m, respectively (Campos-Enríquez et al, 2005; Urrutia et al., 2000; Verma
137 et al., 2012). The system is characterized by an asymmetric structure with NW-SE regional basalt
138 lineaments that belong to the Tepic Zacoalco Rift and local NE-SW fractures in the upper units extending
139 beneath Guadalajara (Alatorre-Zamora and Campos-Enríquez, 1991; Campos-Enríquez and Alatorre-
140 Zamora, 1998). The temperatures, which were measured at the bottom of exploratory wells that were
141 drilled up to 3 km deep, vary from 80 to 300°C (Verma et al., 2012). It appears that heated meteoric water
142 ascends along fault or fracture zones to near surface depths and supplies springs with temperatures of
143 >40°C (Venegas et al., 1985). The hydrothermal fluids are characterized by very high concentrations of Na
144 (679-810 mg l⁻¹), Cl (865-1100 mg l⁻¹), SiO₂ (943-1320 mg l⁻¹), B (75-150 mg l⁻¹) and TDS (2810-4065 mg l⁻¹)
145 (Maciel-Flores and Rosas-Elguera,1992), while the springs are of Na-Cl-HCO₃ type with relatively high

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146 concentrations of Na (260-331 mg l⁻¹), Cl (85-185 mg l⁻¹), SiO₂ (209-253 mg l⁻¹), HCO₃ (395-508 mg l⁻¹), B
147 (10.8-12.3 mg l⁻¹), F (8.5 mg l⁻¹) and TDS (1071-1240 mg l⁻¹), indicating a mixture between hydrothermal
148 fluids and local rainwater origin with ratios of 1:2 to 1:10 (Gutiérrez-Negrín, 1988; Sánchez-Díaz, 2007).

149 **3 Methods**

150 **3.1 Field and laboratory**

151 Water samples were collected from 40 production wells in March 2011 using standard protocols. The
152 samples were analyzed for major and minor ions, trace elements and isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$, ^3H). Field
153 parameters such as temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO), were
154 measured using portable meters (Thermo, Orion). Alkalinity was determined in the field by volumetric
155 titration (0.02N H₂SO₄) of filtered water samples to pH 4.3. At each sampling site, new and pre-rinsed low
156 density polyethylene bottles were filled with filtered (0.45 μm) sample water. Cation and silica samples
157 were acidified with ultrapure HCl to pH<2, and all of the samples were stored in the laboratory at a
158 constant temperature of 4°C. Dissolved cations and anions were determined by inductive-coupled plasma
159 mass spectrometry (ICP-MS) and ion chromatography, respectively. Duplicates of selected samples were
160 analyzed using inductive-coupled plasma optical emission spectrometry (ICP-OES) and ion
161 chromatography, following standard methods (APHA, 2012).

162 [Stable water isotopes](#) were analyzed at Environmental Isotope Laboratory, University of Waterloo,
163 Canada. To conduct deuterium (^2H) analyses, sample water was reduced on hot manganese (512°C) and
164 the released hydrogen was analyzed by GC-MS. To conduct oxygen-18 (^{18}O) analyses, water was
165 equilibrated with CO₂. Preparation and extraction took place on a fully automated system vessel attached
166 to a VG MM 903 mass spectrometer. The ^2H and ^{18}O results are reported as δ -values with respect to the
167 VSMOW (Vienna Standard Mean Ocean Water) standard. [Tritium \(\$^3\text{H}\$ \) was analyzed at Environmental](#)

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168 Isotope Laboratory, University of Arizona, using a liquid scintillation counter after electrolytic enrichment.

169 The average accuracy of tritium analyses was ~0.3 TU.

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170 3.2 Techniques of analysis

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171 A preliminary description of water chemistry and identification of possible processes was performed using
172 a correlation analysis. A hierarchical cluster analysis (HCA) organized samples into classified groups which
173 were evaluated according to their geographic correspondence. A principal component analysis (PCA)
174 elucidated the main controls on groundwater chemistry. All of the statistical calculations were performed
175 using Minitab version 17.1 (Minitab, 2013).

176 The multivariate mixing and mass balance model, or M3 (Laaksoharju et al., 2008), was used to help to
177 understand groundwater composition. The main aim of M3 is to differentiate between what is due to
178 mixing and what is due to water-rock reactions. The M3 method compares the measured groundwater
179 composition of each sample to the selected reference water and reports the changes in terms of mixing
180 and reactions. A PCA is used to summarize the groundwater data by using the majority of the dissolved
181 groundwater constituents Ca, Na, Mg, K, Cl, SO₄ and HCO₃ in combination with the isotopes δ²H, δ¹⁸O and
182 ³H. The outcome of the analyses can be visualized as a scatter plot (PCA plot) for the first two principal
183 components. The observations inside the polygon of the PCA plot are compared to the previously chosen
184 reference water compositions. The mixing calculations create ideal mixing models that use linear
185 distances of the samples from the selected reference waters in the PCA plot.

186 In this study, the following compositions of samples were used as reference waters: i) three deep wells
187 located in the La Primavera geothermic field and representing hydrothermal water; with data taken from
188 Mahood (1983), Maciel-Flores (1992) and Prol-Ledezma (1995): well PP1 (T=255 °C, Cl=851 mg l⁻¹, B=120
189 mg l⁻¹, Li=9.9 mg l⁻¹ and Na= mg l⁻¹), well PP2 (T=265 °C, Cl=1,120 mg l⁻¹, B=131 mg l⁻¹, Li=8.5 mg l⁻¹ and
190 Na=2000 mg l⁻¹), and well PP3 (T=265 °C, Cl=1,500 mg l⁻¹, B=54 mg l⁻¹, Li=3.9 mg l⁻¹ and Na=3310 mg l⁻¹); ii)

191 well AT37 representing local groundwater with low temperature and salinity (Table 1); iii) well AT12 with
192 low temperature and high salinity was taken as polluted reference water (Table 1). Although it is uncertain
193 whether the selected reference waters are end members or close to, they were selected from the
194 available dataset. Well AT37 is an adequate candidate for local groundwater because it is located in the
195 recharge area showing little interaction with rocks. The three deep wells in La Primavera caldera are most
196 probably also an appropriate selection of hydrothermal reference water because their temperatures are
197 in the range of geothermic temperatures according to Verma et al. (2012).

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198 Chloride mass balance was applied with the purpose of validation of the M3 modeling estimates. This
199 method has been discussed and applied in similar environments (e.g. Han et al., 2010) and assumes that
200 extracted groundwater is a mix of two end members (thermal and non-thermal) and that the Cl ion
201 behaves conservative which means that it does not participate in any chemical reactions even at high
202 temperatures.

203 **4 Results and discussion**

204 Sánchez-Díaz (2007) used groundwater temperature and total dissolved solids as criteria to classify wells
205 in hydrothermal water from Toluquilla (HT), hydrothermal water from springs NE of Guadalajara (HG),
206 non-hydrothermal, local groundwater (LG), and mixed groundwater (MG) with both HT and LG (Fig. 4).
207 Considering different sets of historical and new data, this classification is too subjective, especially in the
208 lower TDS range. Furthermore, some inconsistencies between correlation results from different sampling
209 campaigns show that the interpretation is not straightforward. The Mg concentration, for example,
210 decreases with increasing temperature as expected from hydrothermal fluids (Panichi and Gonfiantini,
211 1981); on the other hand, an increasing Mg trend at low temperatures is observed indicating saline
212 groundwater. Finally, it was not clear if there are different sources of hydrothermal or saline waters that
213 affect the local groundwater. These complications motivated us to use multivariate techniques instead of

214 commonly used scatterplots and criteria to divide samples into groups and interpret for potential
215 factors/sources. Because the measured parameters varied considerably from study to study, only data
216 from this study were considered for chemical characterization and multivariate analyses.

