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15 **Groundwater chemistry characterization using multi-criteria approach: the upper Samalà**
16 **River basin (SW Guatemala)**

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27 **Keywords:** groundwater, hydrochemical analyses, chemometrics, principal component analysis,
28 hierarchical clustering analysis, Samalà River

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30

31 **Highlight:**

- 32 • Groundwater of the upper Samalà River basin (SW Guatemala) have been characterized
- 33 • Integrated multi-approach has been used for hydrochemical data interpretation
- 34 • Piper, Schoeller and univariate plots were coupled with chemometric tools (PCA, HCA)
- 35 • Water quality for drinking purposes did not reveal severe concerns

36

37

38 **Abstract**

39 Improving understanding on groundwater chemistry is a key priority for water supply from
40 groundwater resources, especially in developing countries. A hydrochemical study was performed
41 in an area of SW Guatemala (Samalà River basin), where water supply to population is
42 groundwater-based and no systematic studies on its groundwater resources have been performed so
43 far. Traditional hydrochemical analyses on major ions and some trace elements metals coupled with
44 chemometric approach were performed, including principal component analysis and hierarchical
45 clustering analysis. Results evidence that chemical differentiation is linked to the spatial distribution
46 of sampled waters. The most common hydrochemical facies, bicarbonate calcium and magnesium,
47 is linked to infiltration of meteoric waters in recharge areas represented by highlands surrounding
48 Xela caldera, a wide plateau where most of population is concentrated. This trend undergoes
49 chemical evolution in proximity of active volcanic complexes in the southern area, with enrichment
50 in sulphate, chloride and magnesium. Chemical evolution also occurs towards the centre of Xela
51 caldera due to slow circulation in aquifer and consequent sodium enrichment due to ion exchange
52 with the porous medium. Water quality did not reveal severe concerns, even though some sources
53 of contamination could be identified; in particular, agriculture and urban wastewater could be
54 responsible for observed threshold exceedances in nitrate and lead.

55 This integrated multi-approach to hydrochemical data interpretation yielded to the achievement of
56 important information that poses the basis for future groundwater protection in an area where main
57 water features were almost unknown.

58 **1. Introduction**

59 The assessment of groundwater chemistry in hydrogeological studies allows a better understanding
60 of the influence of geological, climatic features and anthropogenic uses on water composition,
61 allowing to assess the water suitability for drinking, agricultural and industrial purposes. Improving

62 hydrochemical understanding is thus a key priority for water supply from groundwater resources,
63 especially for those countries characterized by recent urban development and industrial growth as
64 Guatemala. According to CEPAL (2002), water resources volumes in Guatemala is about 201 km³
65 of surface water and 34 km³ of groundwater. In spite of such large availability, current water
66 distribution does not allow the fulfilment of equity, efficiency and environmental sustainability
67 criteria (SEGEPLAN-BID 2006). The upper Samalá River basin, 200 km SW from the capital city,
68 is a wide urban–industrial agglomeration where the risk of groundwater deterioration is high, due
69 to: uncontrolled withdrawal, intense agricultural exploitation, growing industrial activities,
70 untreated waste disposal and uncontrolled discharge of wastewater (CEPAL 2002). Water for
71 human consumption is withdrawn from aquifers because surface waters are used for wastewater
72 discharge, but limited laboratory facilities force most municipalities to detect only basic quality
73 parameters (e.g. pathogenic microorganisms) and only Quetzaltenango city (140k inhabitants)
74 possesses suitable municipal facilities for periodical controls.

75 Even though groundwater represents the leading resource for human sustainment in Samalà River
76 basin, a chemical characterization at a basin scale for water resources management has not been
77 performed yet. Previous studies give insights about both deep water circulation (Foley et al. 1990,
78 Asturias 2003, Bennati et al. 2011) and groundwater chemistry (Adams et al. 1990, Lima Lobato et
79 al. 2000, Walker et al. 2006). However both studies only aimed at characterizing the fluids of Zunil
80 geothermal reservoir, therefore they are concentrated in a small area 7 km SE from Quetzaltenango.

81 In this scenario, chemical groundwater characterisation would be useful to provide relevant
82 information for groundwater management . In the following, we report the main geological and
83 hydrogeological features of investigation area, which are expected to influence the chemistry of
84 groundwater. Then, the sampling and analytical techniques are described. After that, the main
85 trends of chemical datasets are analysed through classical methods such as classification diagrams
86 (Piper and Schoeller) and bivariate plots. Furthermore an integration with chemometric tools is
87 presented aiming at giving more detailed insights on the hydrochemical features of the investigated

88 area. Indeed, as described by many authors (e.g. Smeti et al. 2009, Kim et al. 2005, 2012,
89 Montcoudiol et al. 2015), large benefits can be obtained in the evaluation of groundwater chemistry
90 and qualitative assessment by joining chemometrics to traditional hydrochemical tools.

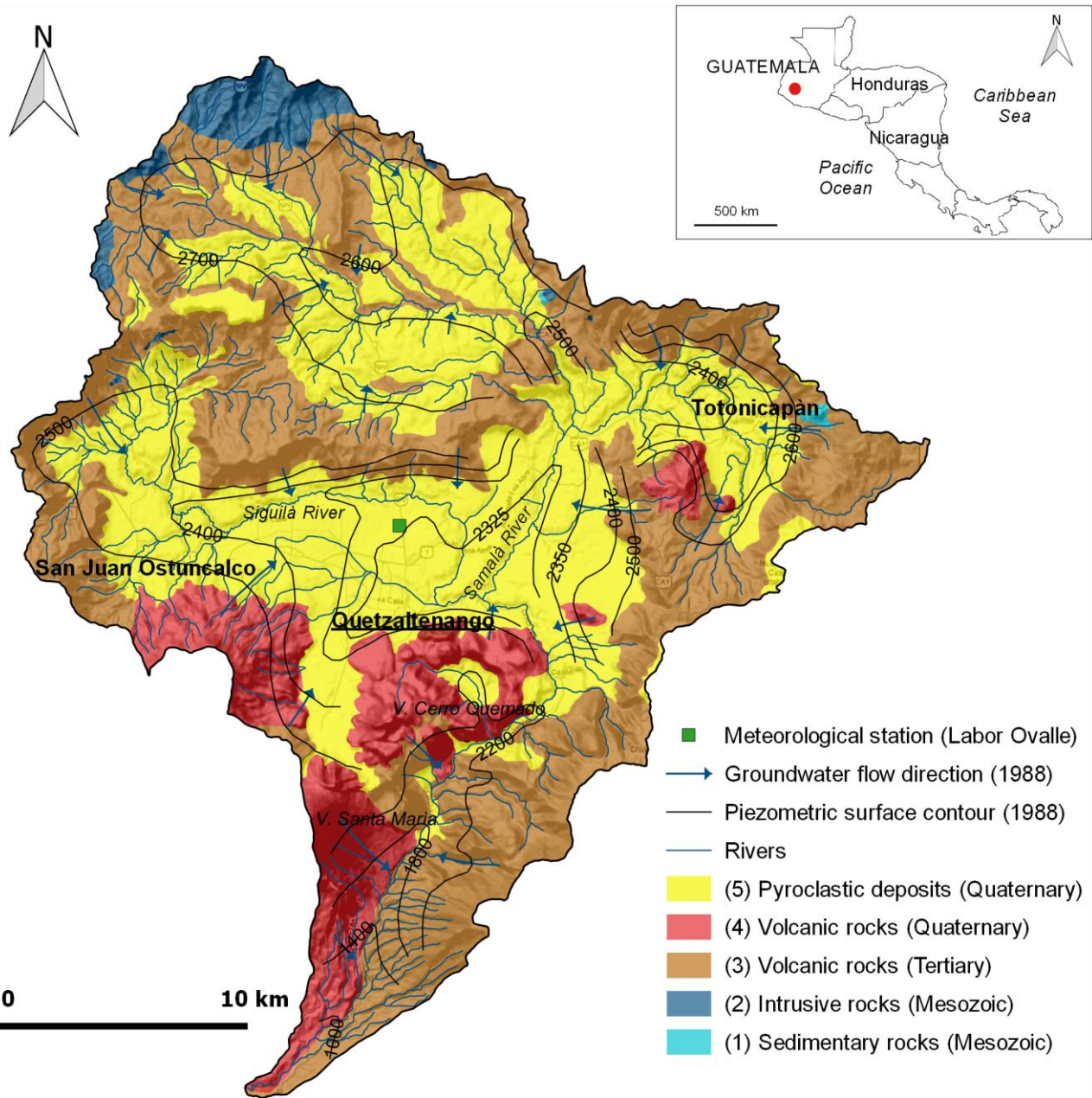
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92 **2. STUDY AREA**

93 **2.1 General setting**

94 Guatemala covers approximately 109,000 km² and the estimated population is about 15 million
95 inhabitants, with a growth rate nearly 2% (CIA, 2014), making it the most populous state in Central
96 America. The study area corresponds to the upper Samalá River basin, located 200 km SW from
97 Guatemala City. It represents one of the most populated regions of Guatemala, reaching more than
98 500k inhabitants, a half of whom lives in rural areas in a large number of villages or little
99 communities. The other half lives in towns, the most important ones being Quetzaltenango,
100 Totonicapán and San Juan Ostuncalco (Figure 1). The local economic development is based on
101 husbandry and agriculture and secondarily on craftsmanship, manufacturing and service industries.

102



103

104

105 **Figure 1.** Hydrogeological map showing hydrogeological complexes and potentiometric surface of
 106 groundwater represented through iso-piezometric lines and flow direction arrows (adapted from
 107 INSIVUMEH 1988)

108

109 2.2 Morphology, hydrology and climate

110 The upper Samalá River basin is located within a volcanic arc called Sierra Madre, where the main
111 volcanoes overtake 3000 meters. The central sector is characterized by a flat or mild morphology,
112 crossed by braided rivers forming fluvial terraces. This region corresponds to an ancient calderic
113 depression (Duffield et al. 1993), named Xela Caldera, remodelled by the rivers action. The
114 hydrographic pattern seems to be essentially controlled by tectonic and volcanic structures, as the
115 Samalá River course displays. It assumes NE-SW direction parallel to Zunil fault zone, then near
116 Quetzaltenango it is deflected by Cerro Quemado volcano and finally it restores NE-SW direction
117 towards south (Figure 1).

118 The regional climate is typical of tropical highlands, thus with a wet and a dry season and
119 significant variations of temperature and rainfall with respect to the altitude (MARN-URL/IARNA-
120 PNUMA, 2009). Meteorological data from INSIVUMEH Labor Ovalle weather station, located 6
121 km north of Quetzaltenango at an altitude of 2380 m a.s.l., are summarized in Table 1 and are
122 referred to the temperature and precipitation events data collected in the 1991-2010 period. The
123 average annual rainfall is about 890 mm and the events are mostly concentrated in the rainy season,
124 from May to October, with the highest rainfall in June. Temperature data range between 12.9 °C in
125 January and 15.8 °C in April, with a yearly average of 14.7 °C, and they display small differences
126 among monthly average values. The moisture reaches the maximum at the end of the rainy season
127 in September, with a monthly average of 81.2%.

