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1 **Geological-geomorphological and geochemical control on low**
2 **arsenic concentration in the Lerma valley groundwater, between the**
3 **two high arsenic geologic provinces of Chaco-Pampean plain and**
4 **Puna**

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25 **Abstract**

26 Argentina is known for having one of the most extensive areas with high arsenic (As)
27 concentration in groundwater in the world. These areas correspond to two main geological
28 provinces, the Puna plateau and the Chaco-Pampean plain. In this large territory, there are some
29 specific environments where the As concentration in groundwater is lower, and in some cases
30 within the recommended limits for drinking water. In our study, we analyze and interpret the low
31 arsenic concentrations reported for the Lerma valley, the easternmost intermontane basin of the
32 Cordillera Oriental, located between the aforementioned high-arsenic geological provinces. The
33 groundwater from this valley is used for the consumption of more than 600.000 inhabitants in the
34 city of Salta and nearby towns. The incipient development of the valley since the late Miocene
35 and the subsequent tectonic and climatic evolution favored low As concentrations with respect to
36 the Puna and the Chaco-Pampean plain. The high-energy sedimentary environments that
37 characterized the area during Plio-Quaternary times and the composition of the sediments have
38 controlled the characteristics of sediments the multilayered aquifer. Moreover, the absence of
39 geogenic arsenic sources, climate, high rain infiltration rate, near neutral pH, redox conditions,
40 and wells construction with screens settled in coarse productive layers favor groundwater of
41 good quality. The geological and tectonic evolution of the Lerma valley could be extrapolated to
42 other similar valleys in the NW of Argentina and can be useful as tool for exploration of good
43 quality groundwater. This is of high importance in Latin American territories with high As
44 concentration in groundwater such as Argentina.

45 **Key words:** Low arsenic in groundwater, Cordillera Oriental, tectonic and sedimentary evolution,
46 groundwater geochemistry, Northwest Argentina

48 **1. Introduction**

49 Arsenic (As) is an element that can be found in groundwater linked to geogenic sources
50 (Nordstrom 2002, Smedley and Kinniburgh 2002). Chronic exposure to high levels of As is toxic
51 for human health producing variety of cancers, cardiovascular disease, and neurologic
52 impairments in exposed populations (Figueiredo et al., 2010; Mitchell, 2014). A large number of
53 people in different parts of the world are exposed to As via drinking water (e.g. China, India,
54 Bangladesh, USA, Mexico, Chile). Argentina was the first Latin American country where As
55 occurrence in groundwater was reported, and the first in the world to document As poisoning
56 from natural sources known as HACRE (Hidro Arsenisismo Crónico Regional Endémico,
57 according to its Spanish initials) (Goyenechea 1917, Bundschuh et al., 2012). In Argentina,
58 extensive areas with high As concentration in surface and groundwater are related mainly to two
59 main geological provinces, the Altiplano-Puna plateau and the Chaco-Pampean plain (Ramos,
60 2017).

61 The origin of As in these environments is linked to geogenic sources derived from Andean
62 orogeny and volcanism, a large scale geological processes affecting in some level most of the
63 Argentinian territory. Only in the Chaco-Pampian plain approximately 2 - 8 million inhabitants
64 are potentially affected by As (Nicolli, 2012). Here, the origin of As (and fluorine) in the
65 groundwater is related to the leaching of volcanic components present in the loess sediments
66 with important quantities of volcanic glass, volcanic minerals and volcanic lithic fragments
67 (Nicolli et al., 2012). Consequently, HACRE develops, sometimes associated with dental and/or
68 skeletal fluorosis. In the Altiplano-Puna plateau, As is found in most of the water types of the
69 region (i.e. groundwater, rivers, lakes, brines, salines, thermal waters, and acid mine drainage)

70 indicating multiple natural (volcanic-mineralogical-geothermal) and anthropogenic origins for
71 As (Murray et al., 2018). San Antonio de Los Cobres town (located 250 km to the west of the
72 Lerma valley) is an emblematic case where As concentrations measured in drinking water are
73 around 200 µg/L.

74 However, in this extended territory, especially in the Chaco-Pampean plain, there are some
75 specific environments (e.g. fluvial plains, sand-dunes) where the As concentration in
76 groundwater is lower than the Argentinian guidelines for As in drinking water of 0.05 mg/L
77 (CAA, 2012), and in some cases lower than the World Health Organization limits of 0.01 mg/L
78 (WHO, 2017) (Becher Quinodóz and Blarasín, 2014; Giacobone et al., 2018) . This is related to
79 hydrogeological and geochemical aspects of the aquifers that promote low As concentration in
80 groundwater. These sites are of special interest due to the lower preventive activities that
81 authorities must promote for preserving public health. However, these areas require of more
82 investigation and delimitation, and a better understanding of the geological-geochemical-
83 hydrological characteristics (Giacobone et al., 2018).

84 This study focuses on the Lerma valley the easternmost intermontane basin of the Cordillera
85 Oriental geological province. The Cordillera Oriental is situated in northwestern Argentina, lying
86 between the Altiplano-Puna plateau and the Chaco-Pampean plain (Fig. 1). The groundwater of
87 the Lerma valley which is the main source of drinking water, has been qualified as good quality
88 (Baudino 1996). The largest urban area corresponds to the city of Salta, located in the northern
89 part of the valley with more than 600.000 inhabitants. It is the capital of the homonymous
90 province and corresponds to the seventh most populated city in Argentine (Argentinian National
91 Census, 2010). Smaller rural towns of the Lerma valley which also consume groundwater are
92 Vaqueros, Rosario de Lerma, Campo Quijano, Cerrillos, La Viña (Fig. 1). The major threatsto

93 groundwater quality are related to urban contamination (Rocha and Baudino, 2002),
94 overexploitation of the aquifers, and in some areas (Arenales Aquifer) anthropogenic
95 contamination with boron, with values that reach 3 mg/L (Bundschuh et al., 1994). Low As
96 concentrations in the Lerma valley groundwaters are described by de Sastre et al. (1992). The
97 authors highlighted the difference with the Puna and the Chaco-Salteña plain (North area of the
98 Chaco-Pampian plain, Fig. 1) where high As concentration in groundwater can be found. In the
99 As-risk map published by the Secretariat of Water Resources of Salta province (Secretaría de
100 Recursos Hídricos), low As concentrations for the Lerma valley are also observed (Hoyos,
101 2013). Moreover, a study of metabolism of inorganic As in children comparing the villages of
102 San Antonio de los Cobres (Altiplano-Puna plateau), Taco Pozo (Chaco-Pampean plain) and
103 Rosario de Lerma (Lerma valley), highlight the difference in As concentrations and health
104 effects among the regions (Concha et al., 1998). The group of children from Rosario de Lerma
105 was selected as a reference group due to their low As intake (0.65 $\mu\text{g/L}$ of As in drinking water),
106 while children from San Antonio de los Cobres, and Taco Pozo ($>200 \mu\text{g As/L}$ in drinking
107 water), had the highest concentration of As in blood and urine ever recorded for children (on
108 average 9 $\mu\text{g/L}$ for blood, and 380 $\mu\text{g/L}$ for urine) (Concha et al., 1998).

109 The aim of this study is to analyze possible geological, structural, sedimentary, hydrological and
110 geochemical, processes that favor low As concentrations in the Lerma valley in a regional
111 context of high As. In order to attain that goal, local and regional factors and processes are
112 analyzed. Among them, the existing data related to the aquifer composition, the origin of the
113 sediments, the geological and structural evolution of the valley, the hydraulics of the aquifer, and
114 the geochemical characteristics of groundwaters. A map of As concentrations in the Lerma
115 valley with data provided by different government offices and from our own sampling work is

116 also presented. In the world-wide context of increasing population, and demand of water
117 resources, this work highlights the importance of a better understanding of the natural processes
118 that create conditions and reservoirs where good quality of groundwater can be found. This is of
119 high importance in territories such as Argentina with extended regions of high arsenic in
120 groundwater.