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217 4.1 Groundwater Chemical Characterization

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218 Table 1 shows the concentrations of measured groundwater chemical elements, field parameters and
219 isotopic data, along with the hydrochemical classification. The classification of waters was performed with
220 HCA using 20 variables (pH, temperature, EC, DO, Na, K, Ca, Mg, Cl, HCO₃, SO₄, NO₃-N, Sr, Si, Fe, F, Zn, ³H,
221 ²H, ¹⁸O). With the help of Ward's linkage rule iteratively neighboring points (samples) were linked through
222 a similarity matrix (Ward, 1963). The squared Euclidian distance was selected as the similarity
223 measurement. The second method was a PCA. For both cluster algorithms, lognormal distributed data
224 were previously log-transformed, and all of the variables standardized (z-scores). The HCA samples were
225 classified into 4 major groups as represented by the dendrogram (Fig. 5) and median values (Table 2). The
226 values for Li, Mn and Ba were not considered in the cluster analysis, because most samples had
227 concentrations below the detection limit.

228 The four groups are plotted on a Piper diagram to demonstrate chemical differences (Fig. 6). Salinity
229 increases as groundwater moves east- and southeastwards from La Primavera field to discharge areas
230 along topographic flow path. EC values reach typically 600 $\mu\text{S cm}^{-1}$ in the discharge areas of urbanized
231 Guadalajara, except for Toluquilla wells where values ascend to 2300 $\mu\text{S cm}^{-1}$. Group 4 (n=19) is a Na-HCO₃
232 water type located in recharge zones in the western portion and reflects a short (local) groundwater flow
233 path with poor circulation. It shows low temperatures (average 25.3 °C) and salinity (254 $\mu\text{S cm}^{-1}$),
234 however elevated NO₃-N (9.1 mg l⁻¹) values, possibly derived from agricultural practices. Groundwater
235 that moves in northern and eastern direction attains a Na-HCO₃ to mixed HCO₃ water type (group 2, n=12),
236 with increased temperatures (30.2 °C) but similar low salinities (300 $\mu\text{S cm}^{-1}$), indicating water-rock

237 interactions. Groundwater in the discharge area in central Guadalajara city evolves to a Na-SO₄ to mixed
238 HCO₃ water type (group 3, n=3), with higher concentrations of several elements indicating an important
239 impact from anthropogenic pollution, i.e. SO₄ (70.6 mg l⁻¹), NO₃-N (12.4 mg l⁻¹), Na (52.2 mg l⁻¹) and Cl
240 (38.9 mg l⁻¹). Finally, water that moves from recharge zone at Primavera caldera southeast towards the
241 central part of Toluquilla valley, attains a Mg-HCO₃ and mixed HCO₃ type (group 1, n=6). These wells show
242 highest temperatures (33.8 °C) and salinity (EC=1,575 µS cm⁻¹), and lowest NO₃-N (0.17 mg l⁻¹) (Fig. 3).

243 This preliminary evaluation of evolution of groundwater chemistry along principal flow paths indicates
244 that groundwater flow is affected by different sources. In the central and northern part of the study area
245 local groundwater from La Primavera caldera undergoes water-rock interactions and mixes with
246 mountain-front recharge as well as return flow from agricultural plots and urban water cycling (Fig. 3,
247 Section I and II), while in the southern portion local water mixes with water from deeper formations that
248 interacts with volcanic rocks of the La Primavera caldera and causes increased mineralization and
249 temperatures (Fig. 3, Section I and II).

250 A factor analysis transformed the 20 variables into a reduced number of factors. The PCA, which loads
251 most of the total variance onto one factor, was used in this study. The factors were extracted through the
252 principal components method. Varimax rotation, where one factor explains mostly one variable, was
253 selected. For fixing the maximum number of factors to be extracted, only factors with eigenvalues higher
254 than one were taken into consideration (Kaiser normalization).

255 Table 3 shows that 4 factors may explain 77% of the variance. Factor 1 (42% of the variance) largely
256 represents high salinity. The correlations of temperature, Na and Cl indicate hydrothermal influence, while
257 HCO₃, Na and Sr could be connected to mineralization and rock dissolution processes, and cationic
258 exchange. In factor 2 (17%) the temperature is inversely related with DO, ³H, and to a lesser degree, NO₃
259 and SO₄, suggesting that this factor represents water affected by human activities, either urban or

260 agricultural. In addition, Table 1 and Figure 7 shows that waters affected by human activities are most
261 evaporated. Sulfate could be related to contamination due to the infiltration of commonly applied sulfate-
262 based fertilizers during the rainy season. This occurs because all the wells are undersaturated with regard
263 to gypsum, indicating that the water does not move through deposits of this mineral. In factor 3 (11%) the
264 relationship between ^2H and ^{18}O reveals the existence of recharge water. This factor is generated almost
265 entirely by the linear relationship between O and H isotopes. The relation with temperature indicates the
266 recharge conditions at different recharge sites. Factor 4 (7%) may be indicative of dissolution of minerals
267 that contain F. The study of Sánchez-Díaz (2007) indicates that rhyolitic rocks and ashes of the study area
268 are responsible for releasing F. Comparable trends have been observed in various similar volcanic
269 environments in central and northern Mexico (Mahlknecht et al., 2004, Mahlknecht et al., 2008).

270 4.2 Isotope hydrology

271 Data from this study and complementary data reported by other investigations (González et al., 1992;
272 GEOEX-SIAPA, 2003) are used to study the origin and evolution of water in the study area (Fig. 7a). The
273 $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ graph shows that groundwater is of meteoric origin with variable evaporation and mixed with
274 hydrothermal fluid. Although all studies show a similar trend, the data reported by González et al. (1992)
275 registered heavier $\delta^{18}\text{O}$ values that may be attributable to evaporation or hydrothermal influence. Similar
276 $\delta^{18}\text{O}$ values in thermal systems have been reported in other studies, e.g. El-Fiky (2009) and Stumpp et al.
277 (2014) with $\delta^{18}\text{O}$ values ranging from -6.7 to -5.6 ‰ and -4.8 to +0.8 ‰, respectively. Water from group 1
278 (hydrothermal influenced) collected in Toluquilla, has a narrow range of $\delta^{18}\text{O}$ (-9.4 to -8.8‰) and $\delta^2\text{H}$ (-67
279 to -68‰) values. They tend to fall slightly below and parallel to the RMWL, possibly indicating different
280 climate conditions during recharge. These samples show isotopic depletion, indicating that recharge by
281 meteoric water is low, as demonstrated by a deuterium excess that ranges from 4 to 8 ‰ with an average
282 of 5.5 ‰ (Fig. 7b). On the other hand, it is possible that only a displacement of $\delta^{18}\text{O}$ is occurring, which

283 could correspond to a geothermal effect and mixing with meteoric waters (Giggenbach and Lyon, 1977;
284 Herrera and Custodio, 2003). The increased Cl concentrations compared to other groups evidences
285 mixture with hydrothermal fluids and longer residence times (Fig. 7c). Group 2 waters, collected in the
286 eastern and southern part of the ATAS, have $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values ranging from -9.6 to -8.6‰ and from -
287 63 to -71‰, respectively. These waters fall along the RMWL. Deuterium excess values vary between 5.3
288 and 8.1 ‰ with an average of 6.7 ‰. These values are similar to other groups (Fig. 7b), therefore, in
289 accordance with the low concentration of Cl, groundwater recharge is of meteoric origin (Fig. 7c). Group
290 3 waters (influenced by anthropogenic pollution) are quite different from the rest; they have heavier $\delta^{18}\text{O}$
291 values ranging from -7.9 to -5.7‰, and $\delta^2\text{H}$ values varying from -59.6 to -47.5‰, and are strongly affected
292 by evaporation. Also a lower deuterium excess in the order of +4‰ is observed (Fig. 6b y 6c). The enriched
293 outlier AT12 represents groundwater from a recreational park with lagoons. In this well there is a negative
294 deuterium excess indicating that rainwater presented evaporative diffusion processes in the soil during
295 recharge process (Custodio, 1997; Manzano et al., 2001). Group 4 waters, mostly from La Primavera
296 recharge area, are covering a relative wide range of values compared to group 1 and 2. Their $\delta^{18}\text{O}$
297 signatures vary from -10.3 to -8.4‰, and their $\delta^2\text{H}$ signatures from -72.2‰ to -63.9‰. Deuterium excess
298 in these wells is the highest and indicate preferential recharge during certain times of the year (Jiménez-
299 Martínez and Custodio, 2008). The overlapping of group 1, 2 and 4 indicates that aquifer formations are
300 mostly hydraulically interconnected. Although altitude variations are in the order of only 400 m around
301 La Primavera caldera, this seems to be enough to generate an altitude effect (Fig 7d).