128

129

130 **Table 1.** Monthly and annual average air temperature, rainfall and moisture the in upper Samalá
131 River Basin (data from INSIVUMEH weather station Labor Ovalle in the period 1991-2010).

132

| | Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | Year |
|------------------|------|------|------|------|-------|-------|------|-------|-------|-------|------|------|-------|
| Temperature (°C) | 12.9 | 13.7 | 14.8 | 15.8 | 15.8 | 15.6 | 15.8 | 15.8 | 15.2 | 15.0 | 13.4 | 13.2 | 14.7 |
| Rainfall (mm) | 2.5 | 2.1 | 12.9 | 41.9 | 142.1 | 173.3 | 99.5 | 115.7 | 161.6 | 107.7 | 21.7 | 11.2 | 892.3 |
| Moisture (%) | 65.7 | 63.1 | 64.5 | 68.4 | 74.5 | 79.4 | 74.5 | 76.1 | 81.2 | 79.3 | 72.7 | 68.6 | 72.2 |

133

134 **2.3 Geological and tectonic setting**

135 The Guatemalan geodynamics consists of a complex interaction between three tectonic plates,
136 North American, Caribbean and Cocos, that originated a NW-SE oriented continental volcanic arc
137 and a wide shear zone with two sub-parallel EW oriented systems of strike-slip faults called
138 Polochic-Motagua (Cáceres et al. 2005, Ortega-Obregón et al. 2008, Phipps Morgan et al. 2008,
139 Bennati et al. 2011). The regional framework is reflected in the study area with the presence of
140 several normal and strike-slip faults, the most significant ones represented by Olinstepeque Fault,
141 EW oriented, and the Zunil Fault zone, NE-SW oriented. The southern sector of the area is bordered
142 by various volcanic complexes: Siete Orejas, Santa María-Santiago, Cerro Quemado (red sectors
143 in Figure 1). Santa María-Santiago and Cerro Quemado complexes showed explosive and
144 effusive activity in historical times (Rose et al. 1987, Conway et al. 1992, Conway et al. 1994,
145 Bennati et al. 2011). The volcanic complexes, together with the aforementioned fault systems,
146 delimit a wide depression identified as Xela Caldera (Duffield et al. 1993). Associated to Zunil fault
147 zone and Xela Caldera eastern margin, a strong hydrothermal activity is found 7 km SE from
148 Quetzaltenango city (Adams et al 1990, Asturias 2003), where several geothermal wells were
149 drilled by the national company for electric supply (INDE).

150 According to Williams (1960), Rose (1987) and INSIVUMEH (1988), the bedrock is composed by
151 Cretaceous sedimentary and intrusive granitic rocks that rarely outcrop in the northern borders of
152 the investigated area. The most part of the area is constituted by large volumes of effusive

153 intermediate-acid rocks, ignimbrites and pyroclastites that were put in place during the Miocene
154 epoch. The recent and Quaternary volcanic activity was responsible of the formation of high
155 stratovolcanoes and calderic depressions, filled by dacitic and andesitic pyroclastic products derived
156 from explosive eruptions (Williams 1960). The rocky products of both Tertiary and Quaternary
157 eruptions are mainly andesites and basaltic andesites with hornblende and frequently one or two
158 pyroxenes and rarely olivine (Williams 1960, Rose et al. 1977, Rose 1987). The Tertiary
159 volcanoclastic rocks have rhyolitic to rhyo-dacitic composition, while the recent pyroclastic
160 deposits have andesitic to dacitic composition.

161

162 **2.4 Hydrogeological setting**

163 The current limited hydrogeological data availability on the surveyed area makes difficult to
164 reconstruct a deepened hydrogeological conceptual model. However, in this paragraph we will
165 propose a conceptual model according to the existing understanding.

166 According to INSIVUMEH (1988) and Bucci et al. (2015) five hydrogeological complexes can be
167 identified in the upper Samalá River basin (Figure 1): (1) Cretaceous intrusive rocks (Mesozoic
168 granites and granodiorites), (2) Cretaceous sedimentary rocks (terrigenous and calcareous products),
169 (3) Tertiary volcanoclastic and crystalline rocks and (4) Quaternary volcanic rocks, for the most
170 part andesites, and (5) Quaternary pyroclastic deposits.

171 The hydraulic properties of rock masses are not easily definable because of the abundance of factors
172 influencing their hydraulic behaviour as fractured media: the number, the openness and the
173 interconnection of fractures. Igneous rocks are generally characterized by a broad range of
174 hydraulic conductivity values, ranging from 10^{-10} m/s in weathered tuffs to 10^{-4} m/s in fractured
175 basalts (Davis & DeWiest 1966, Spitz & Moreno 1996, Fetter 2001). According to that, Franchino
176 et al. (2013) suggested that the hydraulic conductivity of rocky complexes in the studied area range
177 between low and intermediate, respectively for the older rocky complexes (1), (2) (3) and for

178 Quaternary vulcanites (4), more young and fractured. The presence of hydrothermal circulation in
179 Zunil geothermal fields (Foley 1990, Asturias 2003, Bennati et al. 2011) and of several springs,
180 spread all around the Cerro Quemado Complex (Adams et al. 1990, Lima Lobato et al. 2000,
181 Walker et al. 2006), indicates the presence of groundwater and fluids circulation within the volcanic
182 Cenozoic complexes in fractured and faulted sectors.

183 The Quaternary pyroclastic complex (5) is mainly composed by unconsolidated, coarse-sized
184 pyroclastic products reaching at least 250 meters of depth according to stratigraphic logs of water
185 wells. Rocky and fine-grained ash layers with low permeability are found with unknown lateral
186 extension and thus the aquifer is supposed to be undifferentiated or locally confined. The
187 piezometric surface, showed in Figure 1, is steeper in the foothill sectors, that are supposed to
188 represent the recharge areas. The plain sectors, especially the Xela caldera, where smaller hydraulic
189 gradients occur, represent the discharge areas of groundwater flow; generally, rivers perform as
190 drainage axes. The regional groundwater flow is directed from N to S towards the Pacific Ocean,
191 while locally it turns into NW-SE, SW-NE and E-W directions.

192 The depth to water table in the pyroclastic sediments, inferred from unpublished EMAX (*Empresa*
193 *Municipal de Aguas de Xelajú*) reports, ranges from 3 meters in the eastern suburbs of
194 Quetzaltenango to more than 100 meters in the NW sector of the city. The hydraulic properties of
195 the Quaternary pyroclastic complex have been evaluated from pumping tests carried out by
196 INSIVUMEH, EMAX and IIZ (*Instituto para la Cooperación Internacional de Austria*) in the last
197 30 years all over the upper Samalá River basin. The average hydraulic conductivity is equal to
198 $1.5 \cdot 10^{-5}$ m/s and the average transmissivity is $8.7 \cdot 10^{-3}$ m²/s, while the storage coefficient ranges
199 between $3 \cdot 10^{-5}$ and $4 \cdot 10^{-5}$.

200 The Quaternary pyroclastic deposits (5) represent the most exploited aquifer due to its favourable
201 hydraulic properties and to its wide distribution. All the water supply of Quetzaltenango
202 municipality is withdrawn from this complex: one quarter (44,500 m³/day) from Molino Viejo
203 springs -located 7 km NW from Quetzaltenango in Siguilá River Valley- and the remaining from

204 wells. Molino Viejo springs are tens of water outcrops aligned along the right bank of Siguilá River
205 probably linked with the outcrop of a shallow water table. The exploitation is performed through
206 underground drainage tunnels dug into the pyroclastic sediments and the average discharge is 17
207 L/s.

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209

210 **3. MATERIALS AND METHODS**

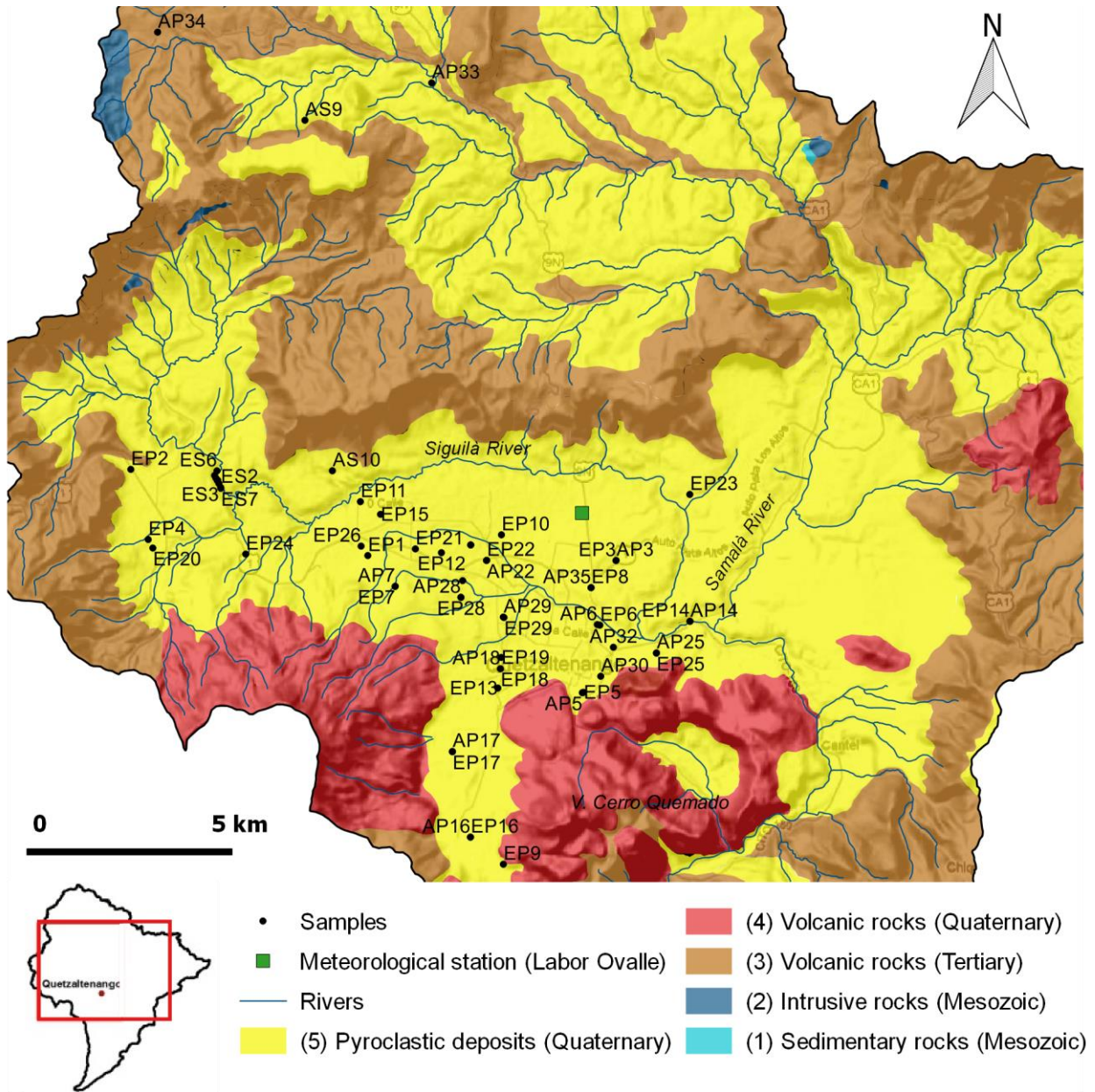
211 **3.1 Sampling and chemical analysis**

