Revision of review 1 (Custodio)

Dear Dr. Custodio,

thank you very much for your interest and comments. Our answers (black and blue colored) are included in the text of your review (red colored) below.

General comments:
1. **The paper presents an interesting point of view on groundwater hydrogeochemisty 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 you, extend the Hydrogeological Settings (section 2.1), modify the Groundwater flow system (section 4.4) and replaced Figure 1 with two new figures (Fig. 1 Hydrogeological settings, Fig. 2 Cross sections) for a better visualization:

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

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

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55   *Pumping wells are drilled in the upper aquifer. Its water table distribution is shown in Fig. 2. In*
56   *the Atemajac valley, groundwater flow direction is oriented mainly from southwest to*
57   *northeast, from the topographically higher areas, towards the Santiago river, with possible*
58   *recharge from normal faults west from Guadalajara city (Fig. 3, section I and II); while in*
59   *Toluquilla the flow of groundwater circulates from northwest to southeast (Fig. 3, section III)*
60   *(SIAPA, 2004; CONAGUA, 2009). However, anthropogenic activity has been changing the*
61   *flow paths, resulting in the formation of different cones of depression. The major discharge is*
62   *given by well pumping activities and springs in the escarpment of the Santiago river (SIAPA,*
63   *2004; CONAGUA, 2009 and 2010). Due to the heavy extractions from the aquifer system,*
64   *water table levels are falling up to 2.2 m/year and 0.3 m/year on average in Atemajac and*
65   *Toluquilla aquifers, respectively (SIAPA, 2004). The constructed well depth is up to 500 m*
66   *and up to 380 m in the valley of Atemajac and Toluquilla, respectively. Depth to water table is*
67   *up to 150 m in the Atemajac valley and typically less than 50 m in Toluquilla valley (SIAPA,*
68   *2004).*
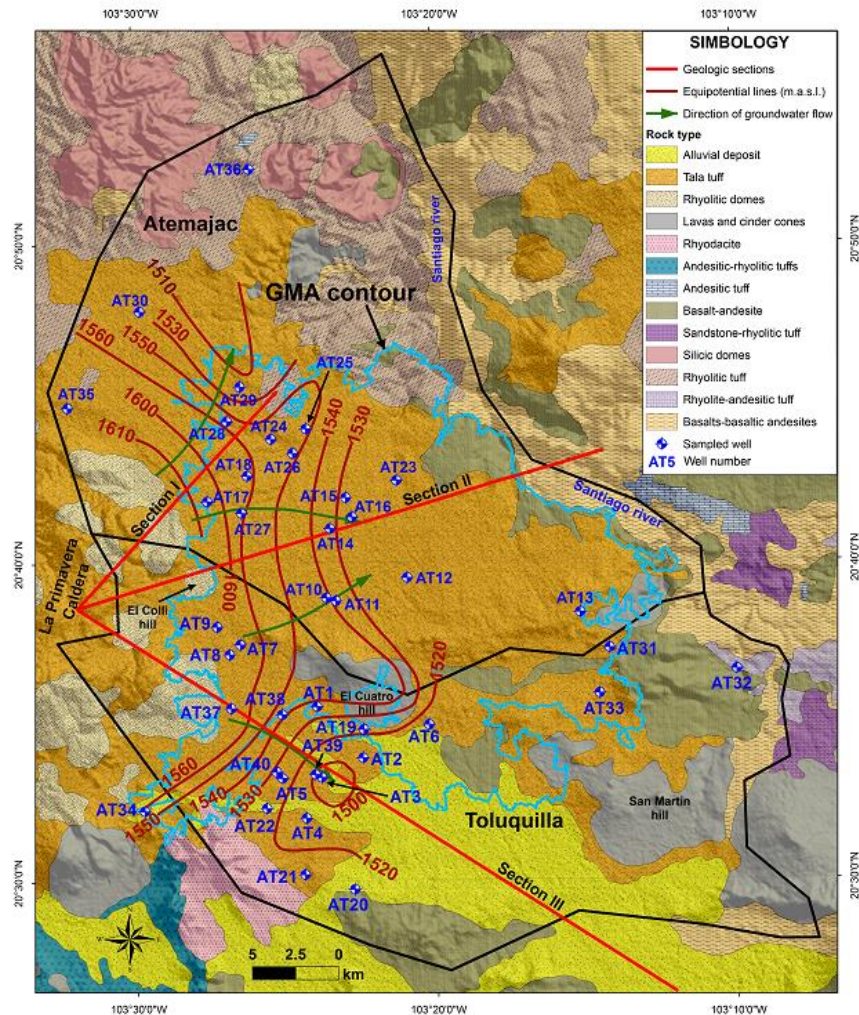
69
70   *Figure 2: Surface geology, water table distribution and location of wells sampled in the study*
71   *area. Note: GMA = Guadalajara metropolitan area*
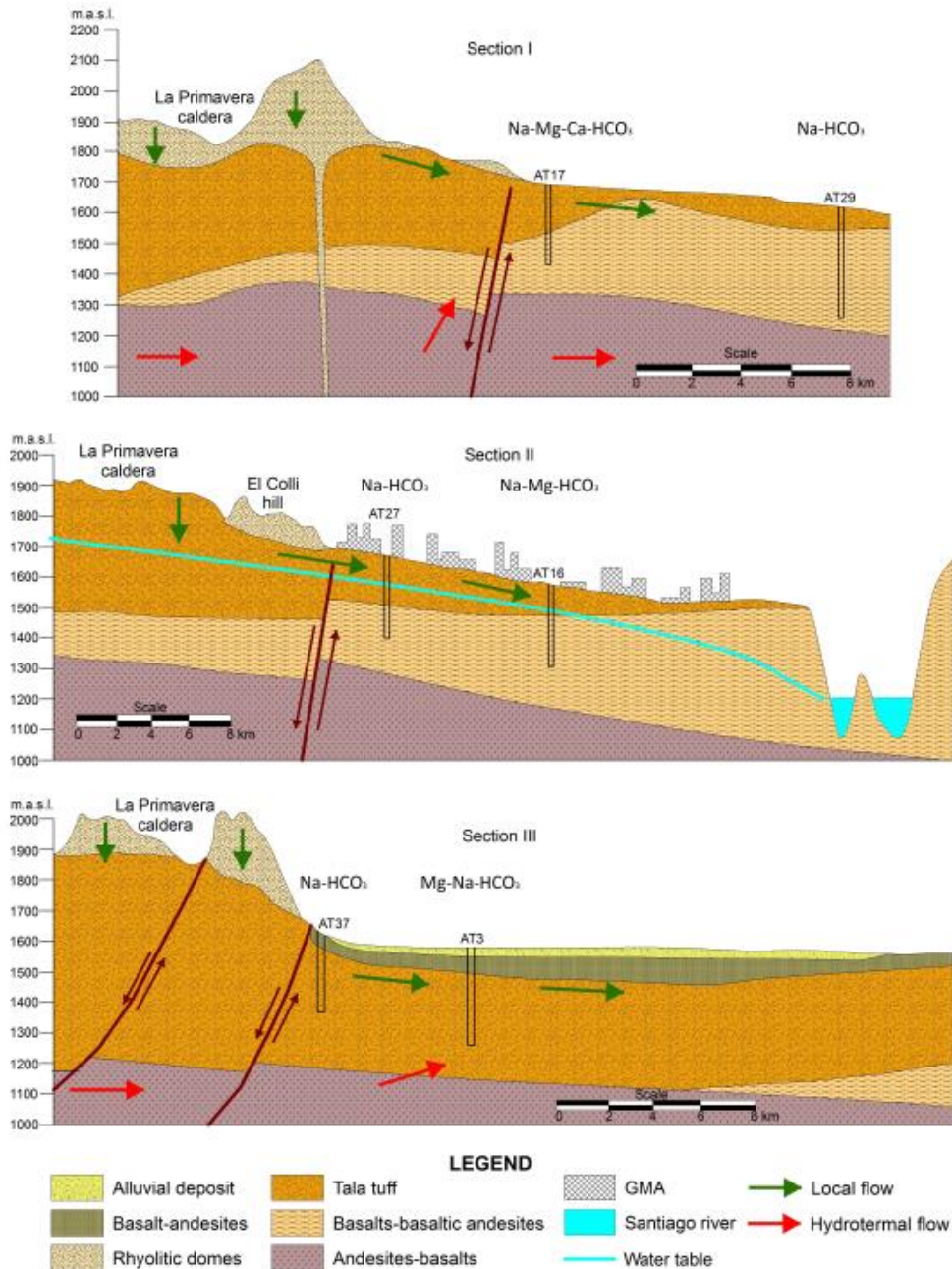
Figure 3: Cross-sections indicated in Fig. 2 and considering hydrogeological settings and water types of selected wells.