302 Tritium results indicate that groundwater within the study area includes both pre-modern (pre-1950s)
303 and modern recharge. The values range from 0.3 to 3.0 TU which suggests a contribution from modern
304 water in most sampled sites (Table 1). Lowest values are in the order of laboratory analysis accuracy, thus
305 these waters may not contain modern water. The majority of waters with ^3H lower than 1.0 TU are in the
306 southern portion of the aquifer system. Elevated ^3H values (>1.5 TU) located mostly in the La Primavera

307 volcanic system represent young waters or recent recharge with little mixing of path lines. Waters with
308 ^3H values <1.5 TU illustrate that these wells may represent mixing of flow paths with modern and pre-
309 modern groundwater residence times. These waters are found mostly in Toluquilla, corresponding to
310 elevated EC, Cl and DIC values. The mixing of water from different ages is expectable because the aquifer
311 is under unconfined conditions, while wells penetrate the saturated zone to a considerable depth, at times
312 up to 500 m, and are almost always completely screened.

313 4.3 Mixing patterns

314 Using a recommended permissible factor of 0.05 (Laaksoharju et al, 2009), all samples are located inside
315 the cover area of the polygon of PCA plot (Fig. 8). The estimated mixing proportions are present in Table
316 4. Results indicate that the proportions of hydrothermal fluids are largest in group 1 varying from 1.9 to
317 12.5%. The hydrothermal mixing proportions according to Cl mass balance method were consistently
318 higher, ranging from 6.2 to 20.6%. Especial AT5 shows important differences between both methods. The
319 other groups show hydrothermal fractions below 1.4% according to M3 modeling and 4.4% obtained from
320 Cl mass balance method. The differences between the two methods is not only due to the distinct
321 underlying algorithm of both methods, but also due the fact that M3 modeling uses 3 reference waters
322 and Cl mass balance only 2 reference waters (thermal/non-thermal). Group 3 represents an insignificant
323 share of hydrothermal water ($\sim 0\%$) due to fact that these wells are located in recharge areas. On the other
324 hand, this group shows an important proportion of anthropogenic impacted water ($>50\%$), while all other
325 groups are less affected ($<37\%$).

326 These results validate the initial selection of groups based on cluster analysis. Geographically,
327 groundwater with elevated hydrothermal proportions is located in the south to southeastern area
328 (Toluquilla), and elevated proportions of polluted groundwater are located mostly in the urbanized area
329 of Guadalajara. Hydrothermal fractions computed with Cl mass balance method are general higher than

330 those with M3 program, while for group 3 (fresh groundwater) there is no correspondence between
331 methods. Differences may be due to the underlying conceptual differences in both approaches. However
332 there is a generally high correlation between both methods ($r^2 = 0.87$) which validates the results.

333 4.4 Groundwater Flow System of Guadalajara

334 The hydrogeological Atemajac-Toluquilla system is located in the northeastern area of the Tepic-Zacoalco
335 Rift, a complex and active neotectonic structure. Local groundwater recharge for Atemajac-Toluquilla
336 Valley originates from rainfall mainly over the La Primavera caldera in the central western portion of the
337 study unit. It flows from the upper alluvial sediments towards the valley floor and Santiago River. Recharge
338 water is of Na-HCO₃ water type with low temperatures, salinities, Cl and Na values, elevated NO₃
339 concentrations, as well as relatively high tritium activities in the range of 0.5 -2.9 TU indicating little mixing
340 of flow paths and recent recharge from pristine soils and return flow from agricultural plots, especially in
341 Toluquilla valley. This result confirms also a relatively fast transport through the unsaturated zone
342 (Herrera and Custodio, 2014). As groundwater circulates in northeastern (Atemajac valley) and eastern
343 direction (Guadalajara city) following the hydraulic gradient, its temperature and salinity increases
344 moderately. The wells are typically drilled in Tala tuff underlain by andesites to basaltic andesite rocks.
345 Locally groundwater evolves to a Na-SO₄ to mixed HCO₃ water type, with relatively high contents of SO₄,
346 NO₃, Na, Cl and tritium (~2TU) indicating an important impact from anthropogenic pollution in urban
347 Guadalajara.

348 Underground heat flow suggests the existence of a magma chamber below the La Primavera caldera,
349 which provides hydrothermal fluids observed on surface expressions such as the La Soledad solfatara and
350 the Cerritos Colorados geothermal field. Regional groundwater that is in contact with these fluids
351 circulates through the lower Atemajac-Toluquilla aquifer specifically below Santa Anita and Toluquilla
352 locations. These Mg-HCO₃ to mixed HCO₃ waters are characterized by elevated temperatures, salinity, Cl,

353 Na and HCO₃ values, low tritium values (<1.7 TU) and contain considerable concentrations of Li, Mn, B and
354 F, indicating thermal influence, circulation through an active volcanic center and fault zones, and water-
355 rock interactions. The corresponding wells are typically drilled in basalt-andesitic rock formations. The
356 well depth of these wells range from 200 to 300 m and depth-to-water table is about 50 m. The low tritium
357 concentration indicates pre-modern infiltration. Low tritium concentrations in deep wells, according to
358 Herrera and Custodio (2014), are due to a mix of water from the upper aquifer and the vertical ascending
359 flow from the lower aquifer. On the other hand, the tritium values show that geochemically speaking, the
360 water predominates as an old fraction (Custodio, 1989). The isotopic composition of groundwater
361 confirms the interconnectivity between water from deeper and shallow rock materials.

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362 5 Conclusions

363 This work represents the first time that groundwater flow dynamics of Guadalajara region have been
364 analyzed and characterized by using a suite of statistical and geochemical methods. Geochemical methods
365 have been combined with multivariate statistical analysis and the multivariate mixing and mass-balance
366 model (M3) to determine the mixing patterns of different fluids when considering fresh groundwater,
367 hydrothermal fluids and human impacted waters. The mixing proportions have been compared to
368 estimates from chloride mass balance method.

369 The initial classification of groundwater groups by cluster analysis has been confirmed by water isotopic
370 technologies, and identifying the controlling factors by principle component analysis is consistent with M3
371 modeling. The origin of groundwater recharge and the mixture of fresh groundwater with hydrothermal
372 fluids and polluted water components was identified. A conceptual flow model was constructed for the
373 Atemajac-Toluquilla aquifer system. The local flow is associated with the infiltration of rainwater that
374 occurs at higher altitudes. Hydrothermal waters are probably related to recharge outside the study area
375 and upward vertical flow in the La Primavera caldera and the valley of Toluquilla. TDS, Cl, Na, Mn and Li,

376 are most indicative of hydrothermal fluids. Modern water polluted with SO_4 and NO_3 can be associated
377 with infiltration of urban sewage and agricultural return flow. According to M3 modeling, the proportion
378 of hydrothermal fluids within older waters was between 1.9% and 12.5%, whereas it was lower than 1.4%
379 within other waters. The proportion of polluted water in groundwater reached up to 52% in urbanized
380 areas.