212 Two sampling surveys were performed in February 2011 and May 2012 within the upper basin of
213 Samalá River. 36 samples were gathered in the first campaign and the remaining 22 during the
214 second one, with 14 common points among the two surveys. The Sampling points consisted of
215 springs and wells owned by municipal authorities and used for drinking purposes. As shown in
216 Table 2, sampled points are mostly wells whose depths range from 70 to 270 meters, while the
217 screens position is mostly unknown. The areal distribution of sampling points (Figure 2) depended
218 on the accessibility of local authorities. Hence, most of the samples were collected in
219 Quetzaltenango city and surroundings. The samples from springs were mostly collected in distal
220 sectors, such as the Molino Viejo group. Each sample point was detailed with a synthetic
221 description and location, acquired through a portable GPS device. Tank and tap sampling points are
222 not included in the presented dataset; when direct sampling was not possible at the water source
223 (well/spring), the water was collected from the inlet pipe upstream the storage tank. The sampled
224 water was collected and stored in 100 mL polyethylene bottles. The main physical-chemical
225 parameters (pH, temperature, electrolytic conductivity, dissolved oxygen) were determined in situ
226 with a HACH portable multi-parameter meter (HQ40d). On the contrary, water analysis were
227 performed in laboratory within few weeks from sample collection. Alkalinity was measured with
228 titration method using 0.1 N HCl. NO_3^- , SO_4^{2-} , Cl^- were determined with a Metrohm ion

229 chromatography with chemical suppression (Metrosep Dual 4), equipped with a monolithic silica
230 gel column (100x4.6 mm). The eluent (sodium hydrogen carbonate) was provided with a 1 ml/min
231 flux. The instrument was equipped with 863 Compact Autosampler with sampling time equal to 120
232 s. Before each analysis water was filtered by a 0.45 μm cellulose nitrate membrane filters and after
233 the network was cleaned for 30 s by ethyl alcohol diluted 70% in high-purity water.

234 The major and minor metal cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Mn, Ni and Pb), once the samples were
235 filtered through 0.45 μm cellulose nitrate membrane filters and acidified with HNO_3 , were
236 determined by a Perkin Elmer, Optima 7000DV model Inductively Coupled Plasma Atomic
237 Emission Spectrometer (ICP-AES). The instrument is provided with a Echelle monochromator, a
238 cyclonic spray chamber and a teflon Mira Mist nebulizer. The instrumental conditions were: plasma
239 power 1.3 kW; sample aspiration rate 15 rpm; argon nebulizer flow 0.6 L/min; argon auxiliary flow
240 0.2 L/min and argon plasma flow 15 L/min. All the reagents used were of analytical grade. All
241 metal solutions were prepared from concentrated stock solutions (Sigma Aldrich). High-purity
242 water (HPW) produced with a Millipore Milli-Q Academic system was used throughout.

243 In order to classify the samples through major ions, data were treated with Piper and Schoeller
244 diagrams and univariate plots. Piper diagram (Piper 1944) is a graphical classification of the
245 chemistry of waters. The cations and anions are plotted in separate ternary plots. The apexes of the
246 cation plot are calcium, magnesium and sodium plus potassium cations. The apexes of the anion
247 plot are sulphate, chloride and carbonate plus hydrogen carbonate anions. The two ternary plots are
248 projected onto a diamond-shape field, that is used to represent the composition of water with respect
249 to both cations and anions. Depending on the position, the hydrochemical facies of the water is
250 defined. The semilogarithmic graph of Schoeller is used to plot the concentrations of anions and
251 cations, in meq/L. The main ionic concentrations are plotted on six equally spaced logarithmic
252 scales, and the points so plotted are joined by straight lines. This diagram gives the absolute
253 concentrations of each ion and allows to make a visual comparison of the compositions of different
254 waters.



256

257 **Figure 2.** Location of sampling points.

258

259

260 **3.2 Chemometric analysis**

261 The chemometric elaboration of the experimental data by principal component analysis (PCA),
 262 hierarchical clustering analysis (HCA) and factor analysis (FA) was performed with XIStat 2007.3
 263 software package.

264 Data set was autoscaled and, when concentrations were below the detection limit, a random value
265 between zero and that limit was inserted in order to be able to thoroughly apply PCA, HCA and FA
266 without losing any data. The variables quantified for less than 70 % of the water samples were not
267 considered further in the chemometric treatment.

268 PCA is a multivariate chemometric technique used to obtain a synthetic representation of
269 experimental data that brings to light correlations between variables considered and similarities
270 present among samples analysed. This technique makes possible to extract the most information
271 possible contained in a set of multivariate data, summarising it in a few linear combinations of the
272 variables (Einax et al., 2004; Otto M., 2007).

273 The interpretation of the PCA results can be facilitated through the graphic representation of
274 loading plot and of score plot; in particular, the loading plot allows one to understand the
275 relationships between the variables (in this case the different elements determined in water
276 samples), emphasising their positive and negative correlations and the role of each variable in the
277 different components; the score plot enables the valuation of behaviour of the objects (in this case
278 the samples of analysed water) towards the different components and their similarities or
279 differences.

280 The aim of HCA is to group data by similarity, taking into account all the information contained in
281 the data set and not only a part of it, as in PCA. Similarity close to 100% indicates high
282 resemblance between the objects, while deviations from a value of 100% indicate differences.

283 Objects that are most similar are “fused” into a single group or cluster and the calculation of
284 similarity is iteratively repeated. The calculation is interrupted when the minimum similarity
285 (maximum dissimilarity) between the objects has been established. Various graphical means exist to
286 evaluate the aggregation in a cluster, but the most widely used is the dendrogram, which highlights
287 not only the various clusters, but also their distance. The level of aggregation of the units or clusters
288 is visualised in ascending order. HCA is an effective statistical method for qualitative study of the

289 composition of the waters and can be used to identify the groupings of samples not well detectable
290 only with PCA.

291 Finally FA is used to explore better the relationship between variables using a Varimax rotation
292 procedure in order to maximise the explained variance.

293

294 **4. RESULTS AND DISCUSSION**

295

296 The results of the in situ parameter measurements and chemical analyses are summarised in Table
297 2. For each sample a list of additional information is given: ID, coordinates, altitude, sampling
298 period, type of sampling point. The sample ID is composed both by letters, that state for the year (E
299 for 2011 and A for 2012) and type of sampling point (S=spring and P=well), and numbers, that
300 identify the sampling location. Water analyses from Adams et al (1990) and Walker et al (2006) are
301 reported in Table 3.

302

303 **4.1 Physical-chemical parameters**

304 Referring to Table 2, temperature shows a broad variety. Springs have the narrowest range and the
305 lowest values, from 14 to 17.4 °C, while wells temperature varies between 16 and 29°C. Compared
306 to mean annual air temperature of 14.7°C (see Table 1), wells temperatures show higher values.
307 Groundwater temperatures are expected to increase with depth with respect to the external regime,
308 due to the presence of a geothermal heat flux. This seems to be confirmed by the measured values,
309 in most cases ranging 20-21°C. The contribution of geothermal gradient is then more significant
310 than the atmospheric heat input at the depths of the investigated wells between 90 and 280 m (see
311 Table 2). Groundwater temperatures also show some peaks between 23and 29°C concentrated near
312 the active volcanic complexes S. María-Santiago and Cerro Quemado. These are likely
313 attributable to anomalous heat fluxes coming from the recent volcanic activity. Nonetheless,
314 correlation between wells depth and temperature is not clear, probably because of water mixing

315 along the well column due to well screens at various depths. The electrolytic conductivity (EC)
316 assumes values between 52 and 499 $\mu\text{S}/\text{cm}$ and an average of 225 $\mu\text{S}/\text{cm}$. The lowest EC values are
317 observed in distal sectors and specifically in springs waters. Conversely, the maxima are
318 concentrated in wells located at the southern sector of the Xela Caldera, near the active volcanic
319 complexes. As for the temperature, a mixing with deep groundwater circuits carrying hot and highly
320 mineralised fluids may be hypothesised. The pH assumes values between 6.98 and 8.10, with a
321 slightly alkaline average of 7.43. Springs generally have slightly acid or neutral pH values, while
322 wells show mostly basic values, with some exceptions from 2012 campaign located close to Cerro
323 Quemado complex.

324

325 **4.2 Major ions**

326 The analysis of major ions represents a key point in order to understand phenomena and processes
327 involved in defining the groundwater chemical trend. Piper diagram is a powerful tool because it
328 allows to classify groundwater in chemical facies and to compare simultaneously a large number of
329 water samples. Piper diagram (Figure 3) shows that the most part of samples belong to the
330 bicarbonate calcic and magnesiatic facies. This is in accordance with typical “young” groundwater
331 composition, that generally starts with alkaline/alkali-earth cations and bicarbonates and gradually
332 evolves towards seawater composition (Appelo & Postma 1996). Thus, the prevalence of HCO_3^- -Ca-
333 Mg ions can suggest that the most part of groundwater in the investigated area has undergone a
334 short flow path or had limited exchange with the surrounding porous medium and thus its chemistry
335 is mainly governed by infiltration waters (meteoric inputs, streams). The Molino Viejo spring
336 waters are the most representative for this facies since they are grouped at the centre of Ca^{2+} - Mg^{2+} -
337 HCO_3^- water type diamond, suggesting a shallow, rapid groundwater circuit.