121 **2. Geological setting**

122 *2.1. Stratigraphy of the Lerma valley*

123 The stratigraphy of the region can be divided in four main sequences (Fig. 2): 1) Early to Middle
124 Cambrian basement (Lerma, Mesón, and Santa Victoria Groups) composed of low grade
125 metamorphic rocks of the Puncoviscana Formation (Turner and Mon, 1979; Escayola et al.,
126 2011); 2) Cretaceous-Paleogene continental strata with conglomerates, sandstones, mudstones
127 and limestones of the Salta Group rift sequence (Marquillas et al., 2005); 3) Synorogenic
128 Neogene to Pleistocene strata composed of reddish sandstones and mudstones, and brownish
129 conglomerates alternated with mudstones of the Guanaco and Piquete Formations (Orán Group),
130 respectively (Gebhard et al., 1974); and 4) Late Quaternary deposits including thick alluvial
131 conglomerates with alternating sandy and muddy layers (La Viña Formation; Gallardo et al.,
132 1996).

133 *2.2. Location and formation of the Lerma valley*

134 The Lerma valley is the easternmost intermontane basin of the geological province of Cordillera
135 Oriental, northwestern Argentina (Fig.1). The Cordillera Oriental is limited by the Altiplano-
136 Puna plateau to the west and by the Subandean ranges and Santa Bárbara System to the east
137 (Fig.1). Eastwards, the Chaco-Pampean plain represent the foreland basin of the Andes. The

138 Lerma valley is bounded by uplifted basement-cored thrust sheets; the Mojotoro and Castillejo
139 ranges to the east (2,500 m) and by the Lesser range (4,800 m) and lower elevations (Vaqueros
140 and Altos de la Laguna ranges) to the west (González Bonorino and Abascal, 2012; García et al.,
141 2013). Low-temperature thermochronology indicates that the Mojotoro and Castillejo ranges
142 started to be exhumed by late Miocene times (Pearson et al., 2013) but probably at low rates as
143 there are no sedimentary evidences of the closure of the valley by that time. The growth strata
144 geometries found both sides of the valley in the upper section of the Piquete Formation
145 synorogenic conglomerates are the main evidence for the establishment of this intermontane
146 basin during late Pliocene-early Pleistocene times (Gallardo et al., 1996, Monaldi et al., 2008;
147 González Bonorino and Abascal, 2012; García et al., 2013, 2019).

148 *2.3. Aquifer systems in the Lerma valley*

149 Seven aquifer systems are recognized in the Lerma valley, from north to south these are named:
150 La Caldera, Arenales, Portezuelo, La Isla, Rosario, La Viña and La Florida (Baudino 1996).
151 Each one has distinctive characteristics such as the recharge area, porous media (grain size), and
152 the chemical water type. However, the levels exploited for drinking water and irrigation
153 correspond to the Quaternary sediments of La Viña Formation (Gallardo et al., 1996). The
154 characteristic of this deposit composed of thick alluvial conglomerates with alternating sandy
155 and muddy layers makes it an heterogeneous multilayered aquifer. The thickness of the La Viña
156 Formation in the basin is difficult to calculate because its transitional contact with the Piquete
157 Formation. A maximum thickness of 240 m has been inferred from water wells located some
158 kilometers southward from Medeiros hills, between the Cerrillos San Miguel and the western
159 edge of the basin (Baudino, 1996) and from seismic records (González Bonorino et al., 2003;

160 Hain et al., 2011). However, most of the drilled wells are around 200 m depth, the wells
161 generally intersect the of different granulometry layers of La Viña Formation.

162 **3. Methodology**

163 *3.1. Data compilation*

164 Water analyses from wells in the Lerma valley has been compiled in this work. The information
165 collected includes data from the Secretariat of Water Resources and Aguas del Norte company
166 from Salta province (Table 1, 2 and 3).

167 *3.1.1 Aguas del Norte company*

168 This company (public and private capital) is the provider of the drinking water and sanitation
169 service of the Salta province. The data obtained correspond to twenty-two (22) well samples of
170 the period 2016 (Table 1). The chemical analyses for As, K, and Na were performed in their own
171 laboratories with ICP-OES (Inductively coupled plasma - optic emission spectroscopy). The
172 detection limits for As were variable according to the calibration curves between <0.015 and
173 <0.035 mg/L. For these samples, Ca, Mg, and HCO₃ were not analyzed.

174 *3.1.2. Secretariat of Water Resources*

175 The Secretariat of Water Resources is the water resources control agency in Salta Province. The
176 company Merco Aguas, performs the well drilling service. The chemical analyses obtained from
177 this source comprises twenty-eight (28) water samples taken between the periods 2008 to 2017
178 from the wells (Table 1). Data of the wells (depth, static level of well, granulometry of the
179 productive layers) was also compiled (Table 1 and 3). Each performed well has between 4 and
180 11 screens. The screens were mainly situated in the coarse sediments layers of the multilayered

181 aquifer that were qualitative described during drilling (Table 3). The transmissivity (T) of the
182 wells (Table 3) were calculated in this study with the information of the technical reports of each
183 well using the Jacob method (Cooper and Jacob, 1953). At each well, the chemical analyses
184 correspond to the mix of waters from the different productive layers where the screens were
185 situated (Table 1 and 2). The water analyses were performed in different external laboratories.
186 The method used for As analysis was spectrophotometry with a detection limit of 0.05 mg/L.
187 This detection limit could be considered high, since the recommended value by the WHO is 0.01
188 mg/L (WHO, 2017). However, it is in the range for local analyses since the permitted value for
189 drinking water in Argentina is 0.05 mg/L (CAA, 2012). Major ions were measured with AAS
190 (Atomic Adsorption Spectrometry) for Na and K with detection limits of 0.5 mg/L. For Ca, Mg,
191 HCO₃, and Cl the method was titration with detection limits of 0.1 mg/L for Ca and Mg, 3 mg/L
192 for bicarbonates and 2 mg/L for chlorine. Finally, SO₄ was determined with turbidimetry with a
193 detection limit of 0.5 mg/L.

194 3.2. Water sampling (this study)

195 Fifteen (15) water samples were collected during 2010 from groundwater and surface water in
196 the northernmost Lerma valley (north of the Vaqueros river) (Fig. 2), and are presented in
197 Table1. The samples were taken *in situ*, the wells were pumped 10 minutes before taken the
198 sample. The samples were filtered with Millex-HV-Durapore-PVDF type of 0.45µm pore size.
199 The samples were acidified with HNO₃, and preserved at 4 °C until being analyzed at ActLabs
200 laboratories (Canada). The analytical method was ICP-MS (Inductively coupled plasma - mass
201 spectroscopy) for and As. The detection limit for As was 0.03 µg/L. Cations and anions were
202 determined by titration according to the standards methods described in Eaton et al., (1998).

203 4. Results

204 The data compiled and obtained in this study correspond mainly to the center and Northern areas
205 of the Lerma valley (Fig. 3). Data provided by the Secretariat of Water Resources, and Aguas del
206 Norte company show that As concentration in groundwater is mostly below detection limits
207 (0.05 mg/L) (Table 1). In the cases where As is detected, samples labeled as 25 and 68, the
208 concentration vary between 0.01 and 0.022 mg/L respectively (Table 1, Fig. 3).