381 M3 is a powerful tool to evaluate the mixing proportions of selected reference waters present in aquifers.
382 We recommend the use of the suite of traditional methods, environmental tracers, statistical analysis and
383 M3 modeling in other aquifers with potentially multiple groundwater origins, especially in active volcanic
384 systems where mixing is an important process. One limitation with this approach, however, is the
385 representativeness of selected reference waters and samples. Part of this uncertainty may be overcome
386 by repeating the field campaign considering seasonal/time variations.

387 These outcomes may help water authorities to identify wells with hydrothermal mixture or polluted water
388 and act accordingly. The information regarding the proportions of fresh groundwater, hydrothermal fluids
389 and polluted waters in each well indicates that the contaminants can be attributed to source waters. For
390 example, Li, Mn, Ba, F and As can be associated with hydrothermal fluids, and SO_4 and NO_3 are related to
391 the production or use of fertilizers, dyes, glass, paper, soaps, textiles, fungicides or insecticides. These
392 results helps authorities to decide whether certain wells have to be isolated or closed in order to provide
393 Guadalajara with the required drinking water quality.

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Table Captions

578 Table 1: Concentrations of measured field parameters, groundwater elements, [isotopic data](#), and
579 hydrochemical classification. Data are given in $mg\ l^{-1}$, except otherwise indicated. Note: T = temperature,
580 DO = dissolved oxygen, EC = electrical conductivity, [Bal.](#) = ion balance error, [S.U.](#) = standard units

581 Table 2: Median values of water chemistry of the groundwater subgroups determined from HCA. Data are
582 given in $mg\ l^{-1}$, except where otherwise indicated.

583 Table 3: Rotated component matrix of the factor analysis for groundwater samples from the Atemajac
584 Toluquilla aquifer system. Coefficients between -0.1 and 0.1 are suppressed. Note: DO = dissolved oxygen,
585 T = temperature, EC = electrical conductivity.

586 [Table 4: Mixing proportions from the multivariate mixing and mass-balance model, M3, using the](#)
587 [following reference waters: deep wells PP1, PP2 and PP3 as a reference for hydrothermal fluids; no. 12 as](#)
588 [a reference for polluted water; and no. 37 as reference for fresh groundwater, and hydrothermal mixing](#)

589 proportions based on Cl mass balance calculations. Note: Avg = average obtained from calculation using
590 the three different hydrothermal reference waters; SD=standard deviation.

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Figure Captions

- 595
- 596 Figure 1: Location of study area (black area) in Mexico and tectonic structures of western Central Mexico.
- 597 Figure 2: Surface geology, water table distribution and location of wells sampled in the study area. Note:
- 598 GMA = Guadalajara metropolitan area
- 599 Figure 3: Cross-sections indicated in Fig. 2 and considering hydrogeological settings and water types of
- 600 selected wells.
- 601 Figure 4: Plot of water temperature vs. total dissolved solids for different groundwater collecting
- 602 campaigns in the study area. The delimitation of classified wells according to Sánchez-Díaz (2007) is also
- 603 shown. Note: HT=hydrothermal water from Toluquilla, HG=hydrothermal water from springs NE of
- 604 Guadalajara, LG=local groundwater, MG = mixed groundwater (HT and LG).
- 605 Figure 5: Dendrogram showing HCA classification with groups and subgroups of samples of the Atemajac-
- 606 Toluquilla aquifer system. The dashed line indicates the “phenon line”, an arbitrary line that defines
- 607 subgroups.
- 608 Figure 6: Piper diagram of groundwater samples from the Atemajac-Toluquilla aquifer system with well
- 609 groups.
- 610 Figure 7: (a) Deuterium and oxygen-18 in groundwater from the ATAS using this and previous studies.
- 611 Note: GMWL = Global Meteoric Water Line (Rozanski et al., 1993), RMWL = Regional Meteoric Water Line
- 612 (Wassenaar et al., 2009); (b) oxygen-18 vs. deuterium excess with labelled altitudes; (c) oxygen-18 vs.
- 613 chloride concentration; and (d) oxygen-18 vs. altitude.
- 614 Figure 8: PCA plots of the M3 model from mixing of hydrothermal fluids with cold groundwater and
- 615 polluted waters.

Table 1:

ID	Well name	Well depth (m)	pH (S.U.)	T (°C)	EC (µS cm ⁻¹)	DO	Na	K	Ca	Mg	Cl	HCO ₃	SO ₄	NO ₃ -N	Sr	SiO ₂	Fe	F	Zn	Li	Mn	Ba	H (TU)	H (‰)	¹⁸ O (‰)	Sal (‰)	Water type
AT1	Toluquilla 1	300	7.3	25	345	5.34	44.2	6.8	13.3	4.9	9.4	146.4	21.5	3.8	0.07	44	0.05	0.95	0.040	0.06	<0.01	0.05	1.70	-64.3	-8.6	-4	Na-Ca-HCO3
AT2	Toluquilla 6	300	7.0	25	1619	5.76	152.0	58	28.9	103	70.1	1068.8	6.5	<0.04	0.38	38.5	0.14	0.33	0.068	0.33	0.26	0.5	0.70	-68.4	-9.3	-8	Mg-Na-HCO3
AT3	Toluquilla 17	200	7.0	25	2310	5.25	114.0	36	58.7	82.9	82.4	1031.3	5.0	0.07	0.45	35.1	0.16	0.65	0.018	0.33	0.51	0.32	0.70	-66.5	-8.8	-10	Mg-Na-HCO3
AT4	Toluquilla 22	300	7.0	31.8	1792	5.1	147.0	40.9	89.7	113	85.4	1415.2	6.6	<0.04	0.61	53.6	0.05	0.99	0.076	0.37	0.22	0.26	1.20	-67.4	-9.1	7	Mg-Na-HCO3
AT5	Toluquilla 7	230	7.0	36.4	1900	5.48	174.0	48.4	80.7	104	229.0	697.6	22.4	<0.04	0.52	61.6	0.37	3.50	0.088	0.47	0.83	0.39	0.40	-66.5	-8.9	3	Mg-Na-HCO3-Cl
AT6	Las Pintas	350	7.2	33.6	718	6.21	102.0	33.9	31.2	16	14.5	435.2	5.9	0.03	0.32	40	0.04	0.26	0.023	<0.05	0.04	0.08	0.90	-64.7	-8.8	6	Na-HCO3
AT7	Garabatos	300	6.8	25	188.9	6.73	16.1	1.2	2	0.4	2.2	24.4	9.7	4.53	0.01	22.8	0.03	1.01	0.020	<0.05	<0.01	<0.02	2.20	-70.5	-9.6	2	Na-HCO3-SO4
AT8	Santa Ana Tepetitán	250	6.9	25.8	240.4	6.02	38.5	2.3	5.8	1	30.6	18.3	34.6	71.6	0.01	45.3	0.02	3.79	0.005	0.08	<0.01	<0.02	0.60	-71.5	-9.9	9	Na-NO3-Cl-SO4
AT9	Tapalco 1	258	6.2	25	310	6.61	67.3	7.2	6.7	2.3	3.7	122.0	12.3	4.68	0.02	52.6	0.03	0.97	0.224	0.09	<0.01	<0.02	1.20	-71.1	-9.8	9	Na-HCO3
AT10	Topasco	235	6.7	21.8	569	6.34	63.8	21	14.3	6.3	5.2	242.2	8.9	0.42	0.1	38.4	0.03	0.84	0.092	<0.05	<0.01	0.05	0.90	-65.2	-8.9	13	Na-Ca-Mg-HCO3-SO4-Cl
AT11	Jardines del Bosque	250	7.1	27.8	309	5.75	26.5	3.5	7.8	2.6	14.0	30.5	29.4	5.76	0.03	29.8	0.02	0.46	0.046	<0.05	<0.01	0.04	2.10	-63.9	-8.4	12	Na-Mg-Ca-HCO3
AT12	Agua Azul	40	7.1	29.1	354	3.3	44.1	8.9	23	7.4	50.3	24.4	95.2	11.8	0.12	41.4	0.02	0.20	0.005	<0.05	<0.01	<0.02	2.40	-47.5	-5.7	0	Na-Mg-Ca-HCO3
AT13	Educadores Jalisco	300	6.5	32.8	1111	3.93	14.8	6.3	16.8	4.8	1.3	102.5	1.1	0.43	0.12	35	0.02	0.21	0.161	<0.05	<0.01	<0.02	0.50	-67.0	-9.1	7	Na-Mg-HCO3
AT14	Tanque Teisistán	292	7.1	32.5	325	4.22	23.3	6	5.1	2.6	4.8	58.6	7.1	1.12	0.04	22.9	0.02	0.72	0.092	<0.05	<0.01	<0.02	1.00	-64.4	-8.8	7	Na-Ca-HCO3
AT15	Górgonos	80	7.4	30.6	231.7	6.5	38.4	4.5	4.2	1.3	11.0	78.1	25.2	5.40	0.02	48.6	0.03	0.81	0.198	<0.05	<0.01	<0.02	1.50	-65.6	-9.0	-5	Na-Ca-Mg-HCO3
AT16	Fray Pedro	70	7.3	30	334	4.28	21.0	6.5	4.6	2.2	5.6	68.3	8.5	1.43	0.03	20.1	0.02	0.34	0.095	<0.05	<0.01	<0.02	0.30	-62.4	-8.7	9	Na-Mg-HCO3
AT17	Bajo La Arena B	80	8.7	24.6	218.5	4.32	20.8	2.8	1.8	0.5	0.7	53.7	2.2	2.40	0.01	48.3	0.04	1.40	0.584	<0.05	<0.01	<0.02	0.90	-72.2	-9.9	4	Na-Mg-Ca-HCO3
AT18	S. Juan de Ocotlán 1	120	7.9	22.5	345	4.95	27.1	8.5	4.5	4.2	2.0	87.8	1.5	0.05	0.02	25.6	0.04	2.49	0.132	<0.05	<0.01	<0.02	0.70	-67.1	-9.4	8	Na-Ca-HCO3-SO4
AT19	Manantial Toluquilla	--	8.3	24.6	143.9	5.8	57.5	13.4	25	12.6	35.6	87.8	65.7	13.8	0.18	38.2	0.07	0.57	0.308	<0.05	<0.01	0.13	2.00	-59.2	-7.9	-1	Na-HCO3-F
AT20	La Estancia 4	150	7.7	23.8	382	2.42	38.1	9.4	13.3	8.6	3.3	162.7	2.5	0.41	0.16	37.7	0.19	0.32	0.294	<0.05	<0.01	0.03	0.40	-67.0	-9.4	12	Na-Ca-HCO3
AT21	La Loma de S. Juan	80	7.5	25.3	569	4.4	38.3	8.6	16.7	12.9	7.2	172.2	6.1	0.95	0.18	44.3	0.03	0.46	0.963	<0.05	<0.01	<0.02	0.80	-67.8	-9.5	5	Na-Mg-Ca-HCO3
AT22	Rancho Alegre	150	7.7	27.5	213.9	4.5	92.6	28.5	37.3	47.8	41.5	467.9	19.6	0.80	0.47	46.6	0.06	0.94	0.397	0.16	0.13	0.12	0.50	-66.3	-9.3	1	Na-HCO3
AT23	Mimbela	50	6.9	28.2	445	5.02	55.0	10.3	18.5	6.1	30.7	97.6	50.8	11.7	0.09	43.4	0.03	0.22	0.008	<0.05	<0.01	0.03	1.90	-59.6	-7.9	-3	Na-HCO3
AT24	Teisistan 14	120	7.0	25.1	305	6.34	33.9	3.5	3.6	1.3	3.1	126.9	13.5	4.20	0.02	45.4	0.05	0.37	0.020	0.06	<0.01	<0.02	1.90	-68.8	-9.6	7	Na-Ca-SO4-HCO3-Cl
AT25	Fovisste	200	6.8	24.4	649	6.68	18.4	7.8	3.1	1.7	1.8	43.9	6.7	2.08	0.02	44.2	0.03	0.35	0.035	<0.05	<0.01	<0.02	0.80	-69.2	-9.5	5	Na-Ca-SO4-Cl
AT26	Power Center	90	7.5	32.6	190.7	5.65	35.3	6.1	7.5	2.7	2.1	113.7	8.6	1.58	0.04	41.9	0.05	0.24	0.033	<0.05	<0.01	<0.02	1.60	-66.3	-9.5	4	Ca-Na-Mg-HCO3
AT27	Vinreyes	300	6.8	29.4	363	4.81	43.9	7.2	5	3.2	1.3	146.4	1.5	0.73	0.02	51.6	0.12	1.18	0.113	0.06	<0.01	<0.02	0.80	-70.9	-10.0	5	Na-HCO3
AT28	Teisistan 61	275	6.7	24.6	222.4	5.94	27.0	4.4	4	1.6	1.4	83.0	3.5	2.07	0.02	47.8	0.35	0.39	0.431	<0.05	<0.01	<0.02	1.60	-69.4	-9.7	1	Na-HCO3-SO4
AT29	Teisistan 56	270	6.9	33.7	298	7.66	16.7	1.7	7.1	2.1	7.6	30.5	21.0	6.75	0.01	19.1	0.02	0.22	0.019	<0.05	<0.01	<0.02	1.70	-66.5	-9.3	6	Na-HCO3
AT30	Teisistan 70	250	7.1	26	107.8	4.83	20.0	8.6	7	1.9	2.9	60.8	12.3	5.72	0.07	47.5	0.03	0.390	0.048	<0.05	<0.01	<0.02	1.70	-67.8	-9.4	-1	Na-HCO3
AT31	Unid. Dep. Tonala	118	6.7	29.8	351	3.5	40.3	12.7	13.3	7.8	3.4	181.8	1.7	1.06	0.14	35.2	0.06	0.26	0.112	<0.05	<0.01	<0.02	0.70	-65.6	-9.0	13	Na-HCO3
AT32	San Ismael	285	6.7	23.9	451	4.37	20.2	7.5	15.8	7.8	0.3	132.2	0.2	0.05	0.17	33.6	0.03	0.06	0.100	<0.05	<0.01	0.03	0.70	-64.8	-8.8	15	Na-Ca-HCO3-SO4-Cl
AT33	Tateposco 2	250	6.8	25.5	192.1	5.46	44.5	13.4	12.6	8	6.3	166.4	2.4	0.7	0.14	35.9	0.03	0.34	0.130	<0.05	<0.01	<0.02	0.70	-64.5	-8.9	-15	Na-HCO3
AT34	El Lindero	55	6.7	26.6	138.9	6.57	22.2	7.4	8.5	5.5	1.2	97.6	6.1	2.02	0.11	40.8	0.03	0.18	0.162	<0.05	<0.01	0.03	2.00	-68.9	-9.6	4	Na-HCO3
AT35	Vivero Los Amigos	24	6.6	27.3	234.7	7.72	19.9	16.6	10.1	4.1	2.7	53.7	40.1	25.4	0.08	30.9	0.02	0.03	0.070	<0.05	<0.01	<0.02	2.90	-64.5	-9.4	5	Na-HCO3
AT36	El Taray	200	6.4	24.7	242	4.37	11.5	7.8	9.3	4.7	0.5	102.5	0.3	0.12	0.04	36	0.03	0.26	0.341	<0.05	<0.01	<0.02	0.70	-67.1	-9.3	3	Na-HCO3
AT37	Viveros del Sur	54	6.3	27.7	160.3	5.63	14.1	9.6	1.9	0.3	2.3	29.3	2.1	1.19	0.01	20.3	0.14	4.90	0.084	<0.05	0.02	<0.02	0.50	-71.6	-10.3	2	Na-HCO3
AT38	Las Pomas	115	6.2	26.4	310	5.74	33.9	1.8	13.5	2.4	9.5	78.1	21.2	5.94	0.02	27.3	0.02	1.67	1.040	0.08	<0.01	<0.02	1.80	-68.5	-9.5	4	Na-Ca-HCO3-SO4
AT39	Potrero La Ordeña	64	6.7	25	165.9	5.93	31.9	8.8	13.2	8.2	10.1	97.6	23.4	17.7	0.15	25.5	0.03	1.25	0.065	<0.05	<0.01	<0.02	1.00	-68.3	-9.4	-22	Na-Ca-HCO3
AT40	Los Gigantes	82	8.0	31.6	182.8	5.65	30.9	2.7	4.7	1.3	2.8	58.6	6.9	4.87	0.02	38.3	0.02	1.71	0.252	0.06	<0.01	<0.02	0.50	-70.4	-9.6	-6	Na-Ca-Mg-HCO3