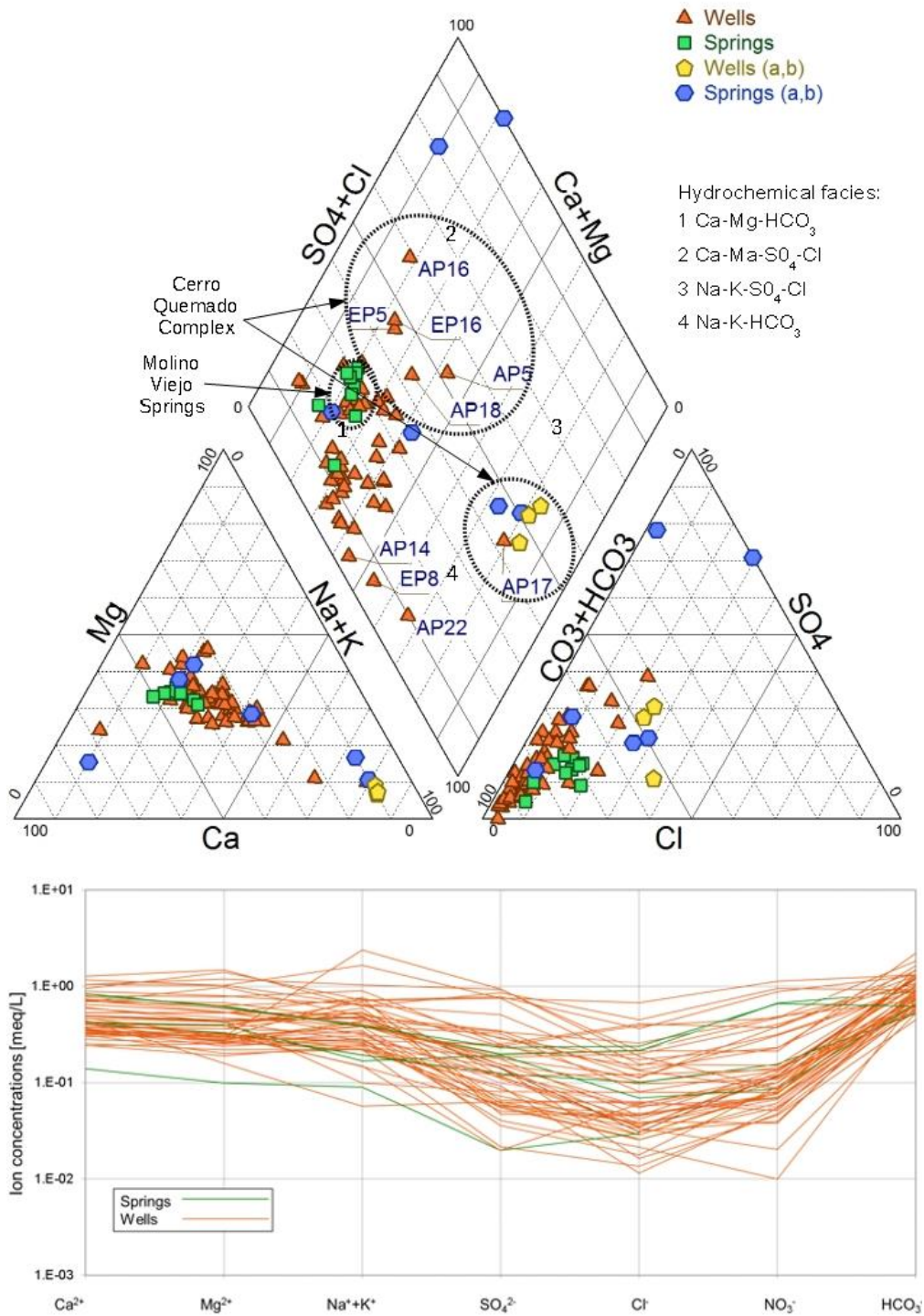
338 Among the waters that display a shift from the general trend, a group of samples -AP5, EP5, AP16,
339 EP16, AP17, AP18- is enriched in Cl^- and SO_4^{2-} and partially in Na^+ and K^+ . These samples,
340 contoured with a dashed line in Figure 3, are all located in the area of Cerro Quemado volcanic

341 complex. This suggests that a possible source of chemical differentiation is related to this active
342 volcano. Here and near Santa María volcano, Walker et al. (2006) observed three main water types:
343 chloride, sulphate, bicarbonate waters. The first ones, according to Adams et al. (1990), were likely
344 originated by various degrees of dilution between shallow, meteoric groundwater and deep
345 hydrothermal Cl⁻ rich waters that can occur in high-pressure and high-density conditions for
346 condensation of volatile acids and alkali halides (Fournier 1981, Goff & Janik 2000). The sulphate
347 waters in volcanic areas were related to condensation and oxidation of hot and sulphur-rich gases in
348 shallow meteoric waters (White, 1957), while the bicarbonate waters were associated to variable
349 mixing rates between meteoric waters and a high Mg²⁺-Ca²⁺ volcanic-magmatic component. The
350 Piper diagram also includes samples from Adams et al. (1990) and Walker et al. (2006). The waters
351 come mostly from springs and show a variable chemistry: starting from Ca²⁺-Mg²⁺-HCO₃⁻ facies a
352 progressive enrichments in Cl⁻ and SO₄²⁻ and in some cases also in Na⁺ is observed, up to a
353 composition that approximates the geothermal wells one (yellow pentagons in Figure 3). The
354 enrichment in Cl⁻, SO₄²⁻ and partially in Na⁺ observed in Piper diagram can be thus originated by
355 mixing between shallow and young groundwater circuits with the volcanic components as end
356 members described by Walker et al. (2006).

357 The Schoeller diagram in Figure 3 displays all the analysed samples in terms of absolute values of
358 ion concentrations expressed in meq/L. Even though Schoeller diagram is generally represented
359 with few samples, in this case it was chosen to gather all the data in order to evidence common
360 trends and to give an overall idea of absolute ion abundance, lacking in Piper diagram. The main
361 trend, contoured with a dashed line, highlights that the maximum concentrations lie in
362 correspondence of Ca²⁺, Mg²⁺ and HCO₃⁻ ions, according to Piper diagram,. The remaining ions
363 generally display lower concentrations, but with more variability. Nitrates, not included in the Piper
364 diagram, show the widest range of concentrations, from 0.001 to approximately 1 meq/L.

365

366



368
 369 **Figure 3.** Top: Piper diagram, including the sampled waters and the literature data (a=Walker et al.
 370 2006, b=Adams et al. 1990). Bottom: Schoeller diagram.
 371

372 In order to better distinguish the factors affecting the chemistry of each water type, major ions were
373 correlated with bivariate diagrams: $\text{Na}^+\text{-Cl}^-$, $\text{Ca}^{2+}\text{-Mg}^{2+}$ and $\text{NO}_3^-\text{-Cl}^-$ (Figure 4). Even in these
374 diagrams we display both ours and Adams et al.'s (1990) and Walker et al.'s (2006) data. The $\text{Na}^+\text{-}$
375 Cl^- plot is useful for inferring possible Na inputs, since Na^+ and Cl^- concentrations are generally
376 similar in atmospheric inputs that represent aquifer recharge: according to Möller (1990),
377 continental rainwaters display Na^+ to Cl^- ratios between 1.1 and 1.8. Since our samples are mostly
378 distributed in the uppermost part of the plot, an imbalance towards Na^+ with respect to the chloride
379 occurs due to sodium enrichment from the parental concentrations in rainwater. One possible source
380 of Na^+ , already discussed in the previous paragraph, is the mixing with deep hydrothermal circuits
381 for the groundwater around Cerro Quemado complex and indeed these samples are mostly
382 distributed in the uppermost part of $\text{Na}^+\text{-Cl}^-$ graph. The same samples are also distributed in the
383 uppermost part of the $\text{Mg}^{2+}\text{-Ca}^{2+}$ plot above the $x=y$ line, indicating that these waters are more
384 enriched in Mg^{2+} . This trend is similar to Walker et al.'s findings, that attributed high $\text{Mg}^{2+}/\text{Ca}^{2+}$
385 ratios to an enhanced interaction between meteoric waters in samples collected around the active
386 volcanic complexes.

387 For the samples far from Cerro Quemado complex, the source of Na^+ ions may be the solid matrix
388 of the main aquifers, formed by andesitic-dacitic pyroclasts and rocks. Strong variations in $\text{Na}^+\text{-Cl}^-$
389 ratio from rainwaters to stream waters and groundwater can occur in reason of ion exchange
390 processes with the solid matrix (Neal & Kirchner 2000). As highlighted by Nagaraju et al. (2014),
391 the base ions exchange between groundwater and hosting material during residence or travel can be
392 better understood by studying the chloro-alkaline index. Schoeller (1967) and Schoeller (1977)
393 suggested the chloro-alkaline index CAI_1 in order to understand the direction of such ion exchange
394 processes during the path of groundwater through the aquifer:

395

396

$$\text{CAI}_1 = [\text{Cl}^- - (\text{Na}^+ + \text{K}^+)]/\text{Cl}^-$$

397

398 Positive values correspond to depletion of Na^+ and K^+ in the water and an enrichment of Mg^{2+} and
399 Ca^{2+} from the hosting material, whereas negative values occur when the exchange direction is
400 inverse: Mg^{2+} and Ca^{2+} decrease in the water and alkali ions are withdrawn from the porous
401 medium. The CAI_1 index for our samples display values between -0.25 and -18.32 (Table 2),
402 revealing a prevalent Na^+ and K^+ exchange from the rock to the water. The smallest values are
403 displayed by the sampling points within the Xela Caldera. The average values of -6.67 for wells
404 samples and -1.37 for springs samples support the hypothesis that springs are characterized by rapid
405 and short groundwater flow paths, whereas samples from the wells are representative of slower
406 and/or longer paths that facilitate ion exchange processes between water and aquifer matrix. As
407 previously mentioned, the Quaternary pyroclastic sediments filling the Xela caldera contain
408 intercalations of fine volcanic ashes and these fine-size beds likely contain clay minerals that are
409 responsible for ion exchange phenomena in the groundwater.

410 The different hydrogeology between well and spring waters can be also inferred by the Mg^{2+} - Ca^{2+}
411 plot. Even if the general trend is represented by a prevalence of Ca^{2+} for the samples far from Cerro
412 Quemado complex, some differences can be highlighted among these samples. Spring waters
413 display a more homogeneous pattern: they display lower Mg^{2+} contents compared to the well waters
414 and the Mg^{2+} - Ca^{2+} ratio is rather constant, as showed by their alignment parallel to the
415 $[\text{Mg}^{2+}]=[\text{Ca}^{2+}]$ line.

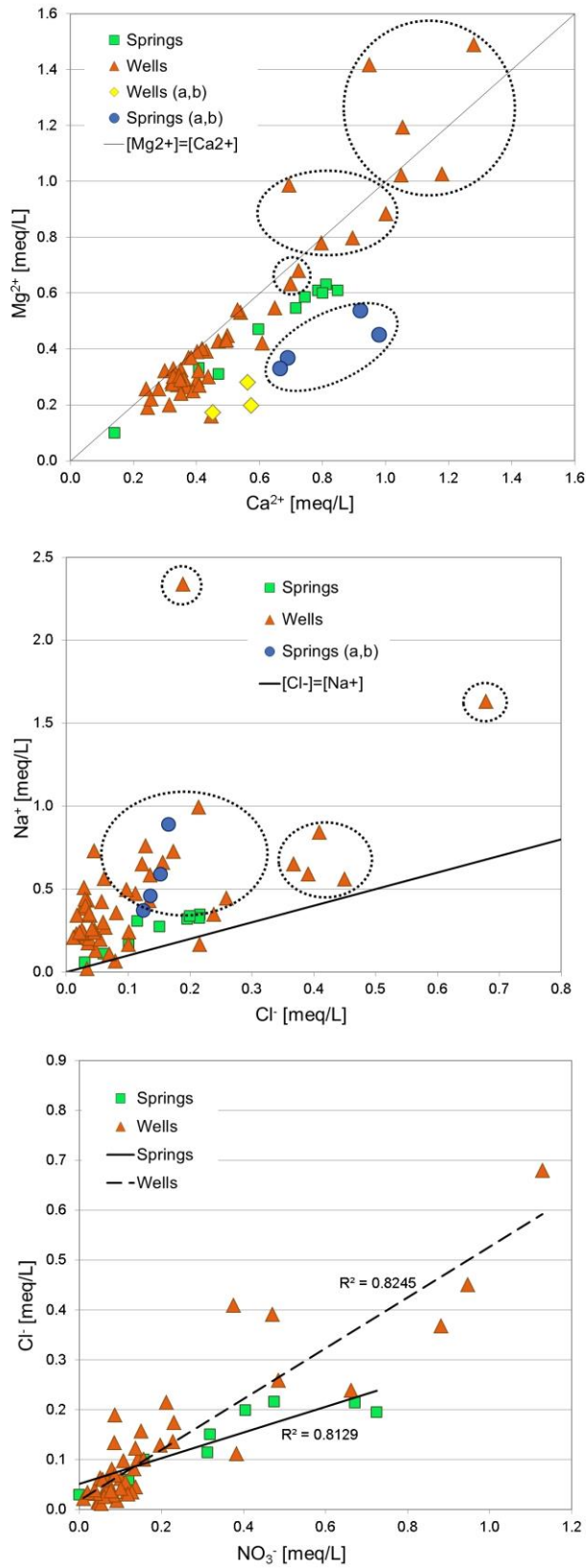
416 As displayed in Table 2, one third of the samples displays nitrates concentrations between 10 and
417 70 mg/l, significantly above the natural background levels which are typically lower than 1 mg/L of
418 N (corresponding to around 4.4 mg/L of NO_3^-) (Agrawal et al. 1999). This feature, together with the
419 positive correlation between NO_3^- and Cl^- (Figure 4), are clues of the anthropic origin of both ions,
420 due to synthetic/organic fertilizers and human effluents. As previously mentioned, the study area is
421 characterized by intense agricultural exploitation and lack of sewage network, thus these activities
422 represent diffuse and point sources of both chlorides and nitrates found into the sampled
423 groundwater.