209 The samples obtained in this study situated in the northernmost Lerma valley (From the
210 Mojotoro river to the North) show low As concentrations between 0.0001 and 0.004 mg/L in
211 groundwater, and between 0.0004 and 0.001 mg/L in rivers (Table 1). This values are within the
212 permitted range of concentrations for As in drinking water of WHO and CAA.

213 The data presented in this study is consistent with previous studies carried out by de Sastre et al.
214 (1992) which map shows samples without As in the Lerma valley in contrast to high natural
215 concentration of As in the Altiplano-Puna plateau and the Chaco-Pampean plain regions. In the
216 map of As risk of the Secretariat of Hydric Resources of Salta province, the samples in the
217 Lerma valley have As concentrations < 0.01 mg/L with some samples between 0.01 and 0.03
218 mg/L (Hoyos, 2013). In a sampling performed during a research of metabolism of As in children
219 from Rosario de Lerma city (Fig. 3), the concentration of As measured in drinking water are
220 around 0.0001 mg/L (Concha et al., 2010).

221 Regarding to the geochemistry of major ions, most of the waters samples are HCO₃-Ca-Mg type
222 with a normal evolution to HCO₃-Na-K (Table 2, Fig. 4). A sample in the North of the valley has
223 SO₄-Ca as dominant ions (sample 82), which is attributed to dissolution of secondary gypsum
224 present in the sediments of the Orán Group (Hoyos, 2005; Lopez, 2017). The sample 63 which
225 has high SO₄ can also interpreted as more evolved since it is located in the central part of the
226 valley. Baudino (1996) associates the presence of SO₄-Cl type groundwaters in La Viña aquifer

227 (Southern portion of the valley) with the dissolution of salts present in the Cretaceous sediments
228 of the Salta group formations (Fig. 2). In groundwater the mean pH value is 7.16 with an extreme
229 value of 8.4 also for the sample 82 located in La Caldera aquifer (Table 1, Fig. 3), the mean
230 value for conductivity is 334 $\mu\text{S}/\text{cm}$, with an extreme of 830 $\mu\text{S}/\text{cm}$ (sample 19) (Table 1, Fig.
231 3). In rivers the mean pH value is 6.33 and the mean conductivity is 182 $\mu\text{S}/\text{cm}$, in both cases
232 lower than in groundwater. Previous data from Baudino (1996) indicates pH values between 5.5
233 and 7.8 and conductivities in a range of 350 – 850 $\mu\text{S}/\text{cm}$ for groundwater.

234 The performed wells have static levels between 11 and 114 m depth from the ground surface
235 with a maximum drilled of 260 m depth (Table 1 and 3, Secretariat of Water Resources data).
236 Concerning the lithology of the productive levels of the wells, these are mainly composed of
237 gravels, conglomerates and sands (Table 3). The transmissivity values calculated for the wells
238 performed by the Secretariat of Water Resources varies between 0.2 m^2/day - 371 m^2/day (Table
239 3). Baudino (1996) indicates medium to very high transmissivity values for the different aquifer
240 systems in the Lerma valley (i.e. Arenales = 250 m^2/day ; El Portezuelo = 55 - 217 m^2/day ; La
241 Isla = 140 - 2,000 m^2/day ; La Viña = 170 - 280 m^2/day).

242 **5. Discussion**

243 For the low As concentration in the groundwater of the northern Lerma valley we analyze the
244 following possibilities: The absence of geogenic sources of arsenic in comparison to the situation
245 in the Puna and the Chaco-Pampian plain, and the climate contributions to the geological
246 processes, the characteristics of the aquifer, and groundwater geochemistry.

247 *5.1. Comparison of the Lerma valley with the surrounding areas of high arsenic content*

248 *5.1.1. Puna*

249 In general, the sources of As in groundwater and drinking water in the Altiplano-Puna plateau
250 are attributed to the weathering of the extensive Cenozoic volcanic rocks (de Sastre et al., 1992;
251 Farías et al., 2009), sulfide deposits, mining wastes, and the discharge of thermal waters (Tapia
252 et al., 2019, this issue; Murray et al., 2019 this issue).

253 The Altiplano-Puna plateau (Fig. 1), has been characterized by active volcanism since, at least,
254 Oligocene times. In general, the sources of As in groundwater and drinking water in the
255 Altiplano-Puna plateau are attributed to the weathering of the extensive Cenozoic volcanic rocks
256 cropping out there (de Sastre et al., 1992; Farías et al., 2009). The Cenozoic volcanism, is one of
257 the distinctive features of this region (Ramos, 2017). Volcanism in the Puna has records from
258 ~26 Ma, and it intensified from ~15 Ma to the present (Grosse and Guzmán, 2018). During the
259 Miocene, volcanic calderas generated important volumes of pyroclastic flows deposits
260 (ignimbrites), but domes and stratovolcanoes were also important (Grosse and Guzmán, 2018;
261 Guzmán and Montero-López 2015). The Miocene to Quaternary silicic ignimbrite field in the
262 Altiplano-Puna plateau forms one of the largest ignimbrite provinces on Earth (Kay et al., 2010).
263 Tapia et al., (2019, this issue) indicates that fluvial sediments originated from Neogene volcanic
264 rocks erosion in the Altiplano-Puna exhibit the highest concentrations of As (351 mg/kg) when
265 compared to fluvial sediments originated from erosion of other geologic periods and/or rock
266 types (112 mg/kg). This last value is already higher than the average of the upper continental
267 crust (5.7 mg/kg; Hu and Gao, 2008) highlighting the Altiplano-Puna anomaly in As, especially
268 related to Neogene volcanic rocks.

269 In the Lerma valley there is a lack of Cenozoic volcanism as known in the Puna. Despite the
270 Neogene volcanism had episodes of expansion with volcanic manifestations that reached the
271 eastern edge of the Puna including the Cordillera Oriental geological province (Hongn et al.,

272 2018), the lack of volcanic rocks is observed in the stratigraphy of the Lerma valley (section
273 2.1). During the middle to upper Miocene, the Lerma valley was included in the fragmented
274 foreland basin after the exhumation of the Mojotoro and Pascha mountain ranges and between 12
275 and 8 Ma the fluvial dynamics in the valley was very energetic (conglomerates in the Guanaco
276 and Piquete Formations) (Gallardo et al., 1996, Monaldi et al., 1996; González Bonorino and
277 Abascal, 2012; Pearson et al., 2013) (Fig. 5). The synorogenic Neogene sediments in the Lerma
278 valley are composed of reddish sandstones and mudstones, and brownish conglomerates
279 interbedded with mudstones of the Guanaco and Piquete formations, respectively (Gebhard et al.,
280 1974) with a general lack of volcanic components. The distinctive geomorphology of the Puna
281 with closed and endorreic basin systems make the Puna an isolated geological province where
282 there is a lack of transference of sediments and chemical components such as As outside of the
283 system. This natural characteristic of the Puna preserves the surrounding areas such as the Lerma
284 valley out of the direct transference of As. Instead, in the Puna region, the closed basin and its
285 high evaporation rates produces an enrichment in the depocenter of the basins reflected in high
286 concentration of As in brines, salines, and lakes (Tapia et al., 2019, this issue).