619 **Table 2:**

Group	N	Parameter	pH (S.U.)	T ($^{\circ}$ C)	EC (μ S cm $^{-1}$)	TDS	DO	3 H (TU)	δ^2 H (‰)	δ^{18} O (‰)	HCO $_3^-$	K	Mg	Si	Ca	Fe	Na	Sr	Zn	F	Cl	NO $_3$ -N	SO $_4$	Li	Ba	Mn
1	6	Average	6.9	33.8	1575	733	5.4	0.73	-66.65	-9.02	852.7	41.0	79.5	45.9	54.4	0.14	130.3	0.46	0.11	1.11	87.2	0.17	11.0	0.29	0.28	0.33
		Median	7.0	33.6	1706	710	5.4	0.70	-66.52	-8.98	864.5	38.5	98.0	43.3	48.0	0.10	130.5	0.46	0.07	0.80	76.3	0.05	6.5	0.33	0.29	0.24
2	12	Average	7.2	30.2	300	95	4.5	0.66	-66.09	-9.10	128.0	9.2	5.9	33.6	10.9	0.04	31.2	0.10	0.23	0.67	3.5	0.97	3.9	0.01	0.04	0.01
		Median	7.1	29.9	317	89	4.4	0.70	-66.27	-9.07	117.4	8.2	5.6	35.6	13.0	0.03	29.0	0.11	0.13	0.34	3.3	0.57	2.4	0.00	0.03	0.01
3	3	Average	6.8	23.4	556	229	4.7	2.1	-55.5	-7.2	69.9	10.9	8.7	41.0	22.2	0.04	52.2	0.13	0.11	0.3	38.9	12.4	70.6	0.00	0.08	0.01
		Median	6.7	23.9	569	241	5.0	2.0	-59.2	-7.9	87.8	10.3	7.4	41.4	23.0	0.03	55.0	0.12	0.01	0.2	35.6	11.8	65.7	0.00	0.08	0.01
4	19	Average	7.0	25.3	254	84	6.0	1.5	-68.5	-9.5	75.5	5.4	2.5	38.6	6.6	0.06	29.4	0.04	0.17	1.1	6.2	9.1	15.5	0.02	0.04	0.01
		Median	6.8	25.0	235	77	5.9	1.6	-68.8	-9.5	78.1	4.5	2.1	44.0	6.7	0.03	27.0	0.02	0.07	0.8	2.9	4.5	12.3	0.00	0.04	0.01

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621 **Table 3:**

Variable	PC1	PC2	PC3	PC4
pH				0.47
T	0.24	0.23	0.29	
EC	0.32			
DO		-0.25		
³ H		-0.37		0.15
² H			0.45	-0.20
¹⁸ O			0.45	
HCO ₃	0.32			
K	0.32			
Mg	0.33			
SiO ₂				-0.23
Ca	0.32			
Fe				-0.37
Na	0.33			
Sr	0.32			0.13
Zn				
F				-0.371
Cl	0.3			
NO ₃		-0.40		
SO ₄		-0.50		
Eigenvalue	8.43	3.38	2.21	1.34
% of variance	42	17	11	7
Cum. % variance	42	59	70	77

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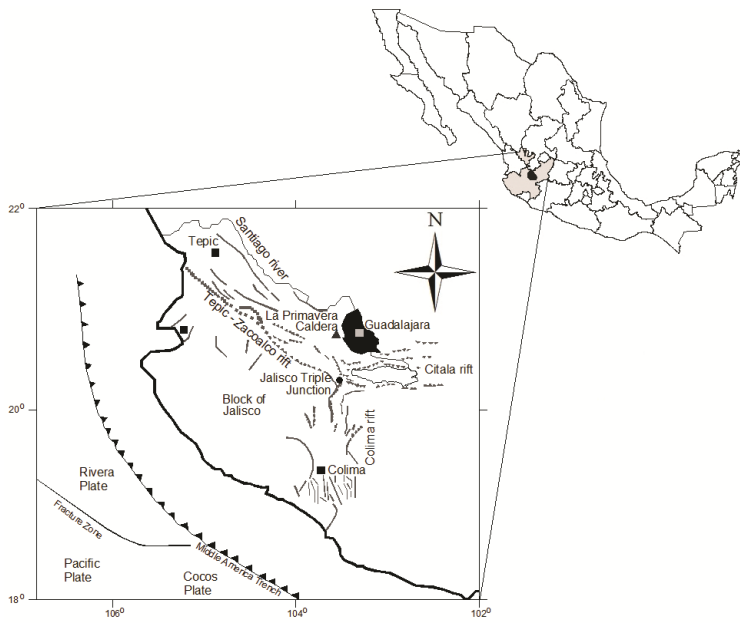
623 **Table 4:**