424 As displayed in Table 2, toxic heavy metals concentrations are mostly around or below 1 ppb.
425 Similar values are typical of non-polluted groundwater and thus significant anthropogenic metal
426 inputs can be excluded in the investigated area. Concerning lead and nickel, the highest
427 concentrations are around 10^{-2} mg/L. In this case an anthropogenic origin is likely, since they were
428 collected within the urbanised area of Quetzaltenango, e.g. for infiltration of urban waste waters
429 enriched in heavy metals. In remote and poorly populated regions some samples (AP33, ES3, ES4,
430 ES7) show higher manganese concentrations around 10^{-2} mg/L compared to the lower quantities of
431 the remaining samples . This higher content of Mn may be due to natural mechanisms of the
432 delicate manganese oxides equilibrium in aquifers, rather than anthropogenic causes.

433 Table 2 also compares the parameters with Italian and Guatemalan quality standards for drinking
434 purposes. Grey cells highlight exceedances with respect to the assigned thresholds. The two
435 samples exceeding the threshold of lead, already mentioned in the previous paragraph, are linked to
436 urban sources, while the other parameter exceeding the regulatory limits, the nitrates concentration,
437 is often above 50 mg/L. Nitrates are linked to the intense and poorly regulated
438 agricultural/husbandry activities occurring in Quetzaltenango area and to the lack of depuration
439 systems for human wastewaters. A large number of samples shows exceedance for Guatemalan
440 regulation because the nitrates threshold is very strict (10 mg/l), whereas at global level the most
441 frequent limit is 50 mg/L.

442

443



444

445 **Figure 4.** Bivariate plots including sampled waters and literature data. Concentrations are expressed

446 in meq/L. For symbol significance see Fig.3.

447 **Table 2.** Design features of sampling points and main chemical parameters of groundwater samples. Thresholds of drinking water standards are
 448 reported in second and third row, for Italy (Legislative Decree 31/2001) and Guatemala (COGUANOR NGO 29.001.98, 1999) respectively.

449

| SAMPLE ID | Z (m asl) | TYPE | DEPTH (m bgl) | YEAR | MONTH | T (°C) | EC (µS/cm) | PH | O ₂ % | O ₂ (mg/L) | Ca ²⁺ (mg/L) | Mg ²⁺ (mg/L) | Na ⁺ (mg/L) | K ⁺ (mg/L) | HCO ₃ ⁻ (mg/L) | CO ₃ ²⁻ (mg/L) | SO ₄ ²⁻ (mg/L) | Cl ⁻ (mg/L) | NO ₃ ⁻ (mg/L) | TDS (mg/L) | Pb (mg/L) | Ni (mg/L) | Mn (mg/L) | CAI |
|---------------------|-----------|--------|---------------|------|----------|--------|------------|---------|------------------|-----------------------|-------------------------|-------------------------|------------------------|-----------------------|--------------------------------------|--------------------------------------|--------------------------------------|------------------------|-------------------------------------|------------|------------|------------|-----------|--------|
| IT (D.lgs 31/2001) | | | | | | 34 | 1500 | 6.5-8.5 | | | 150 | 100 | | | | | 250 | 250 | 50 | 1000 | 0.01 | | | |
| GT (Coguanor, 1999) | | | | | | | 2500 | 6.5-9.5 | | | | | 250 | | | | 250 | 250 | 10 | | 0.01 | | 0.05 | |
| AP14 | 2327 | well | 91 | 2012 | May | 21.90 | 158 | 7.48 | 58 | 3.76 | 5.64 | 3.13 | 9.20 | 1.10 | 50.32 | - | 0.00 | 1.12 | 2.47 | 73.04 | <0.045E-03 | <0.015E-03 | 2.09E-03 | -12.52 |
| AP16 | 2442 | well | 213 | 2012 | May | 17.40 | 390 | 6.97 | 83 | 5.84 | 25.60 | 18.08 | 12.87 | 2.39 | 56.15 | - | 41.34 | 15.97 | 58.74 | 214.79 | <0.045E-03 | <0.015E-03 | 1.12E-03 | -0.38 |
| AP17 | 2412 | well | 230 | 2012 | May | 20.80 | 378 | 7.68 | 29 | 1.98 | 6.54 | 3.66 | 9.97 | 1.75 | 91.89 | - | 45.44 | 6.70 | 5.39 | 171.74 | <0.045E-03 | <0.015E-03 | 1.67E-03 | -11.59 |
| AP18 | 2391 | well | 183 | 2012 | May | 23.80 | 322 | 7.31 | 69 | 4.33 | 14.01 | 7.70 | 15.16 | 1.97 | 72.20 | - | 36.17 | 5.55 | 9.39 | 162.23 | <0.045E-03 | <0.015E-03 | 1.10E-03 | -3.53 |
| AP22 | 2402 | well | 185 | 2012 | May | 24.20 | 175 | 7.45 | 83 | 5.23 | 4.73 | 1.39 | 14.58 | 2.12 | 54.69 | - | 2.76 | 1.39 | 2.34 | 84.06 | <0.045E-03 | <0.015E-03 | 1.09E-03 | -8.83 |
| AP25 | 2393 | well | 171 | 2012 | May | 26.10 | 230 | 7.59 | 76 | 4.58 | 10.60 | 6.48 | 9.89 | 3.39 | 56.15 | - | 14.17 | 4.75 | 5.28 | 100.27 | <0.045E-03 | <0.015E-03 | 1.23E-03 | -2.85 |
| AP27 | 2419 | well | 247 | 2012 | May | 23.20 | 174 | 7.32 | 80 | 4.94 | 7.80 | 3.04 | 6.90 | 1.43 | 49.59 | - | 4.77 | 2.12 | 3.54 | 79.24 | 3.29E-03 | <0.015E-03 | 1.54E-03 | -4.64 |
| AP28 | 2462 | well | | 2012 | May | 22.10 | 172 | 7.47 | 89 | 5.65 | 6.13 | 4.11 | 9.82 | 2.24 | 47.40 | - | 5.54 | 1.49 | 6.27 | 83.08 | <0.045E-03 | <0.015E-03 | 1.82E-03 | -6.34 |
| AP29 | 2405 | well | 183 | 2012 | May | 23.00 | 178 | 7.39 | 87 | 5.56 | 6.90 | 3.45 | 8.05 | 1.90 | 50.32 | - | 6.98 | 1.31 | 4.81 | 92.01 | <0.045E-03 | <0.015E-03 | 1.15E-03 | -9.54 |
| AP3 | 2349 | well | 213 | 2012 | May | 20.50 | 174 | 7.48 | 78 | 5.20 | 9.92 | 5.25 | 1.50 | 1.35 | 51.63 | - | 3.88 | 2.83 | 4.92 | 81.44 | <0.045E-03 | <0.015E-03 | 1.11E-03 | -0.25 |
| AP30 | 2361 | well | 137 | 2012 | May | 22.50 | 266 | 7.41 | - | - | 10.83 | 6.45 | 16.73 | 1.57 | 64.17 | - | 13.80 | 6.16 | 14.30 | 134.08 | 6.33E-03 | 6.33E-06 | 1.56E-03 | -3.42 |
| AP31 | 2432 | well | 160 | 2012 | May | 21.30 | 193 | 7.35 | 77 | 6.95 | 7.52 | 4.47 | 11.41 | 1.71 | 53.24 | - | 7.44 | 3.45 | 6.72 | 96.07 | <0.045E-03 | <0.015E-03 | 9.84E-04 | -4.55 |
| AP32 | 2329 | well | 140 | 2012 | May | 23.30 | 219 | 7.47 | 84 | 5.35 | 8.07 | 4.74 | 14.94 | 1.28 | 61.99 | - | 5.69 | 4.35 | 8.49 | 109.62 | 1.35E-02 | 1.35E-05 | 2.69E-03 | -4.56 |
| AP33 | 2612 | well | | 2012 | May | 24.70 | 141 | 7.49 | 26 | 1.57 | 7.04 | 2.92 | 5.49 | 1.92 | 44.48 | - | 1.94 | 0.76 | 0.62 | 61.31 | 5.07E-04 | 5.07E-07 | 1.86E-02 | -12.46 |
| AP34 | 2788 | well | | 2012 | May | 15.90 | 97 | 7.24 | 105 | 7.54 | 8.96 | 1.94 | 0.46 | 1.44 | 32.09 | - | 3.07 | 1.20 | 1.26 | 50.44 | <0.045E-03 | <0.015E-03 | 1.23E-03 | -0.68 |
| AP35 | 2309 | well | 183 | 2012 | May | 26.70 | 178 | 7.70 | 69 | 4.09 | 7.68 | 4.47 | 6.21 | 2.26 | 55.42 | - | 3.00 | 2.24 | 3.16 | 84.52 | 1.28E-03 | <0.015E-03 | 1.74E-03 | -4.18 |
| AP5 | 2314 | well | 122 | 2012 | May | 21.10 | 398 | 7.02 | 74 | 4.76 | 23.62 | 12.47 | 37.51 | 1.24 | 80.95 | - | 36.43 | 24.07 | 69.97 | 286.51 | <0.045E-03 | <0.015E-03 | 1.14E-03 | -1.45 |
| AP6 | 2349 | well | 76 | 2012 | May | 21.80 | 349 | 7.28 | 76 | 5.07 | 15.97 | 9.46 | 19.36 | 2.22 | 78.61 | - | 12.17 | 14.52 | 23.28 | 175.73 | <0.045E-03 | <0.015E-03 | 2.38E-03 | -1.19 |
| AP7 | 2514 | well | 201 | 2012 | May | 20.20 | 150 | 7.52 | 100 | 6.95 | 8.40 | 4.86 | 2.46 | 2.40 | 40.84 | - | 9.25 | 2.47 | 5.36 | 76.14 | <0.045E-03 | <0.015E-03 | 1.09E-03 | -1.42 |
| AS10 | 2427 | spring | | 2012 | May | 16.90 | 147 | 7.10 | 85 | 5.95 | 9.43 | 3.75 | 10.35 | 1.75 | 40.11 | - | 3.81 | 2.01 | 7.16 | 78.40 | <0.045E-03 | <0.015E-03 | 1.29E-03 | -1.50 |
| AS4 | 2436 | spring | | 2012 | May | 16.30 | 238 | 6.73 | 91 | 6.47 | 18.56 | 8.16 | 6.67 | 3.24 | 55.42 | - | 5.53 | 8.46 | 41.07 | 132.74 | <0.045E-03 | <0.015E-03 | 9.56E-04 | -0.63 |
| AS9 | 2766 | spring | | 2012 | May | 13.80 | 52 | 7.29 | 97 | 7.27 | 2.71 | 1.25 | 1.41 | 1.28 | 18.23 | - | 0.77 | 0.96 | 0.06 | 26.71 | <0.045E-03 | 2.64E-03 | 1.50E-03 | -2.00 |
| EP1 | 2486 | well | | 2011 | February | 22.70 | 202 | 7.91 | 104 | 6.83 | 4.92 | 2.31 | 5.27 | 0.58 | 27.58 | - | 6.94 | 0.58 | 2.84 | 51.02 | 3.80E-03 | <0.015E-03 | 8.83E-03 | -13.86 |