287 Another important geogenic source of arsenic in the Puna are sulfide mines (Tapia et al., 2019,
288 this issue). Sulfide mines (Pb, Zn, Cu, Au, Ag, Sn) in the Puna are in many cases related to the
289 Cenozoic volcanism (Allmendinger et al., 1997; Richards et al., 2006; Caffè and Coira, 2008).
290 These mineral deposits contain As in gangue minerals as well as in ore minerals. Arsenic is
291 present in pyrite, arsenopyrite, and other rich As mineral accessories. Rich As-pyrite and
292 arsenopyrite is also present in epithermal and alluvial rich gold mineralization hosted in marine
293 shales from the Ordovician period (Rodríguez et al., 2010). The natural weathering of these
294 sulfide deposits releases As into the surrounding environment in the Pozuelos basin (Murray et

295 al., 2019, this issue). Arsenic is also present in the mining wastes of sulfide mining sites that
296 were exploited between the 70' and 90' decades, as well as in the acid mine drainage (AMD)
297 generated by oxidation of the wastes. Examples of inactive mines and AMD generation in the
298 Puna are La Poma treatment plant, La Concordia, and Pan de Azúcar mines, which affect the
299 basins of San Antonio, Tajamar, and Cincel rivers, respectively (Kirschbaum et al., 2012;
300 Murray et al., 2014; Murray et al., 2019 this issue).

301 In the Lerma valley there is a lack of sulfide deposits (García et al., 1997). In comparison with
302 the Puna, the absence of this important geogenic source appears to be another important reason
303 that favors the low arsenic concentration in groundwater and surface water. However, the strong
304 arsenic anomaly related to the sulfide mineralization in the Puna which is also extended to the
305 Bolivian Altiplano, is reflected in the geochemical composition of rainwater in the city of in the
306 Lerma valley. Gaiero et al., (2013) indicates that strong WNW winds from the Altiplano-Puna to
307 the Atlantic Ocean generates deflation and transport of important volumes of dust. Romero et al.,
308 (2017) indicate that anomalies of As ($0.63 \mu\text{g/L}$) and other elements (Ca, Cu, Zn, Sb, and Pb)
309 create a unique signature of rainwater in the Lerma valley. The origin of these metals in the rain
310 water is associated to the rainout of dust that is transported from the Altiplano-Puna plateau to
311 the east, in particular during the dry season where scarce vegetation cover, and strong westerly
312 winds favor the transport of rich As and metallic dust to the east of the Altiplano-Puna.
313 Statistical analyses indicate a direct correlation between As and Ca, Cu, Zn, Sb, and Pb, similar
314 to those observed in the polymetallic ore deposits hosted in the Altiplano-Puna.

315 The Puna region is also characterized by the presence of numerous hot springs (Pesce and
316 Miranda, 2003). Thermal waters are also natural sources of arsenic (Nordstrom 2002; Smedley
317 and Kinniburgh 2002; Howell et al., 2014). Despite only few studies measured As in the thermal

318 waters, some examples can be mentioned in the Argentinian Puna such as the hot springs near
319 San Antonio de Los Cobres (9,490 $\mu\text{g/L}$) (Hudson-Edwards and Archer, 2012) and in Vilama
320 (6,170 $\mu\text{g/L}$) (Peralta Arnold et al., 2017). El Tatio geothermal site in the Chilean Puna is also
321 well known by the high arsenic concentrations (45,000 – 50,000 $\mu\text{g/L}$) (Webster and Nordstrom
322 2003). There are no hot spring sites registered for the Lerma valley (Pesce and Miranda 2003).

323 *5.1.2. Chaco-Pampian plain*

324 All areas of the Chaco-Pampean plain are affected in different grade by the presence of As in
325 groundwater, especially the north-northwest and the center-south regions show the highest
326 concentrations (Nicolli et al., 2012). In the Chaco-Salteña plain (northern Chaco-Pampian plain),
327 limited by the Pilcomayo River in the North, the Salado river in the South, and the Paraguay and
328 Paraná rivers in the East (Fig. 1), As concentrations in groundwater vary from 10 to 800 $\mu\text{g/L}$
329 affecting the peri-urban and rural population (about 311,500 inhabitants). In the town of Taco
330 Pozo As concentrations in the blood of local inhabitants ranged from 9.1 to 11 $\mu\text{g/L}$ after a long-
331 term consumption of groundwater containing >200 $\mu\text{g/L}$ As (Nicolli et al., 2012). The aquifers
332 are hosted in superposed sequences of aeolian loess and fluvial sediments of Tertiary and
333 Quaternary ages. The geogenic source of arsenic are volcanic components present in the aeolian
334 loess and loessoid (reworked loess or loess-like deposits). In the Chaco-Pampean plain the
335 aeolian loess and loessoid cover an area of approximately 500,000 km^2 , with a thickness of 40 –
336 50 m making it one of the biggest sedimentary basin in the southern hemisphere for loessic or
337 loessoid sediments deposited during the Cenozoic (Zarate 2003).

338 The beginning of the loessoid sedimentation cycle has been related to a phase of Late Miocene
339 (~10 Ma) orogeny of the Andes resulting in the elevation of the Cordillera, which acted as a
340 barrier to moisture-laden Pacific winds (Zarate, 2003). According to Ramos (1999),

341 accumulations of synorogenic sediments several hundred meters thick, derived from erosion of
342 the uplifted Cordillera were deposited during the Late Miocene and the Pliocene. Loess
343 deposition was furthermore related to a multistage transport mechanism, involving fluvial and
344 aeolian processes with westerly and southwesterly wind directions, as dominant carriers of the
345 aeolian deposits (Zarate 2003). However, westerly tropospheric winds and northerly winds were
346 also important (Iriondo, 1990, 1997)

347 In the Lerma valley Lapiana et al. (2016) interpreted the lower section of Lumbrera Superior
348 Formation (Eocene-Oligocene) as a pre-Miocene sandy-loess. These deposits with participation
349 of volcanic ashes are located in the southern part of the valley and are thought to be related to the
350 first stage of a proto volcanic arc located to the west. There is not data of wells located in the
351 south area of the valley in this work (Fig. 3). However, in the As-risk map published by the
352 Secretariat of Water Resources, the concentration of As in this region show values <0.01 mg/L
353 (Hoyos, 2013). These Eocene-Oligocene loess sediments are probably deep in the stratigraphic
354 column of the valley, and the exploited groundwater only reaches the Quaternary aquifer
355 sediments. Regarding to the Miocene arsenic-rich loess (as known in the Chaco-Pampian plain),
356 there is no mention of its presence in the Lerma valley. This is probably related to the structural
357 and sedimentary evolution of the valley at that time. During the middle to upper Miocene, the
358 incorporation of the Lerma valley in the fragmented foreland basin established a very energetic
359 fluvial dynamics characterized by conglomeratic deposits of Guanaco and Piquete Formations
360 (Fig. 2 and Fig. 5). This environment was not favorable for the accumulation of thick successions
361 of silty material. This situation was maintained throughout the Pleistocene, when conglomerates
362 of the Calvimonte (conglomerates, sandstones and brown-reddish pellets), La Viña and
363 Portezuelo Formations were deposited (Gallardo et al., 1996). Only towards the end of the

364 Pleistocene (ca. 16 kyr) the sedimentation environment changed to a much less energetic one,
365 controlled by the partial closure of the drainage of the valley towards the foreland that made the
366 accumulation of fine material possible (Fig. 5). The northern Lerma valley is coated by silty-
367 sandy sediments with a variable thickness ranging from 2 to 4 meters, and developing soils and
368 representing the arable land of the region. These deposits were studied by García et al. (2019) in
369 the Carabajal farm (west of Rosario de Lerma town) (Fig. 1) obtaining AMS ¹⁴C ages ranging
370 between 9,593 to 10,176 years cal BP and correlating them with the loess of the Urundel
371 Formation (Iriondo, 1997). The stratum type of Urundel formation is located in the Chaco-
372 Salteña Plain with a maximum thickness of 16 meters and an age of 16 kyr (¹⁴C, Iriondo, 1990,
373 1997). It is composed of quartz (60/80%), hornblende, altered plagioclases, no volcanic glass
374 shards, and has an origin in the Bolivian Andes rocks during glaciations periods (Iriondo, 1990,
375 1997). In the Lerma valley the thickness of these fine deposits increases southwards. In the
376 extreme north of Finca Carabajal it is 2-3 meters thick including some soil levels, while in
377 Guachipas-La Viña area, it reaches 5-6 meters, and the original sedimentary structures (lake
378 environment) are better preserved. There is not data about the presence/absence of volcanic ash
379 or arsenic content for this new loess.