Well ID	Well group	M3 calculations						Cl m-b calculations	
		% fresh groundwater		% polluted water		% hydrothermal water		% hydrothermal water	
		Avg	SD	Avg	SD	Avg	SD	Avg	SD
2	1	78.1	0.6	17.0	0.1	4.9	0.7	6.2	1.4
3	1	68.1	0.7	26.4	0.1	5.5	0.7	7.3	1.7
4	1	73.6	0.7	21.3	0.1	5.1	0.8	7.6	1.7
5	1	63.1	2.0	24.4	0.2	12.5	2.2	20.6	4.8
6	1	67.7	0.0	30.4	0.0	1.9	0.0	1.1	0.3
22	1	75.6	0.3	21.4	0.0	3.0	0.3	3.6	0.8
10	2	71.1	0.1	28.5	0.0	0.4	0.1	0.3	0.1
33	2	69.5	0.1	29.8	0.0	0.7	0.1	0.4	0.1
18	2	80.3	0.1	19.0	0.0	0.7	0.1	0.0	0.0
40	2	89.0	0.0	10.2	0.0	0.8	0.0	0.1	0.0
14	2	68.3	0.1	31.2	0.0	0.6	0.1	0.2	0.1
16	2	62.6	0.1	36.1	0.0	1.2	0.1	0.3	0.1
13	2	76.1	0.1	22.5	0.0	1.4	0.1	0.0	0.0
32	2	69.0	0.1	30.4	0.0	0.7	0.1	0.0	0.0
36	2	78.9	0.1	20.1	0.0	1.1	0.1	0.0	0.0
21	2	82.7	0.0	16.5	0.0	0.9	0.0	0.5	0.1
31	2	72.3	0.1	26.4	0.0	1.3	0.1	0.1	0.0
20	2	80.4	0.1	19.3	0.0	0.3	0.1	0.1	0.0
12	3	0.0	0.0	100.0	0.0	0.0	0.0	4.4	1.0
19	3	48.2	0.0	51.8	0.0	0.0	0.0	3.1	0.7
23	3	48.8	0.0	51.0	0.0	0.1	0.0	2.6	0.6
1	4	66.3	0.0	33.7	0.0	0.0	0.0	0.7	0.2
15	4	73.4	0.0	26.6	0.0	0.0	0.0	0.8	0.2
11	4	63.0	0.0	36.8	0.0	0.2	0.1	1.1	0.2
38	4	84.8	0.0	15.2	0.0	0.0	0.0	0.7	0.2
39	4	82.9	0.0	16.7	0.0	0.3	0.0	0.7	0.2
7	4	89.7	0.0	10.1	0.0	0.2	0.0	0.0	0.0
29	4	78.4	0.0	21.4	0.0	0.2	0.0	0.5	0.1
34	4	86.7	0.0	13.3	0.0	0.0	0.0	0.0	0.0
35	4	75.8	0.0	24.2	0.0	0.0	0.0	0.1	0.0
9	4	93.1	0.0	6.6	0.0	0.3	0.0	0.1	0.0
25	4	85.9	0.1	13.8	0.0	0.4	0.1	0.0	0.0
24	4	86.5	0.0	13.5	0.0	0.1	0.0	0.1	0.0
26	4	84.1	0.1	15.5	0.0	0.4	0.1	0.0	0.0
30	4	82.3	0.0	17.7	0.0	0.0	0.0	0.1	0.0
17	4	96.2	0.0	3.3	0.0	0.5	0.0	0.0	0.0
27	4	95.2	0.0	4.8	0.0	0.0	0.0	0.0	0.0
28	4	88.4	0.0	11.1	0.0	0.5	0.0	0.0	0.0
8	4	93.8	0.2	4.5	0.0	1.7	0.3	2.6	0.6
37	4	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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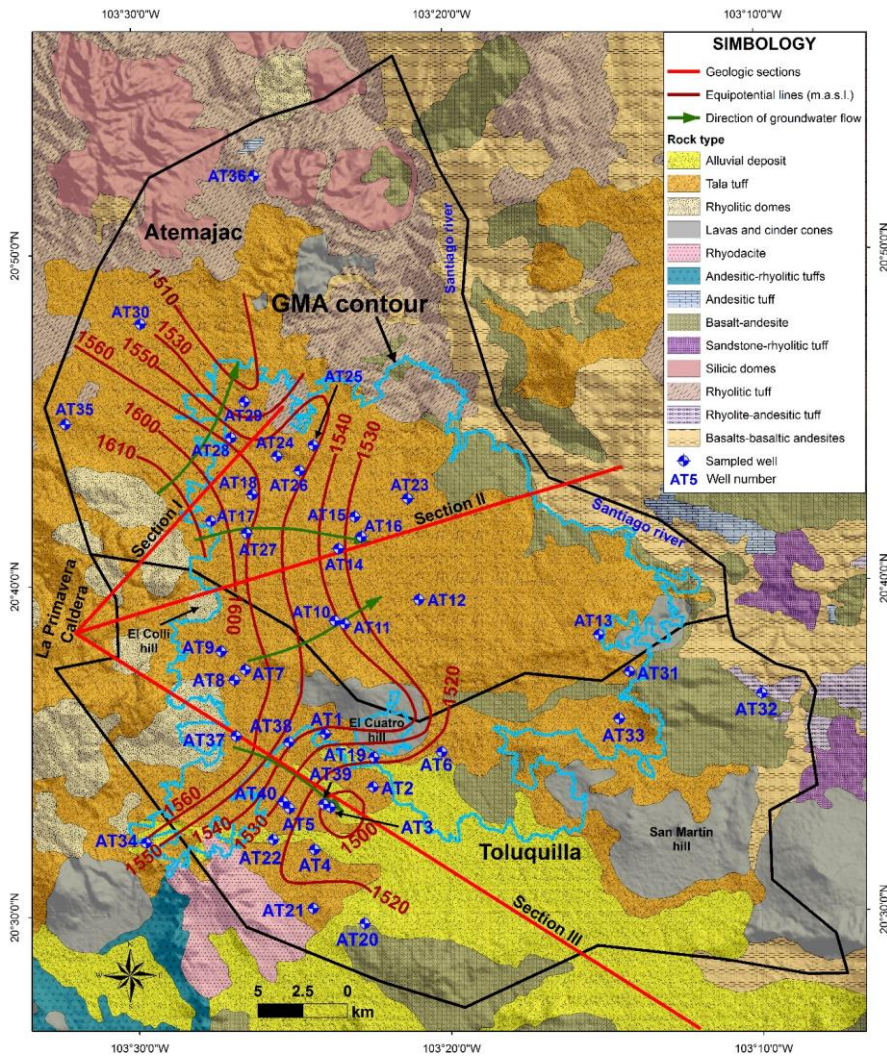
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626 **Figure 1:**

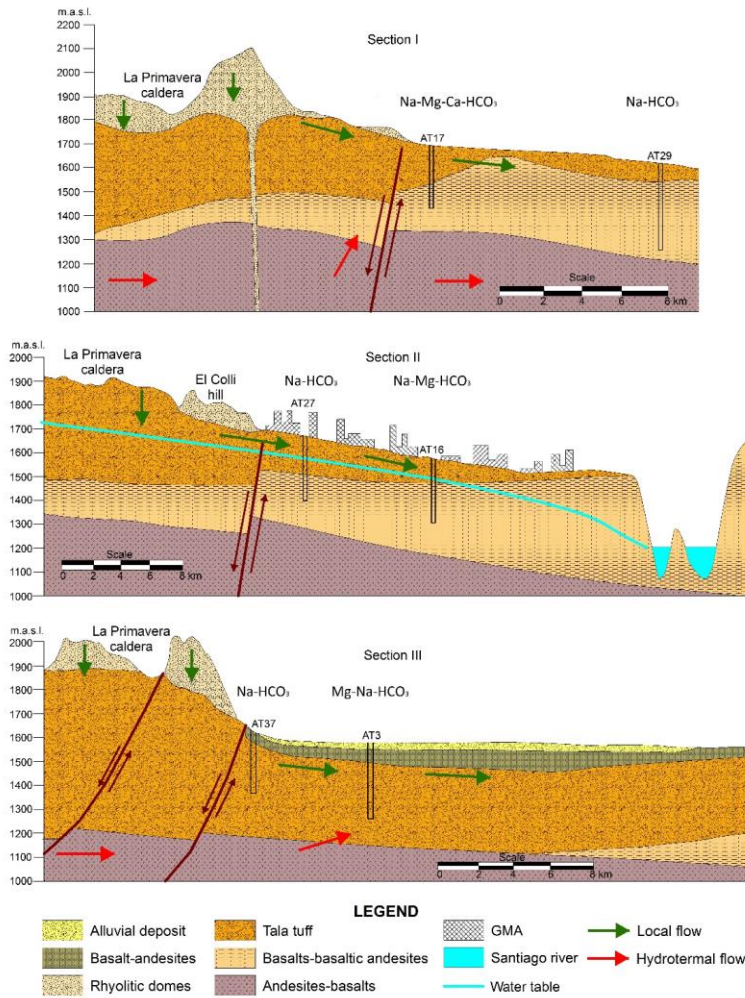


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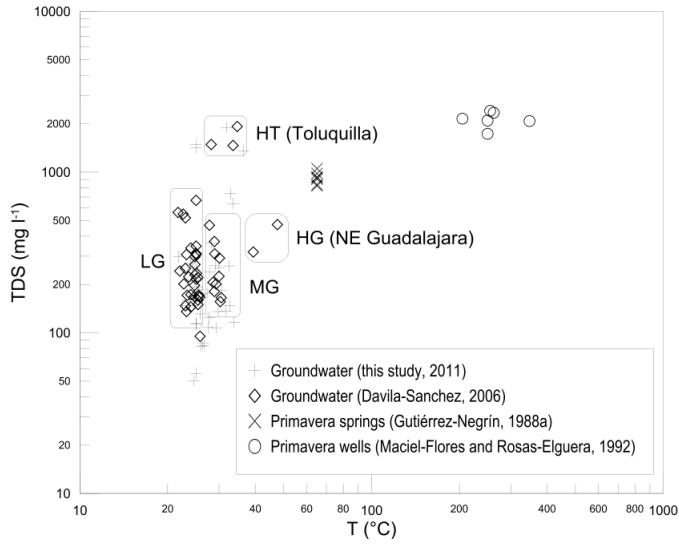
628 Figure 2:



630 Figure 3:



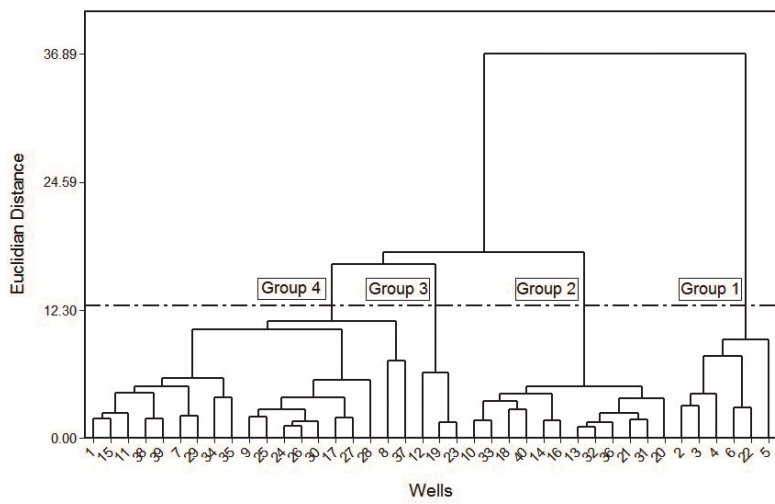
632 **Figure 4:**



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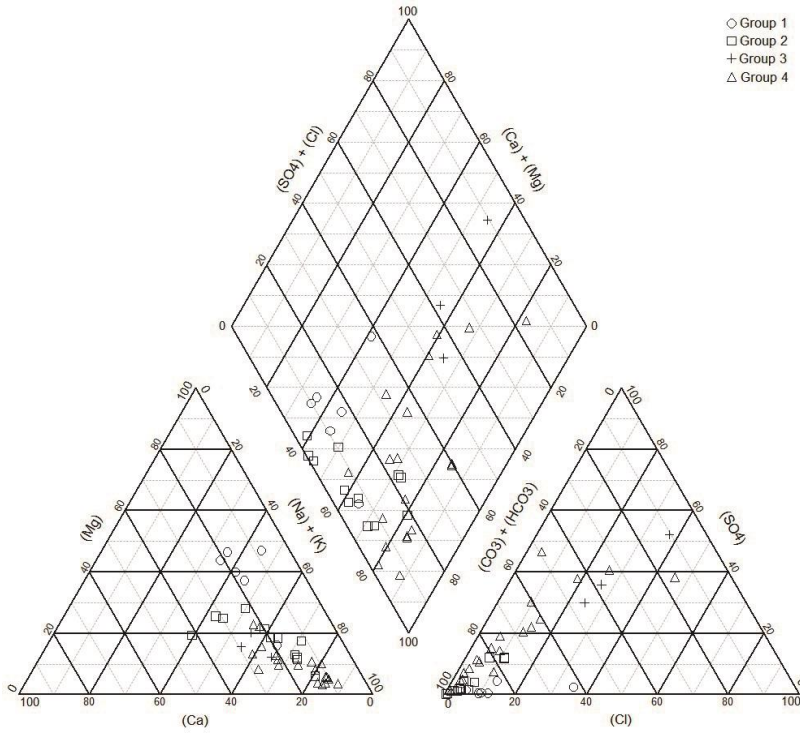
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635 **Figure 5:**



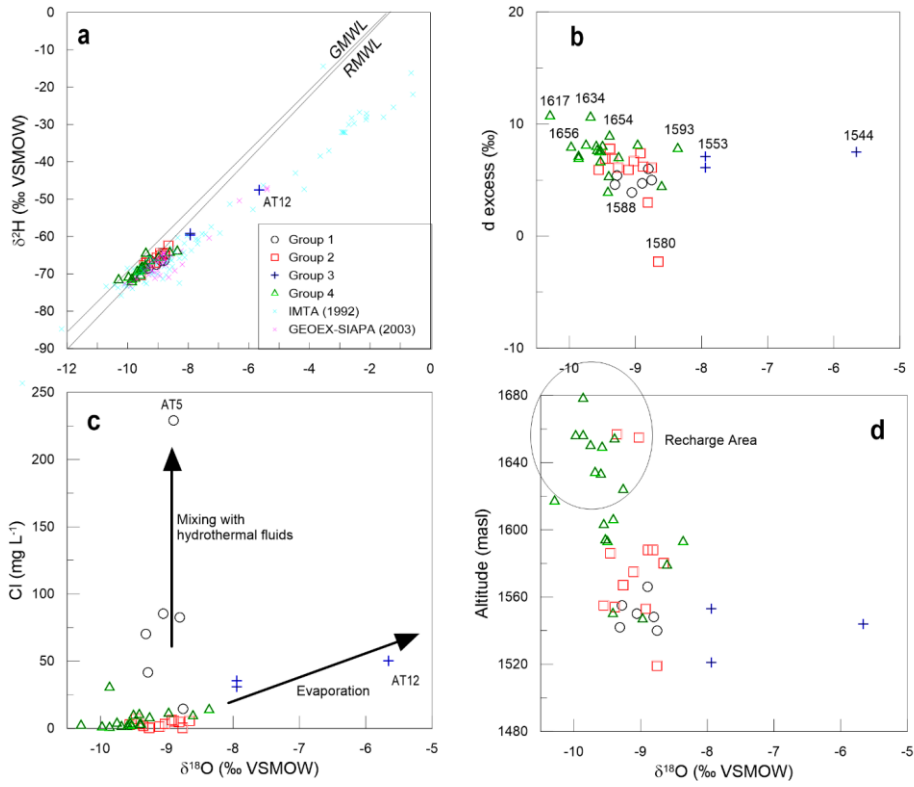
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637 Figure 6:



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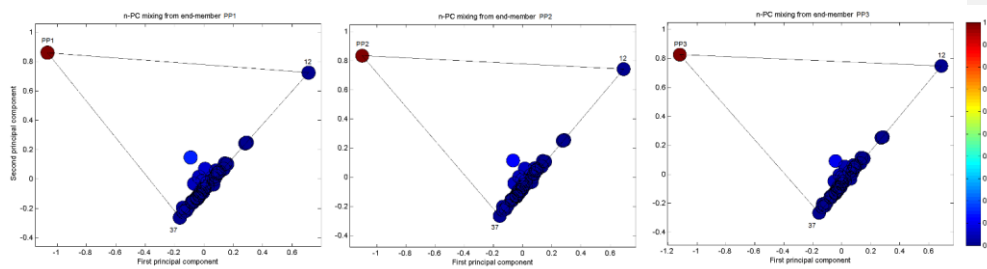
639 **Figure 7:**



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642 **Figure 8:**



643