| | | | | | | | | | | | | | | | | | | | | | | | | |
|------|------|--------|-----|------|----------|-------|-----|------|-----|------|-------|-------|-------|------|--------|------|-------|-------|-------|--------|----------|------------|----------|--------|
| EP10 | 2402 | well | 183 | 2011 | February | 24.80 | 160 | 7.70 | 91 | 5.62 | 5.13 | 2.68 | 4.76 | 0.57 | 36.73 | - | 1.04 | 0.48 | 2.95 | 54.35 | 7.55E-03 | <0.015E-03 | <2.0E-06 | -15.34 |
| EP11 | 2480 | well | 168 | 2011 | February | 21.50 | 198 | 7.30 | 64 | 4.36 | 8.07 | 3.52 | 8.81 | 1.28 | 47.11 | - | 10.37 | 0.93 | 4.04 | 84.12 | 6.39E-03 | <0.015E-03 | <2.0E-06 | -14.92 |
| EP12 | 2443 | well | 138 | 2011 | February | 23.50 | 204 | 7.54 | 80 | 5.12 | 7.38 | 3.21 | 4.66 | 0.62 | 39.84 | - | 3.47 | 1.32 | 4.17 | 64.68 | 1.84E-03 | <0.015E-03 | <2.0E-06 | -4.88 |
| EP13 | 2370 | well | 213 | 2011 | February | 29.30 | 282 | 7.51 | 88 | 5.02 | 17.95 | 9.68 | 13.42 | 2.23 | 100.19 | - | 24.46 | 4.82 | 14.13 | 186.89 | 6.84E-03 | 1.61E-03 | 1.10E-03 | -3.71 |
| EP14 | 2318 | well | 91 | 2011 | February | 20.60 | 160 | 7.72 | 65 | 4.43 | 6.47 | 3.42 | 7.86 | 0.42 | 48.14 | - | 1.72 | 0.63 | 5.69 | 74.35 | 1.38E-03 | <0.015E-03 | 8.66E-03 | -18.75 |
| EP15 | 2479 | well | 156 | 2011 | February | 22.50 | 191 | 7.67 | 76 | 4.92 | 6.31 | 2.43 | 4.81 | 0.53 | 39.03 | - | 4.50 | 0.41 | 3.33 | 61.35 | 3.01E-03 | <0.015E-03 | <2.0E-06 | -18.32 |
| EP16 | 2457 | well | 213 | 2011 | February | 16.80 | 387 | 7.19 | 80 | 5.64 | 19.02 | 17.22 | 15.00 | 2.70 | 80.18 | - | 37.56 | 13.03 | 54.65 | 239.36 | 7.11E-03 | 1.71E-03 | 1.45E-03 | -0.96 |
| EP17 | 2406 | well | 230 | 2011 | February | 20.20 | 453 | 8.10 | 78 | 5.16 | 21.12 | 14.51 | 22.86 | 1.84 | 122.83 | 5.70 | 44.82 | 7.60 | 13.14 | 254.42 | 6.84E-03 | 1.74E-03 | 5.70E-03 | -3.86 |
| EP18 | 2362 | well | 183 | 2011 | February | 24.30 | 334 | 7.65 | 73 | 4.58 | 20.07 | 10.75 | 17.45 | 2.09 | 111.30 | - | 34.32 | 4.56 | 12.28 | 212.81 | 2.75E-03 | 1.16E-03 | 2.93E-04 | -5.32 |
| EP19 | 2375 | well | 67 | 2011 | February | 21.70 | 284 | 7.62 | 85 | 5.61 | 12.99 | 6.64 | 8.22 | 1.25 | 59.74 | - | 15.71 | 2.88 | 8.27 | 115.69 | 3.67E-03 | <0.015E-03 | 5.49E-04 | -3.80 |
| EP2 | 2520 | well | 213 | 2011 | February | 17.50 | 199 | 7.00 | 89 | 6.29 | 6.01 | 3.92 | 2.98 | 0.70 | 33.19 | - | 2.79 | 1.70 | 4.39 | 55.68 | 6.94E-03 | <0.015E-03 | <2.0E-06 | -2.08 |
| EP20 | 2506 | well | 187 | 2011 | February | 20.60 | 175 | 7.36 | 99 | 6.61 | 7.05 | 3.95 | 4.48 | 1.11 | 35.15 | - | 6.02 | 1.95 | 6.99 | 66.70 | 5.61E-03 | <0.015E-03 | <2.0E-06 | -3.06 |
| EP21 | 2455 | well | 183 | 2011 | February | 23.90 | 183 | 7.58 | 87 | 5.47 | 6.81 | 3.30 | 5.33 | 0.87 | 39.91 | - | 4.17 | 1.03 | 4.93 | 66.35 | 3.94E-03 | <0.015E-03 | 4.99E-03 | -7.75 |
| EP22 | 2411 | well | 185 | 2011 | February | 26.00 | 171 | 7.72 | 83 | 5.13 | 9.40 | 5.20 | 11.66 | 1.41 | 82.43 | - | 2.93 | 1.03 | 5.15 | 119.21 | 9.01E-03 | 1.35E-03 | 8.69E-03 | -17.78 |
| EP23 | 2336 | well | 78 | 2011 | February | 17.50 | 168 | 7.85 | 85 | 6.08 | 8.17 | 3.91 | 5.80 | 0.37 | 47.96 | - | 2.43 | 1.65 | 4.29 | 74.58 | 5.04E-03 | <0.015E-03 | 5.66E-03 | -4.64 |
| EP24 | 2502 | well | 198 | 2011 | February | 18.80 | 225 | 6.72 | 97 | 6.72 | 12.21 | 5.12 | 5.57 | 1.37 | 43.44 | - | 12.03 | 3.61 | 8.86 | 92.22 | 3.89E-03 | <0.015E-03 | <2.0E-06 | -1.72 |
| EP25 | 2401 | well | 171 | 2011 | February | 21.00 | 238 | 7.74 | 68 | 4.63 | 6.49 | 3.34 | 9.75 | 0.78 | 45.03 | - | 7.42 | 2.03 | 4.36 | 79.20 | 9.31E-04 | <0.015E-03 | 1.12E-03 | -6.76 |
| EP26 | 2468 | well | 156 | 2011 | February | 18.70 | 218 | 7.94 | 103 | 7.10 | 8.76 | 3.65 | 5.52 | 0.95 | 37.53 | - | 8.49 | 1.60 | 8.48 | 74.98 | 8.18E-03 | <0.015E-03 | <2.0E-06 | -4.84 |
| EP27 | 2423 | well | 247 | 2011 | February | 26.90 | 164 | 7.54 | 83 | 5.03 | 7.22 | 3.55 | 5.86 | 0.86 | 46.25 | - | 2.66 | 0.91 | 3.80 | 71.11 | 8.72E-04 | <0.015E-03 | <2.0E-06 | -9.80 |
| EP28 | 2446 | well | | 2011 | February | 21.90 | 173 | 7.79 | 88 | 5.74 | 9.85 | 5.23 | 9.92 | 1.58 | 74.07 | - | 5.33 | 1.23 | 7.95 | 115.17 | 5.50E-03 | 1.68E-03 | 5.96E-03 | -12.65 |
| EP29 | 2411 | well | 183 | 2011 | February | 22.80 | 177 | 7.80 | 96 | 6.19 | 10.00 | 5.45 | 10.12 | 1.68 | 76.03 | - | 6.77 | 1.09 | 7.36 | 118.51 | 9.06E-03 | 1.52E-03 | 1.09E-03 | -14.65 |
| EP3 | 2382 | well | 213 | 2011 | February | 17.10 | 166 | 7.74 | 71 | 5.20 | 8.65 | 4.76 | 12.96 | 1.20 | 81.03 | - | 3.16 | 2.19 | 6.27 | 120.21 | 2.17E-03 | 1.19E-03 | 7.98E-04 | -8.63 |
| EP4 | 2533 | well | 183 | 2011 | February | 24.80 | 174 | 7.51 | 93 | 5.66 | 4.84 | 3.12 | 4.80 | 1.19 | 34.66 | - | 2.74 | 0.93 | 3.44 | 55.72 | 5.27E-03 | <0.015E-03 | <2.0E-06 | -8.09 |
| EP5 | 2341 | well | 122 | 2011 | February | 20.90 | 499 | 7.38 | 65 | 4.44 | 14.52 | 8.26 | 10.23 | 0.26 | 43.87 | - | 16.32 | 9.17 | 30.11 | 132.74 | 9.42E-04 | <0.015E-03 | 1.14E-03 | -0.75 |
| EP6 | 2327 | well | 76 | 2011 | February | 21.80 | 340 | 7.55 | 80 | 5.30 | 21.02 | 12.43 | 13.57 | 2.03 | 111.84 | - | 11.46 | 13.88 | 29.21 | 215.44 | 6.09E-03 | 2.24E-03 | 3.39E-03 | -0.64 |
| EP7 | 2506 | well | 201 | 2011 | February | 20.00 | 151 | 7.76 | 98 | 6.48 | 6.57 | 3.99 | 3.99 | 0.83 | 34.96 | - | 5.66 | 1.25 | 7.19 | 64.44 | 6.18E-03 | <0.015E-03 | 1.59E-04 | -4.53 |
| EP8 | 2381 | well | 183 | 2011 | February | 26.20 | 175 | 7.91 | 99 | 6.40 | 7.15 | 3.66 | 16.79 | 1.12 | 81.88 | - | 2.26 | 1.60 | 4.73 | 119.20 | 2.77E-03 | 4.08E-04 | 1.49E-03 | -15.85 |
| EP9 | 2466 | well | 244 | 2011 | February | 20.50 | 271 | 7.03 | 84 | 5.74 | 13.92 | 11.98 | 10.88 | 0.78 | 89.45 | - | 16.62 | 3.97 | 23.75 | 171.35 | 2.07E-02 | 1.30E-02 | 3.25E-04 | -3.41 |
| ES1 | 2443 | spring | | 2011 | February | 16.50 | 210 | 6.98 | 94 | 6.89 | 8.17 | 4.04 | 3.82 | 1.12 | 32.09 | - | 5.97 | 3.57 | 9.70 | 68.49 | 4.40E-03 | <0.015E-03 | <2.0E-06 | -0.94 |
| ES2 | 2440 | spring | | 2011 | February | 16.80 | 230 | 7.04 | 93 | 6.81 | 15.73 | 7.42 | 8.02 | 2.31 | 65.35 | - | 9.58 | 7.67 | 29.42 | 145.50 | 3.54E-03 | 1.43E-03 | 2.05E-03 | -0.89 |
| ES3 | 2445 | spring | | 2011 | February | 15.90 | 238 | 7.18 | 92 | 6.75 | 16.25 | 7.67 | 7.50 | 2.22 | 54.67 | - | 9.45 | 7.62 | 41.63 | 147.01 | 6.35E-03 | 1.70E-03 | 2.60E-02 | -0.78 |
| ES4 | 2448 | spring | | 2011 | February | 16.10 | 230 | 7.02 | 92 | 6.70 | 16.03 | 7.31 | 7.40 | 2.07 | 52.23 | - | 8.49 | 6.94 | 44.94 | 145.41 | 4.08E-03 | 1.27E-03 | 1.02E-02 | -0.92 |
| ES5 | 2442 | spring | | 2011 | February | 16.30 | 178 | 7.11 | 92 | 6.72 | 11.95 | 5.72 | 7.06 | 3.27 | 55.59 | - | 8.59 | 4.06 | 19.33 | 115.57 | 6.94E-03 | 1.21E-03 | 6.15E-05 | -2.41 |
| ES6 | 2437 | spring | | 2011 | February | 16.40 | 230 | 7.03 | 91 | 6.71 | 14.32 | 6.64 | 6.29 | 1.75 | 59.92 | - | 11.32 | 5.35 | 19.76 | 125.34 | 5.18E-03 | 2.21E-03 | 6.60E-03 | -1.11 |
| ES7 | 2435 | spring | | 2011 | February | 16.70 | 206 | 7.26 | 95 | 6.80 | 14.90 | 7.13 | 7.76 | 2.27 | 66.14 | - | 8.87 | 7.07 | 25.07 | 139.21 | 6.45E-03 | 2.39E-03 | 4.83E-02 | -0.98 |