380 *5.2. Influence of weather, aquifer composition and granulometry, and groundwater* 381 *geochemistry*

382 The Lerma valley is characterized by a meso-thermal and sub-humid climate with dry season and
383 little annual change in temperature (Burgos and Vidal, 1951). The wet season occurs during the
384 austral summer from November to March. In contrast with the Chaco-Pampian plain and the
385 Puna regions with arid or semiarid regimes and a low annual rainfall and a high evaporation
386 (Nicolli et al., 2012; Tapia et al., 2019) The Lerma valley has an average annual precipitation

387 between 700-800 mm (Romero Oru  et al., 2017). Most of the recharge of the exploited aquifers
388 occurs due to infiltration of rainfall (Baudino, 1996). The infiltration of rainwater measured in La
389 Caldera aquifer in the North of the valley (where samples with < 0.01 mg/L of As were obtained)
390 is high > 60% and contribute to fresh water recharge (L pez, 2017). In The Chaco-Pampian plain
391 and the Puna, climate plays an important role, affecting dissolved As through evaporation during
392 the dry season (Nicolli et al., 2012; Tapia et al., 2019 this issue; Murray et al., 2019 this issue).
393 Moreover, in those regions, poorly drained flat plains, lowlands and closed depressions that
394 concentrate shallow unconfined groundwater, of form salars depressions, are affected by a slow
395 drainage and a delayed runoff, or closed systems making them preferential landforms for As-
396 accumulation (Nicolli et al., 2012, Tapia et al., 2019 this issue; Murray et al., 2019 this issue).
397 The conductivities of the groundwater (350 – 850 $\mu\text{s}/\text{cm}$), the pH (5.5 – 7.8), and the
398 composition of major ions ($\text{HCO}_3\text{-Ca-Mg}$ with normal evolution to $\text{HCO}_3\text{-Na}$) (Table 1, Fig. 4)
399 indicates that these groundwaters are little evolved as well as indicated by Baudino (1996) who
400 also suggest a little time of circulation and/or circulation by inert materials. In the Lerma valley,
401 the most productive levels of the multilayered aquifer are placed in Quaternary layers composed
402 of fine gravels and sands to fine sands Baudino (1996). The grain size favor high porosity,
403 permeability and circulation of the groundwater with medium to high transmissivity values
404 which implies low residence times (Table 3).

405 Another important fact for lowe As in groundwaters is that the aquifer sediments in the Lerma
406 valley have an origin in the erosion of the early to middle Cambrian basement composed of low
407 grade metamorphic rocks of the Puncoviscana Formation, the Cretaceous-Paleogene continental
408 strata with conglomerates, sandstones, mudstones and the limestones of the Salta Group rift with
409 a lack of geogenic arsenic sources (sections 5.1.1 and 5.1.2). An example of similar free arsenic

410 conditions can be observed in the Chaco-Pampean plain in some specific environments where
411 low As concentration in groundwater can be found. These natural free arsenic conditions are
412 created by the presence of fluvial sediments layers interbed in the aeolian loess deposits. The
413 fluvial sediments do not contain arsenic and contribute to higher porosity and permeability and
414 circulation of the groundwater. In the paleo-channels of the Cuarto river located in Córdoba
415 Province, Giacobone et al. (2018) describe a scarcely evolved groundwater of HCO₃-Ca to
416 HCO₃-Na type. These waters result from high velocities flows that circulate in coarse fluvial
417 sediments composed of inert mineralogy with low interaction time resulting in a low As (1 – 10
418 µg/L) concentrations in groundwater. In the south of Córdoba province, Becher Quinodoz and
419 Blarasin (2014) described fresh HCO₃-type groundwater in active dunes sediments that conform
420 a fluvial-aeolian environment linked to local flows with current precipitation recharge. In this
421 case, As concentrations are still above the limits for human consumption, but with lower values
422 than in the surrounding loessoid environments, where high concentrations of As are related to
423 brackish-salty groundwater (SO₄-Cl type), as the result of long existing regional flows and long
424 interaction time with the loess.

425 In the Lerma valley, even if sediments with As minerals in very small quantities were present in
426 the silty-sandy sediments comparable to Urundel Formation, the geochemical environment most
427 probably do not entirely contribute to put As in solution. If volcanic glass with As were present
428 in the loess, the pH range of the groundwater (5.5 – 7.8) is not high enough to favor the
429 processes of dissolution of volcanic glass and As leaching as described in the Chaco-Pampian
430 plain where groundwaters with pH from near 7.00 up to 9.24 favor that process (Nicolli et al.,
431 2012).

432 Moreover, under the circum-neutral pH of the Lerma valley groundwater if As is present, it is
433 favorable adsorbed onto the surface of Al- Fe- and Mn-oxides and hydroxides (such as hematite,
434 goethite, $\text{Fe}(\text{OH})_3(\text{a})$, magnetite, and gibbsite) that could precipitate in the aquifer and be
435 removed from groundwater. In the Chaco-Pampian plain the oxidation-reduction (redox)
436 potential phenomena is observed as mechanism of regulation of As concentration (Nicolli et al.,
437 2012). There is no data of redox potential for the compiled samples of the Lerma valley, which is
438 of high importance to understand the mobility of As. In the case of oxidative conditions, which is
439 most likely possible in the coarse productive layers, As sorption processes by secondary Al- Fe-
440 and Mn-oxides and hydroxides minerals will be enhanced. However, coarse aquifer materials
441 have less surface area for adsorbing arsenic, and thus less arsenic available for potential
442 mobilization (Erickson and Barnes, 2005). If As is present in the loess sediments of the Lerma
443 valley (i.g. the loess comparable to Urundel Formation) and groundwaters were under reductive
444 conditions, the release of As to groundwater could be favored via reductive dissolution of metal
445 hydroxides and reductive desorption. This process has been observed in the fine sediments
446 aquitards layers of the multilayered glacial aquifers described by Erickson and Barnes (2005);
447 Thomas et al. (2008); and Nicholas et al. (2017) in the Northeast of United States. However, in
448 these environments, arsenic was also observed to be removed from groundwater by precipitation
449 of sulfide minerals, which occurs under sulfate-reducing conditions (Thomas et al., 2008). All
450 these examples show that oxidation-reduction (redox) potential is an important factor to have in
451 account to understand As mobility, and should be analyzed with more detail in the Lerma valley.