Section 4.4: Groundwater Flow System of Guadalajara

The hydrogeological Atemajac-Toluquilla system is located in the northeastern area of the Tepic-Zacoalco Rift, a complex and active neotectonic structure. Local groundwater recharge for Atemajac-Toluquilla Valley originates from rainfall mainly over the La Primavera caldera in the central western portion of the study unit. It flows from the upper alluvial sediments towards the valley floor and Santiago River. Recharge water is of Na-HCO$_3$ water type with low

temperatures, salinities, Cl and Na values, elevated NO_3 concentrations, as well as relatively high tritium activities in the range of 0.5 -2.9 TU indicating little mixing of flow paths and recent recharge from pristine soils and infiltration from agricultural plots. This result confirms also a relatively fast transport through the unsaturated zone (Herrera and Custodio, 2014). As groundwater circulates in northeastern (Atemajac valley) and eastern direction (Guadalajara city) following the hydraulic gradient, its temperature and salinity increases moderately. The wells are typically drilled in Tala tuff underlain by andesites to basaltic andesite rocks. Locally groundwater evolves to a Na-SO_4 to mixed HCO_3 water type, with relatively high contents of SO_4, NO_3, Na, Cl and tritium (~2TU) indicating an important impact from anthropogenic pollution in urban Guadalajara.

Underground heat flow suggests the existence of a magma chamber below the La Primavera caldera, which provides hydrothermal fluids observed on surface expressions such as the La Soledad solfatara and the Cerritos Colorados geothermal field. Regional groundwater that is in contact with these fluids circulates through the lower Atemajac-Toluquilla aquifer specifically below Santa Anita and Toluquilla (Sánchez-Díaz, 2007). These Mg-HCO_3 to mixed HCO_3 waters are characterized by elevated temperatures, salinity, Cl, Na and HCO_3 values, low tritium values (<1.7 TU) and contain considerable concentrations of Li, Mn, B and F, indicating thermal influence, circulation through an active volcanic center and fault zones, and water-rock interactions. The corresponding wells are typically drilled in basalt-andesitic rock formations. The well depth of these wells range from 200 to 300 m and depth-to-water table is about 50 m. The low tritium concentration indicates pre-modern infiltration. Low tritium concentrations in deep wells, according to Herrera and Custodio (2014), are due to a mix of water from the upper aquifer and the vertical ascending flow from the lower aquifer. On the other hand, the tritium shows that geochemically speaking, the water predominates as an old fraction (Custodio, 1989)

The isotopic composition of groundwater confirms the interconnectivity between water from deeper and shallow rock materials. Practically all groundwater sampled contains at least a small fraction of modern water. The proportions of hydrothermal fluids in sampled well waters ranged from 13 (cold groundwater) to 87% (hydrothermal water), while the proportion of polluted water is between 0 and 63%.

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 as follows:

4.1 Groundwater Chemical Characterization

Table 1 shows the concentrations of measured groundwater elements, field parameters and isotopic ratios, along with the hydrochemical classification. The classification of waters was performed with HCA using 20 variables (pH, temperature, EC, DO, Na, K, Ca, Mg, Cl,

HCO$_3$, SO$_4$, NO$_3$-N, Sr, SiO$_2$, Fe, F, Zn, ^{3}H, ^{2}H, ^{18}O). With the help of Ward's linkage rule iteratively neighboring points (samples) were linked through a similarity matrix (Ward, 1963). The squared Euclidian distance was selected as the similarity measurement. The second method was a PCA. For both cluster algorithms, lognormal distributed data were previously log-transformed, and all of the variables standardized (z-scores). The HCA samples were classified into 4 major groups as represented by the dendrogram in Fig. 4 and median values (Table 2). The values for Li, Mn and Ba were not considered in the cluster analysis, because most samples had concentrations below the detection limit.

The four groups are plotted on a Piper diagram to demonstrate chemical differences (Fig. 5). Salinity increases as groundwater moves east- and southeastwards from the Primavera to discharge areas along topographic flow path. EC values reach typically 600 μS cm^{-1} in the discharge areas urbanized Guadalajara, except for Toluquilla wells where values ascend to 2300 μS cm^{-1}. Group 4 (n=19) is a Na-HCO$_3$ water type located in recharge zones in the western portion and reflects a short (local) groundwater flow path with poor circulation. It shows low temperatures (average 25.3 °C) and salinity (254 μS cm^{-1}), however elevated NO$_3$-N (9.1 mg l^{-1}) values, possibly derived from agricultural practices. Groundwater that moves in northern and eastern direction attains a Na-HCO$_3$ to mixed HCO$_3$ water type (group 2, n=12), with increased temperatures (30.2 °C) but similar low salinities (300 μS cm^{-1}), indicating water-rock interactions. Groundwater in the discharge area in central Guadalajara city evolves to a Na-SO$_4$ to mixed HCO$_3$ water type (group 3, n=3), with higher concentrations of several elements indicating an important impact from anthropogenic pollution, i.e. SO$_4$ (70.6 mg l^{-1}), NO$_3$-N (12.4 mg l^{-1}), Na (52.2 mg l^{-1}) and Cl (38.9 mg l^{-1}). Finally, water that moves from recharge zone at Primavera caldera southeast towards the central part of Toluquilla valley, attains a Mg-HCO$_3$ and mixed HCO$_3$ type (group 1, n=6). These wells show highest temperatures (33.8 °C), high salinity (EC=1,575 μS cm^{-1}), and lowest NO$_3$-N (0.17 mg l^{-1}) (Fig. 3).