450 **Table 3.** Chemical parameters of groundwater investigated by Adams (1990) and Walker (2006).

451 Analyses are not balanced.

452

| SAMPLE ID | TYPE | LOCATION NAME | Ca ²⁺ (mg/L) | Mg ²⁺ (mg/L) | Na ⁺ (mg/L) | K ⁺ (mg/L) | HCO ₃ ⁻ (mg/L) | SO ₄ ²⁻ (mg/L) | Cl ⁻ (mg/L) | TDS | T (°C) | pH |
|-----------|--------|---------------------|-------------------------|-------------------------|------------------------|-----------------------|--------------------------------------|--------------------------------------|------------------------|--------|--------|------|
| ZTG-38 | spring | Llano del Pinal | 92.9 | 11.6 | 13.5 | 2.0 | 72.0 | 230.0 | 5.3 | 427.3 | 14.9 | 6.0 |
| ZTG-15 | spring | Chicua | 19.6 | 10.8 | 8.5 | 4.5 | 98.8 | 12.7 | 4.4 | 159.3 | 14.4 | 6.5 |
| ZTG-19 | spring | Zunil | 40.2 | 40.0 | 313.0 | 32.0 | 665.0 | 202.0 | 186.0 | 1478.2 | 74.4 | 7.8 |
| ZTG-28 | spring | Zunil | 13.8 | 8.8 | 116.0 | 14.4 | 210.0 | 73.2 | 70.8 | 507.0 | 61.4 | 7.0 |
| 95-B4 | spring | Zunil | 18.4 | 12.9 | 10.5 | 3.9 | 0.0 | 15.8 | 4.8 | 68.0 | 25.5 | 6.3 |
| 95-B2 | well | Almolonga | 11.3 | 6.7 | 110.1 | 6.2 | 182.9 | 82.5 | 55.1 | 455.8 | 38.9 | 6.2 |
| 95-B9 | well | Baños Cirilo Flores | 11.5 | 4.7 | 105.8 | 7.5 | 140.5 | 77.1 | 48.4 | 395.9 | 48.5 | 6.9 |
| 95-B10 | well | Baños Chocovi | 9.0 | 4.1 | 82.6 | 12.3 | 141.7 | 22.6 | 54.6 | 327.0 | 47.1 | 7.5 |
| 95-B28 | spring | Inde Dam | 13.3 | 7.9 | 20.4 | 3.5 | 83.64 | 28.4 | 5.8 | 172.2 | 18.7 | 10.0 |

453

454

455 **4.3 Results of chemometric analysis**

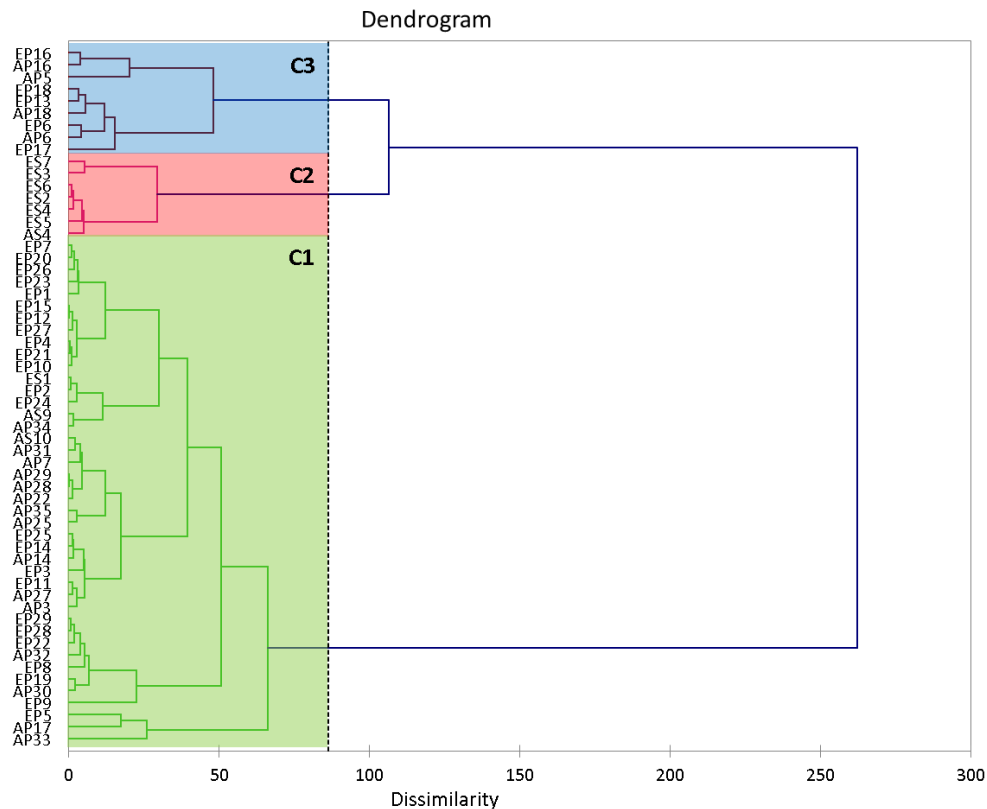
456 The univariate analysis of the chemical dataset presented in the previous paragraph was not
457 sufficient to fully describe the groundwater features. A clear identification of the factors influencing
458 the hydrogeochemistry of the studied area, as well as the relationship between chemical behaviour
459 and spatial distribution of samples, were still missing. Thus, a new approach to the dataset through
460 multivariate techniques was adopted.

461 In order to distinguish similar chemical behaviours among the sampled waters, not detected through
462 univariate analysis described in the previous paragraph, a HCA was performed. The similarity
463 between objects was measured by squared Euclidean distances, and the Ward's method of
464 agglomerative HCA was used. Figure 5 displays the results of the HCA analysis on the whole
465 sample set. Three clusters, named C1, C2 and C3 from the bottom to the top of the dendrogram, can
466 be distinguished. The majority of samples (43) are grouped in cluster C1. These samples come from
467 31 different wells, almost entirely located in the central sector of Xela Caldera, among which 8
468 were sampled in both the two campaigns and three springs (ES1, AS9, AS10). At bottom of this
469 cluster it is possible to distinguish a smaller grouping characterized by higher dissimilarity and

470 composed by three samples: EP17, AP5 whose location is nearby the active volcanic complexes,
471 and AP33, collected in the northern part of the study area, 15 km from the others.

472 The cluster C2 is entirely composed by springs water in Molino Viejo area.

473



474

475 **Figure 5.** Dendrogram obtained by hierarchical clustering analysis HCA .

476

477 The C3 includes 10 samples located in the south-western border of the area, near the active volcanic
478 complexes. Their similarity could support the hypothesis of a common evolutionary trend related to
479 the recent volcanic history of this area. Two samples (AP5 and AP16) correspond to those points
480 that belong to the Cl-SO₄-Ca-Mg type showed in Piper diagram (Figure 3). Three couples (EP18-
481 AP18, AP6-EP6, AP16-EP16) represent the same sampling points in two different years. The good
482 agreement of chemical features among the two sampling campaigns reflects unchanged chemical
483 characteristics of the groundwater collected in those points. Conversely, AP17 and EP5, that are the
484 same sampling points of respectively EP17 and AP5 found in C3, are located in cluster C1. This

485 indicates an inter-annual variability for these points that can be explained with a decreasing ion
486 concentration and EC from 2011 to 2012, likely due to the fact that the samples of 2012 were
487 collected in May, at the beginning of the rainy season, while the 2011 samples in February during
488 the dry season (see Table 1) and thus the azimuthal groundwater recharge regime was different.

489 The HCA revealed the possibility of recognizing a geographical criterion among sampled
490 groundwater. Nevertheless, a more detailed focus is needed on the parameters influencing the
491 sampled waters and thus a PCA was performed. Figure 6 shows the combined plot of scores and
492 loadings obtained by PCA considering the waters collected in both sampling campaigns. Taking
493 into account the scree plot, we reported only the first two principal components that contain a total
494 variance of about 62 %; the remaining PCs contain a low, and therefore not significant, percentage
495 of information.