452 Finally, the characteristics of the wells construction with several screens situated in the coarse
453 sediments layers can also favor to low As concentration in the Lerma valley. That is the case in
454 multilayered glacial aquifers where construction practices such as exploiting a thick, coarse

455 aquifer and installing a long well screen yield good water quantity for public water system wells
456 (Erickson and Barnes, 2005). Moreover, in that environment wells with long screens set at a
457 distance from an upper confining unit are at lower risk of exposure to geochemical conditions
458 conducive to arsenic mobilization via reductive mechanisms such as reductive dissolution of
459 metal hydroxides and reductive desorption of arsenic. Exploiting the coarse sediments in the
460 Lerma valley seems to ensure extraction of the good quality groundwaters. However, the wells
461 with higher As values of 0.01 and 0.02 mg/L (wells 25 and 68) could indicate that may exist
462 groundwater with higher As content (released either by local higher pH or reductive conditions).
463 Therefore, a better understanding of the redox conditions, mineralogy and geochemistry of the
464 sediments (i.e. the loess present in the Lerma valley) and a better correlation between the wells
465 characteristics and the exploited levels will be necessary to understand the processes that
466 increase As concentrations in the mentioned wells.

467 *5.3. Other similar intermountain valleys in Northwest Argentina*

468 Low As concentrations in surface and groundwaters are also reported in the Sub Andine valleys
469 located to the north of the Lerma valley in the Cordillera Oriental and Subandinas geological
470 provinces where As range between 6 – 10 µg/L (de Sastre et al., 1992; Farías et al., 2009). Some
471 examples are Las Maderas, Los Alisos, and La Cienaga dams; groundwater in Jujuy and Palpalá
472 cities; and Xibi-Xibi, Perico, and del Molvado rivers (Farías et al., 2009). Even though
473 Cordillera Oriental and Subandinas geological provinces have different structural and
474 geomorphological characteristics, their intermountain valleys share similar conditions for the
475 deposition of Mid-late Miocene to Quaternary sediments (Ramos, 2017). Further understanding
476 of the natural processes that have created these natural reservoirs of low As concentration and
477 how similar or different are with respect to the Lerma valley is necessary.

478 **6. Conclusion**

479 The concentrations of As in Lerma valley are within the recommended values for drinking water
480 in Argentina (0.05 mg/L) and are remarkably lower in comparison to the Puna and the Chaco-
481 Pampian plain surrounding regions. Low As concentration in the groundwater of the Lerma
482 valley can be attributed to a combination of natural processes related to the geochemistry of
483 groundwater (mainly HCO₃-Ca type, near neutral pH, and most probably oxidative conditions),
484 the absence of the typical geogenic sources (Cenozoic volcanism, sulfide deposits, thermal water
485 sources, and the rich-As volcanic ash Miocene loess), high fresh rain water infiltration rates, low
486 residence times, and the characteristics of the wells construction (with screens settled in coarse
487 inert sediments layers). The absence of the Mio-Pliocene loess was favored by the high-energy
488 sedimentary environments that characterized this region during that time. However, a better
489 understanding of the redox conditions, mineralogy, and geochemistry of the sediments (i.e. the
490 loess present in the Lerma valley) with a better correlation between the wells characteristics will
491 be necessary to understand the wells with the higher As values (0.01 and 0.02 mg/L). The
492 geological, geochemical, and tectonic characteristics of the Lerma valley could be extrapolated
493 to other similar valleys in NW of Argentina such as the Cordillera Oriental and Subandinas
494 geological provinces. In the context of increasing population, and demand of water resources, a
495 better understanding of the natural processes that create reservoirs for groundwater of good
496 quality can be useful as an exploration tool. This is of high importance in territories with high As
497 concentration in groundwater such as Argentina.

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504 **Author Contributions**

505 JM, redacted the manuscript and contributed to the interpretation, discussion of the data, and
506 figures confectioning. MRO and EML contributed to the obtainment and classification of data,
507 figures confectioning, and discussion. VG and AK contributed to the discussion and conclusion
508 sections of the manuscript.

509 **Conflict of Interest**

510 The authors declare no conflicts of interest

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721

722 Figure captions

723 Fig. 1. Areas with high arsenic content in South America (Bundschuh et al., 2012) and the
724 location of the Lerma valley.

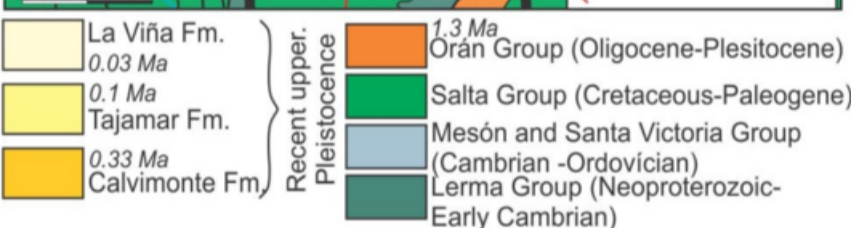
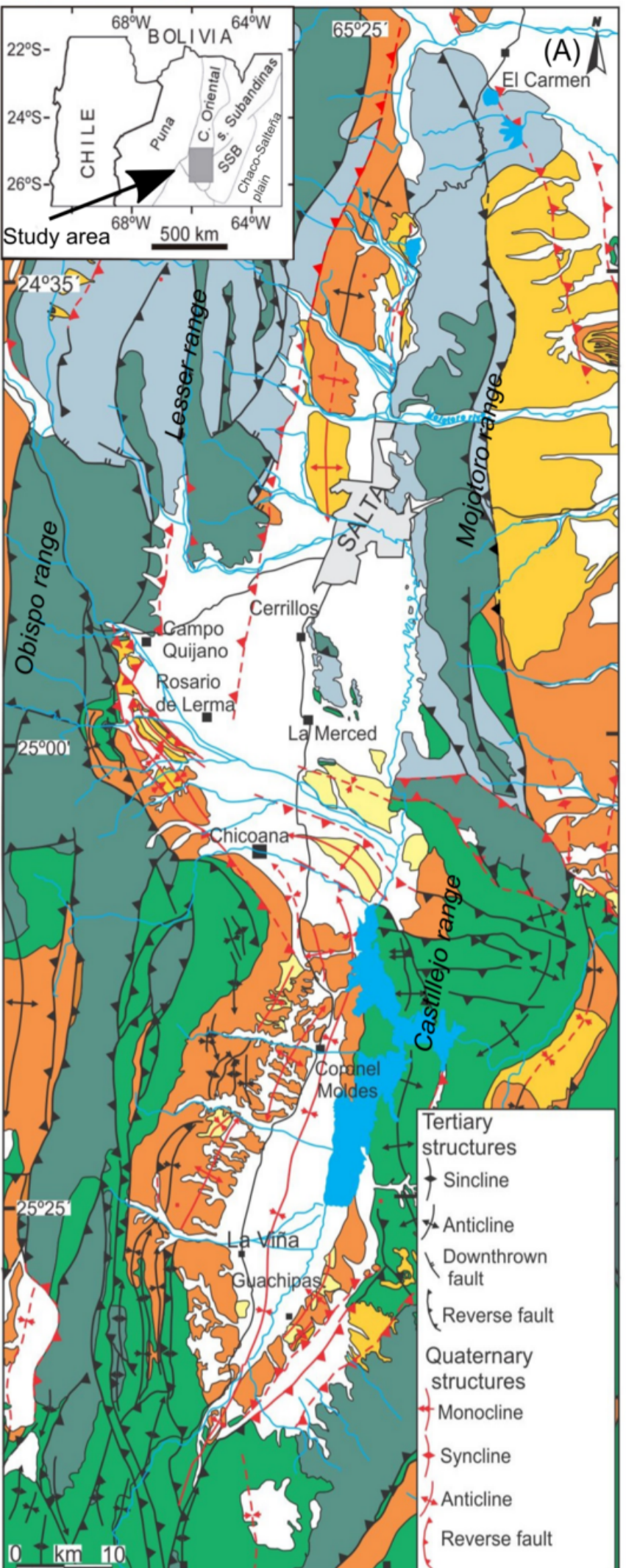
725 Fig. 2. (A)- Geological map of the Lerma valley. (B)- Stratigraphic column with a detail of the
726 Cenozoic in the Lerma valley, modified from Barrientos et al. (2018).