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

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

Table 3 shows that 4 factors may explain 77% of the variance. Factor 1 (42% of the variance) largely represents high salinity. The correlations of temperature, Na and Cl indicate hydrothermal influence, while HCO3, Na and Sr could be connected to mineralization and rock dissolution processes, and cationic exchange. In factor 2 (17%) the temperature is inversely related with DO, ^{3}H, and to a lesser degree, NO$_3$ and SO$_4$, suggesting that this factor represents water affected by human activities, either urban or agricultural. In addition, Table 1 shows that waters affected by human activities are most

181 *evaporated. Sulfate could be related to contamination due to the infiltration of commonly*
182 *applied sulfate-based fertilizers during the rainy season. This occurs because all the wells*
183 *are undersaturated with regard to gypsum, indicating that the water does not move through*
184 *deposits of this mineral. In factor 3 (11%) the relationship between ^2H and ^{18}O reveals the*
185 *existence of recharge water. This factor is generated almost entirely by the linear*
186 *relationship between O and H isotopes. The relation with temperature indicates the recharge*
187 *conditions at different recharge sites. Factor 4 (7%) may be indicative of dissolution of*
188 *minerals that contain F. The study of Sánchez-Díaz (2007) indicates that rhyolitic rocks and*
189 *ashes of the study area are responsible for releasing F. Comparable trends have been*
190 *observed in similar volcanic environments in central and northern Mexico (Mahlknecht et al.,*
191 *2004, Mahlknecht et al., 2008).*

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193

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

197

198 **Answer:**
199 We understand that there is a shift to heavier values, however it is relatively small. Recharge
200 water from La Primavera (group 4) has a signature of (-68.5/-9.5 permil), while thermally
201 affected water has a signature of (-66.7/-9.0 permil). The small difference may be explained
202 by the effect that most waters have at least a small component of thermal affected waters,
203 as also confirmed by the mixing model M3 (Table 4). On the other hand, Gutierrez et al.
204 (1994) reports values of -8.7-9.2 permil for thermal waters in the study area with
205 temperatures between 64 and 85 °C (Sanchez-Diaz, 2007).

206

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

209

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

213

214 **5. 3H content is what is expectable from an unconfined system recharged from the**
215 **surface taking into account the mixing produced by a spring or a long screened**
216 **pumped well. This is not addressed. It seems that the groundwater equivalent water**
217 **depth is relatively small. This is also not addressed.**

218

219 **Answer:**
220 We agree that this issue is not addressed and propose to add the following paragraph which
221 describes 3H results in the section "4.2 Isotope hydrology":

222

223 *…*

224

225 *Tritium results indicate that groundwater within the study area includes both pre-modern (pre-*
226 *1950s) and modern recharge. The values range from 0.3 to 3.0 TU which suggests a*
227 *contribution from modern water in every sampled site (Table 1). The majority of waters with*
228 *^3H lower than 1.0 TU are in the southern portion of the aquifer system. Elevated ^3H values*
229 *(>1.5 TU) located mostly in the La Primavera volcanic system represent young waters or*
230 *recent recharge with little mixing of path lines. Waters with ^3H values <1.5 TU illustrates that*
231 *these wells may represent mixing of flow paths with modern and pre-modern groundwater*

232 *residence times. These waters are found mostly in Toluquilla, corresponding to elevated EC,*
233 *Cl and DIC values. The mixing of water from different ages is expectable because the aquifer*
234 *is under unconfined conditions, while wells penetrate the saturated zone to a considerable*
235 *depth, at times up to 500 m, and are almost always completely screened.*
236
237 *…*
238
239
240 **6. Technical comments: in tables say that pH has no units. Make clear if what is given is**
241 **SiO2 or Si; both are used with close figures. TDS is as STD in the tables. The two**
242 **cross sections of figure 8 are shown in figure 2 and not in figure 1; they seem too**
243 **simplistic; some added hydrogeological information will be welcome. The two cross**
244 **sections of figure 8 are shown in figure 2 and not in figure 1; they seem too**
245 **simplistic; some added hydrogeological information will be welcome.**
246
247 **Answer:**
248 We attend these technical comments correspondingly in the manuscript as well as all other
249 modification as result of the required changes. The two cross sections have been re-
250 elaborated considerably and can be seen in new Figure 3.
251
252