496 Regarding the variables, a correlation among the main dissolved species (major ions, EC, TDS) and
497 the PC1 is evident. Furthermore, all the samples collected in the area near the active volcanic
498 complexes (cluster C3) are distributed along the positive PC1 axis. O₂ and O₂% variables are
499 represented by vectors having opposite direction relative to pH and T variables on PC2. This
500 indicates that high concentrations of dissolved oxygen appear with low pH and temperature. K⁺, Pb
501 and Mn variables are characterized by vectors having different directions with respect to those of
502 the other variables, indicating a their uncommon behavior in the different aquatic systems
503 considered.

504 Clusters derived from HCA were overlapped as coloured areas in order to compare the two
505 chemometric approaches and to associate the physico-chemical parameters to the clusters detected
506 by HCA. The cluster C1, representing waters collected in the central sector of Xela caldera, are
507 weakly influenced by the main chemistry of groundwater, since they are located to the opposite side
508 of TDS, EC and main ions vectors. This is probably linked to the fact that they are more diluted
509 than the groundwater close to volcanic area, where sampled waters (cluster C3) have higher
510 contents of solutes. Hence, their origin might be related to different flow paths that are composed by

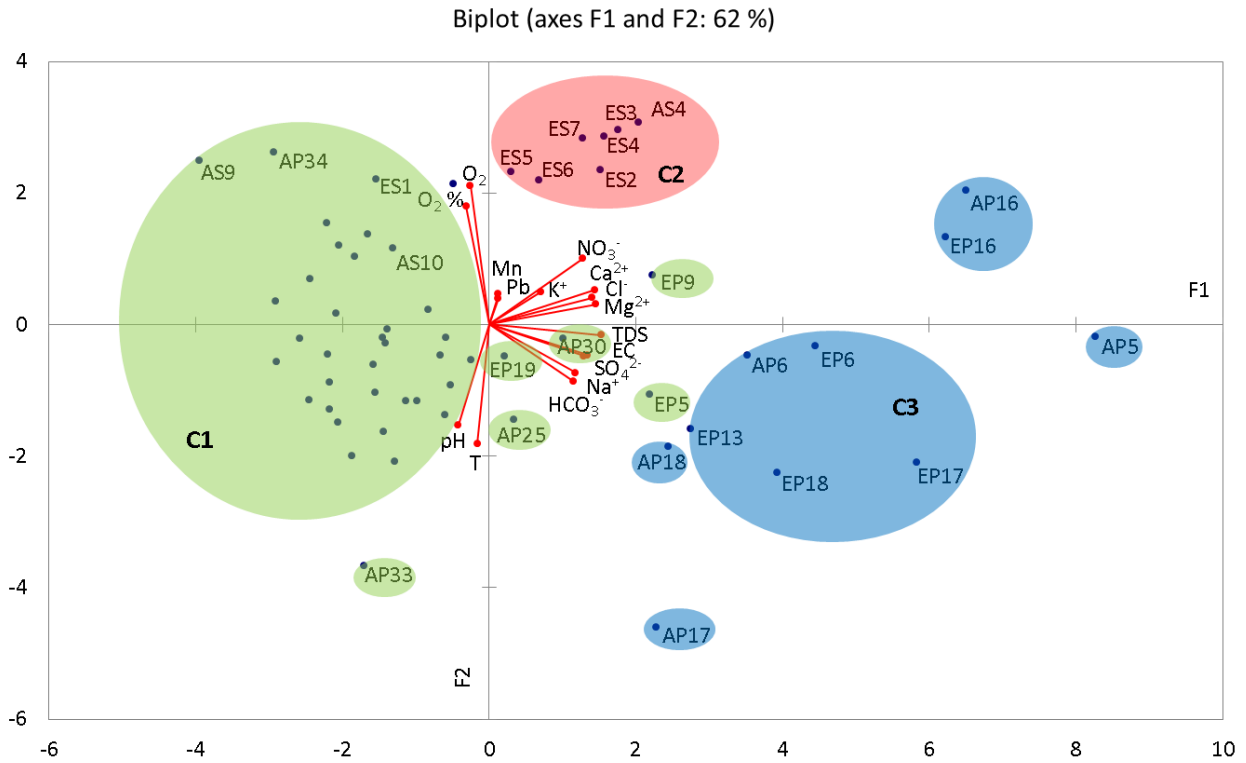
511 more diluted groundwater infiltrated in recharge areas. Conversely, some points belonging to C1 of
512 HCA (EP5, EP9, EP19, AP17, AP25, AP30) lay on the right side of PC2 axis, indicating that they
513 might be influenced by the main dissolved species. Among these, AP33 and AP17 occupy a
514 separated position in the lowermost part of the plot because of low O₂ concentrations. This explains
515 particularly the different position for AP17 and EP17 samples: even though collected in the same
516 well, they show a relevant decrease in O₂ concentration in one year (from 5.16 to 1.98 mg/L). As in
517 the case of sample AP33, that remains isolated because of its high temperature and low O₂
518 concentration, low oxygen values may be explained by the presence of organic pollutants in
519 aquifers, linked to local inputs from wastewater discharges.

520 The group C2, formed by spring waters, is well identified also in PCA, as it is greatly influenced by
521 the variables identified by the vectors of the dissolved oxygen. This is confirmed by the high values
522 of O₂ found in those waters (6.47÷6.89 mg/L).

523 The samples in cluster C3 are relatively scattered but the behaviour is quite homogeneous since
524 they occupy the leftmost part of the plot. They are strongly dependent on the main dissolved ionic
525 species because they are aligned with the direction of the vectors representing the major ions, CE
526 and TDS. As in HCA, differences among the two years of sampling can be found, but this does not
527 significantly affect their position. An exception is represented by AP17 and EP5: in HCA they were
528 listed in C1 but they seem to be much closer to their correspondents EP17 and AP5 the EP5 sample
529 can be here considered belonging to the C3 cluster. The analyses results (Table 2) confirm the
530 similarity between EP5 and samples belonging to C3 cluster.

531 Table 4 presents the factor loadings obtained for the groundwater samples collected in the
532 investigated area. Four factors were obtained summing more than 70% of the total variance in the
533 entire data set. The first factor, accounting for 42% of the total variance, presents highest loading
534 for EC, Ca²⁺, Mg²⁺, Na⁺, HCO₃⁻, SO₄²⁻, Cl⁻, NO₃⁻, TDS. Hence, this factor represents the main
535 components of groundwater. The second factor is characterized by high loadings of dissolved
536 oxygen and Pb²⁺. For this reason we hypothesized that this factor describes the behavior of the

537 oxygenated groundwater usually more rich in heavy metals such as lead. Indeed lead is often found
538 in sediments like sulfide in reducing conditions but it can be released into the waters under
539 oxidizing conditions due the fact that the sulfidic component is oxidized to sulfate. In factor 3 pH,
540 temperature and HCO_3^- have a positive factor loading: this indicates a strong interconnection among
541 these variables. This finding confirms the strict dependence of bicarbonate equilibrium on pH and
542 temperature: neutral or slightly acid or basic conditions foster HCO_3^- dissolution, while at constant
543 pH HCO_3^- is more soluble at low temperatures. Finally the last factor presents high and moderate
544 loading for K^+ and Mn respectively. It can be then associated with the behavior of some
545 groundwater characterized by relatively high concentration of potassium and, to a lesser extent,
546 manganese but not of other principal ions. Such finding is partially confirmed by the presence in
547 analyses results of samples with K^+ concentrations >3 mg/l and moderate concentrations of other
548 ionic species. This suggests the presence of an independent source of K^+ in the considered
549 groundwater system. Considering that these are few cases and that the main rock formations are
550 sources of Na^+ , the source may be anthropogenic and with local significance, for instance nutrient-
551 related inputs.



552

553 Figure 6. Biplot obtained by principal component analysis PCA. Coloured areas correspond to the
 554 clusters detected in hierarchical clustering analysis HCA.

555

556 **Table 4.** Variable loadings in the factors obtained by FA for groundwater samples. The bold values
 557 correspond for each variable to the factor having the largest cosine square

558

| Variables | F1 | F2 | F3 | F4 |
|-------------------------------|--------------|--------------|--------------|--------------|
| T | -0.142 | -0.408 | 0.515 | -0.131 |
| E.C. | 0.871 | -0.241 | 0.022 | -0.200 |
| pH | -0.263 | -0.219 | 0.592 | -0.282 |
| O2 % | -0.103 | 0.895 | 0.010 | -0.025 |
| O2 | -0.064 | 0.984 | -0.165 | 0.034 |
| Ca ²⁺ | 0.918 | 0.104 | -0.037 | 0.230 |
| Mg ²⁺ | 0.929 | 0.071 | 0.047 | 0.106 |
| Na ⁺ | 0.706 | -0.224 | 0.257 | -0.033 |
| K ⁺ | 0.338 | 0.004 | -0.037 | 0.728 |
| HCO ₃ ⁻ | 0.681 | -0.160 | 0.644 | 0.195 |
| SO ₄ ²⁻ | 0.786 | -0.236 | 0.088 | -0.006 |
| Cl ⁻ | 0.895 | -0.054 | -0.265 | 0.097 |
| NO ₃ ⁻ | 0.831 | 0.163 | -0.367 | 0.143 |
| TDS | 0.967 | -0.079 | 0.204 | 0.131 |
| Pb | 0.123 | 0.337 | 0.279 | -0.159 |
| Mn | 0.050 | 0.076 | -0.044 | 0.199 |

559

560 **5. CONCLUSIONS**

561 The present study aimed to improve the knowledge of the hydrochemical setting of a large area in
562 central America, where groundwater features were almost unknown. The hydrochemical results
563 show the prevalence of the meteoric influence, according to the Ca-Mg-HCO₃ facies. Further
564 processes such as mixing with hydrothermal fluids in the volcanic areas and ion exchange with clay
565 minerals in the aquifer solid matrix, are likely responsible for the Na enrichment of some waters.
566 Along with that, a Mg enrichment was also detected in the southern sector, due to the circulation in
567 the andesitic rocky complexes of Santa Maria and Cerro Quemado volcanic complexes.
568 Furthermore, anthropogenic inputs were detected: nitrates in rural areas and lead in urban areas that
569 in some cases are above the quality standards.

570 The research highlighted the importance of coupling Piper and Schoeller diagrams and univariate
571 plots with chemometric tools (PCA and HCA). From one side the hydrochemical facies of
572 groundwater were defined and the reason for different water composition were hypothesized, while
573 on the other side the multivariate analysis allowed to better distinguish more features of
574 groundwater thanks to the comparison between physical and chemical parameters. HCA revealed
575 that the majority of samples can be ordered following a geographical criterion and PCA allowed a
576 more detailed focus on the parameters influencing the analysed waters. Principal ions, as well as
577 oxygen content, were envisaged as the most discriminating parameters influencing the water
578 composition. The latter is possibly influenced by the presence of organic contamination and by the
579 temperature value. Furthermore, data evidenced the almost complete absence of contamination
580 sources for toxic heavy elements, with only two exceptions (nitrate and lead), likely connected to
581 agriculture and urban wastewater.

582 This first chemical characterisation of the area may be used by both researchers for further studies
583 and by the stakeholders for the management of groundwater, for instance posing the basis for the
584 development of a groundwater monitoring network.

585

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591

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