727 Fig. 3. Arsenic concentrations in surface and groundwaters of the Lerma valley.

728 Fig. 4. Piper diagram for surface and groundwaters of the Lerma valley.

729 Fig. 5. Schematic overview of the tectonic evolution and sedimentation dynamics
730 from the Miocene to the Quaternary in the Lerma valley. Adapted from Hain et al. (2011).





Period / Epoch		Stratigraphic unit	Lithology
Quaternary	Holocene	Portezuelo Fm.	Accumulation of sand, pelites and gravels. Unbound sediments.
	Pleistocene	La Viña Fm.	
		Tajamar Fm.	
Neogene	Pliocene	Orán Group	Piquete Fm.
			Guanaco Fm.
	Miocene		Anta Fm.
	Rio Seco Fm.		
Paleogene	Oligocene	Salta Group	Lumbrera Fm.
	Eocene		

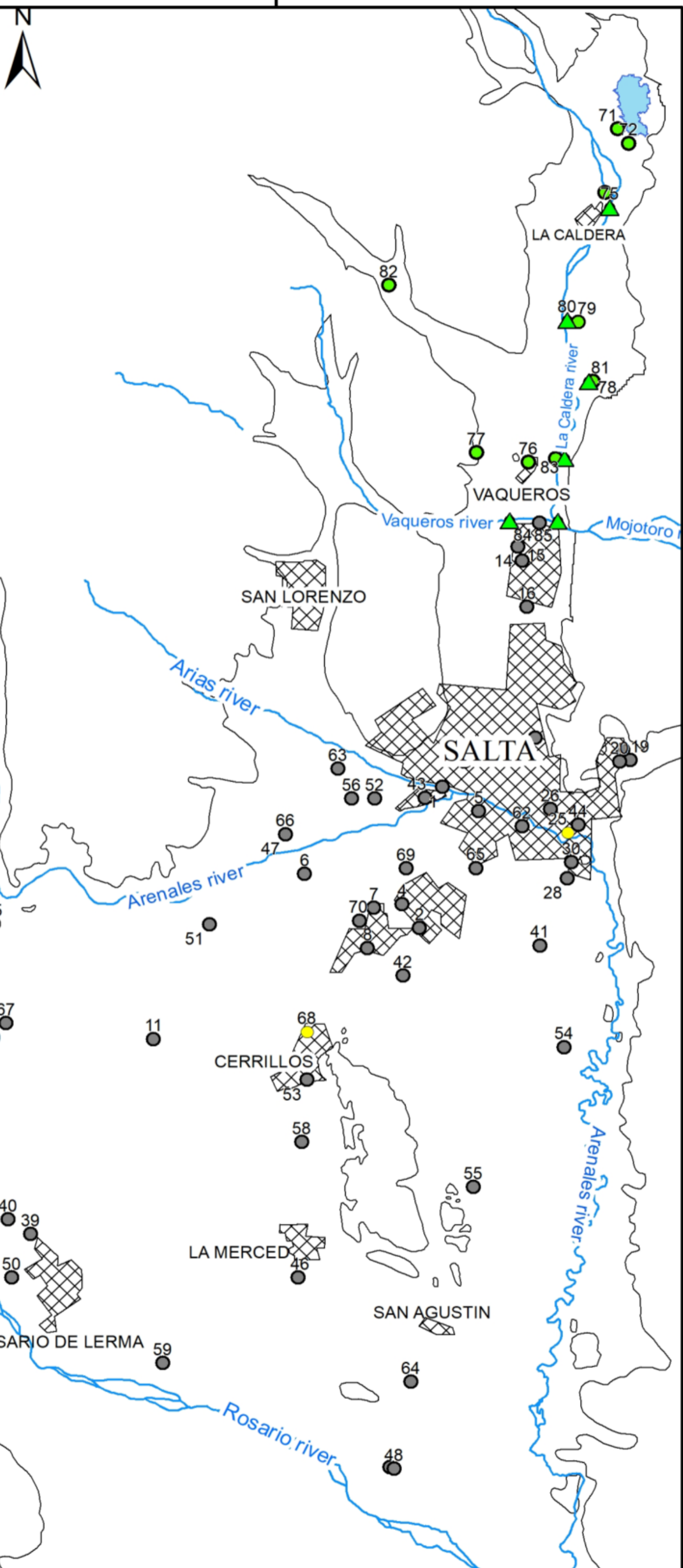
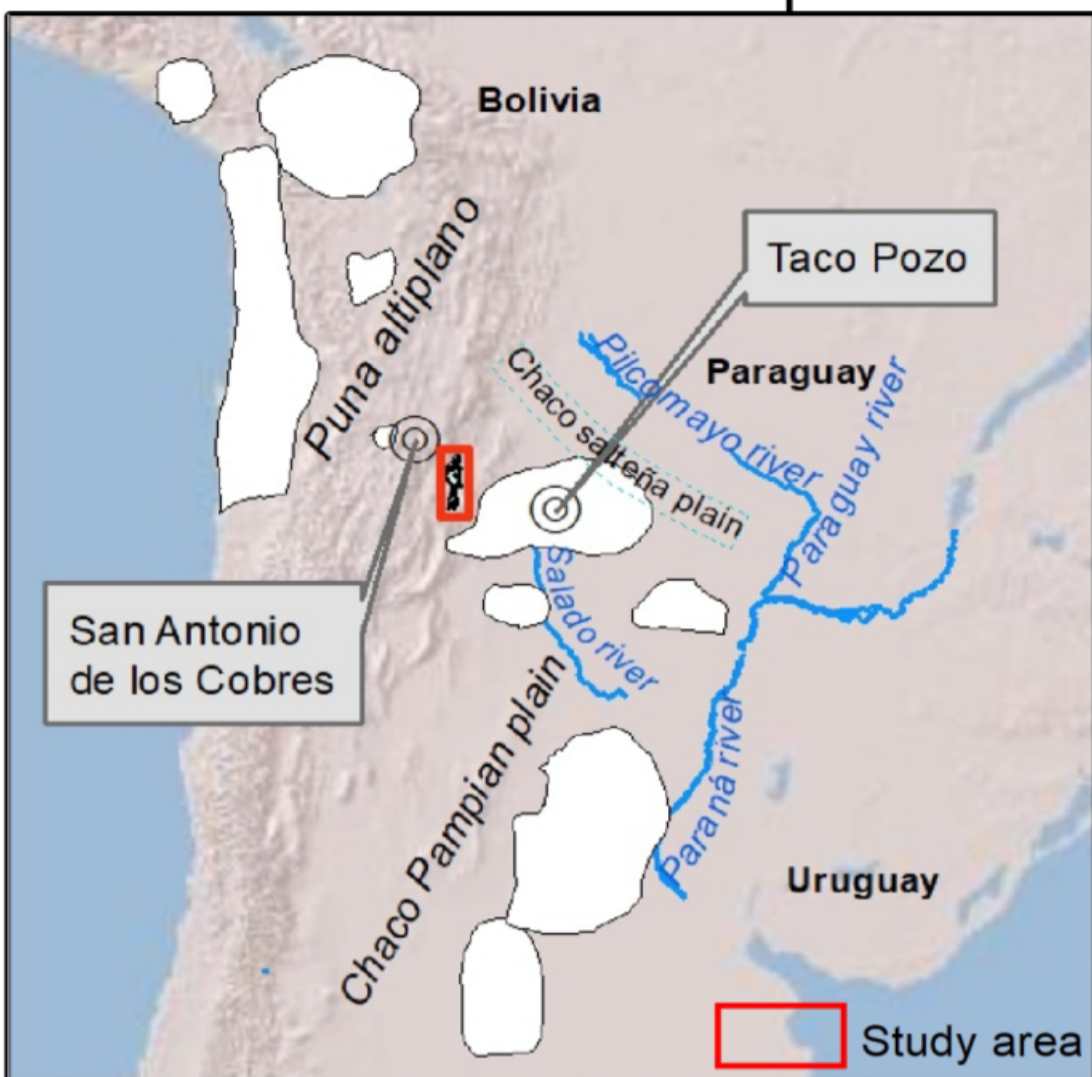
(B)

References



65°40'0"O

65°30'0"O



Legend

- Rivers
- Urban areas
- Limit of Lerma valley
- Dams
- Surface water sample
- Groundwater sample

As concentration (mg/L)

- < 0.010 mg/L
- 0.010 - 0.050 mg/L
- > 0.050 mg/L
- below detection limits



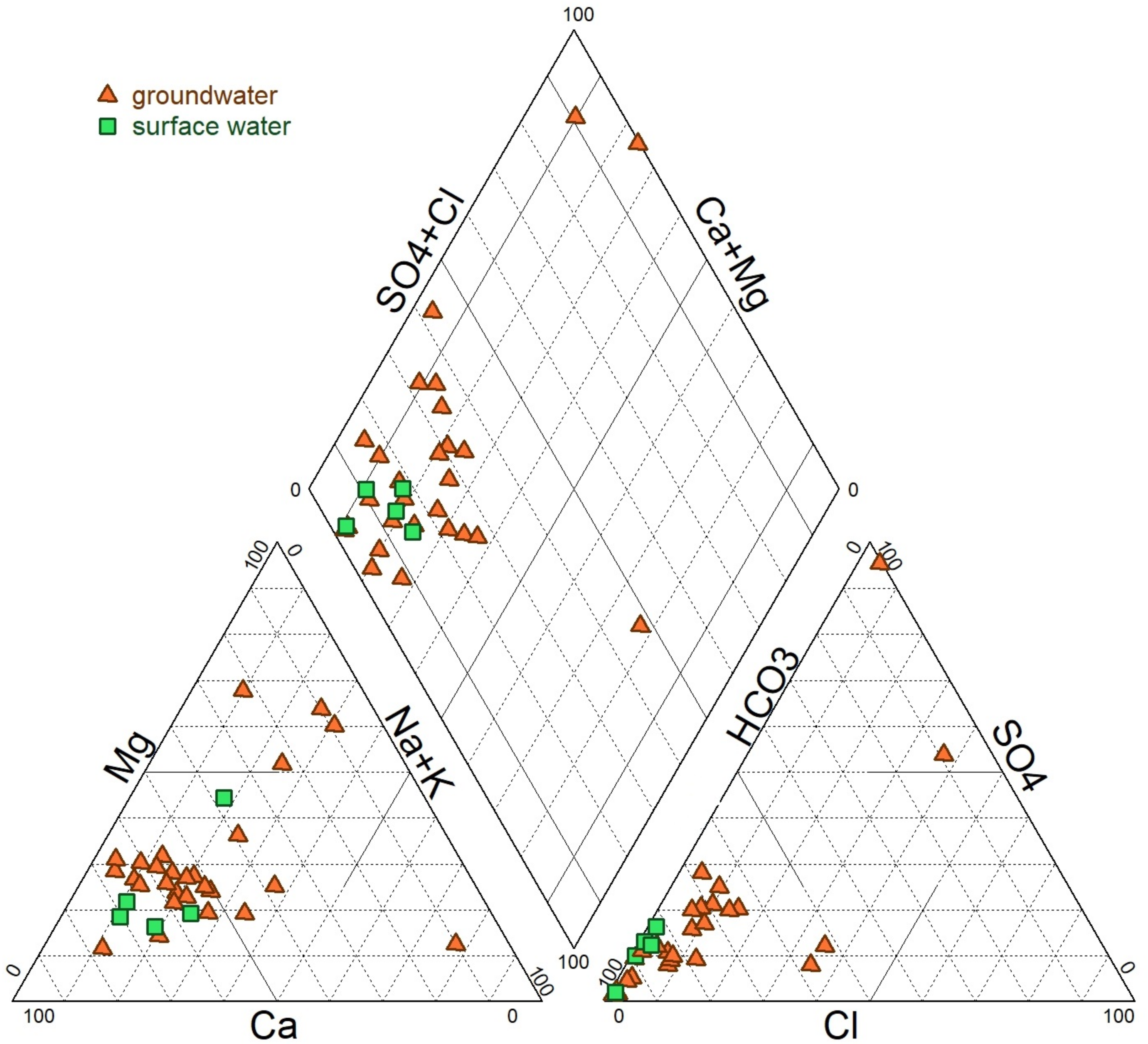
65°40'0"O

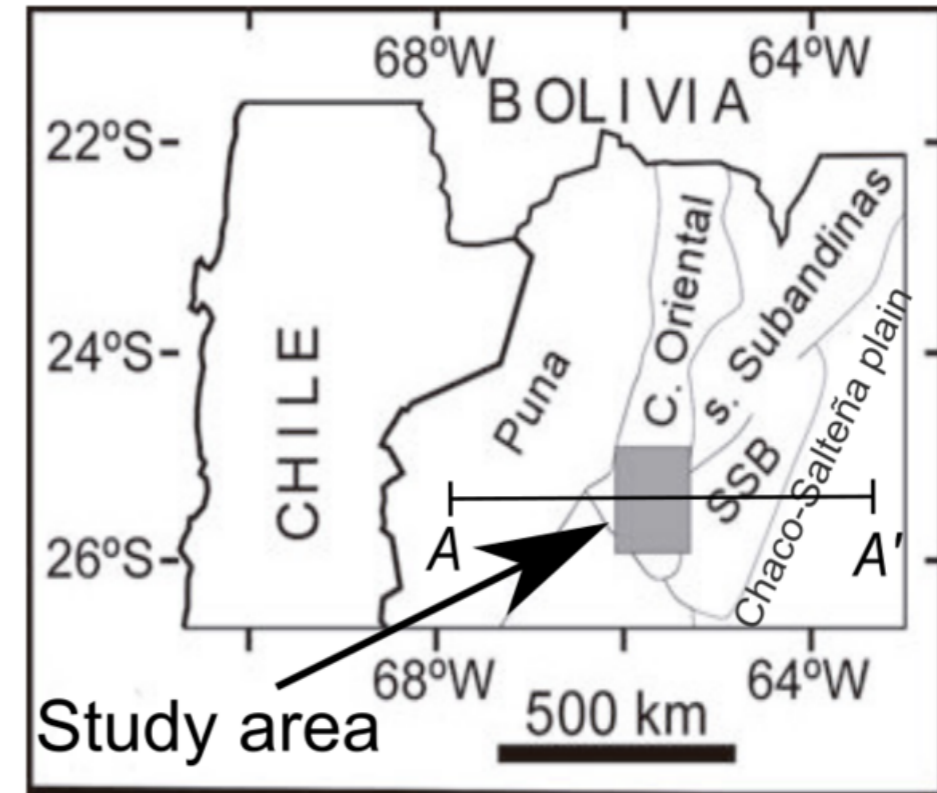
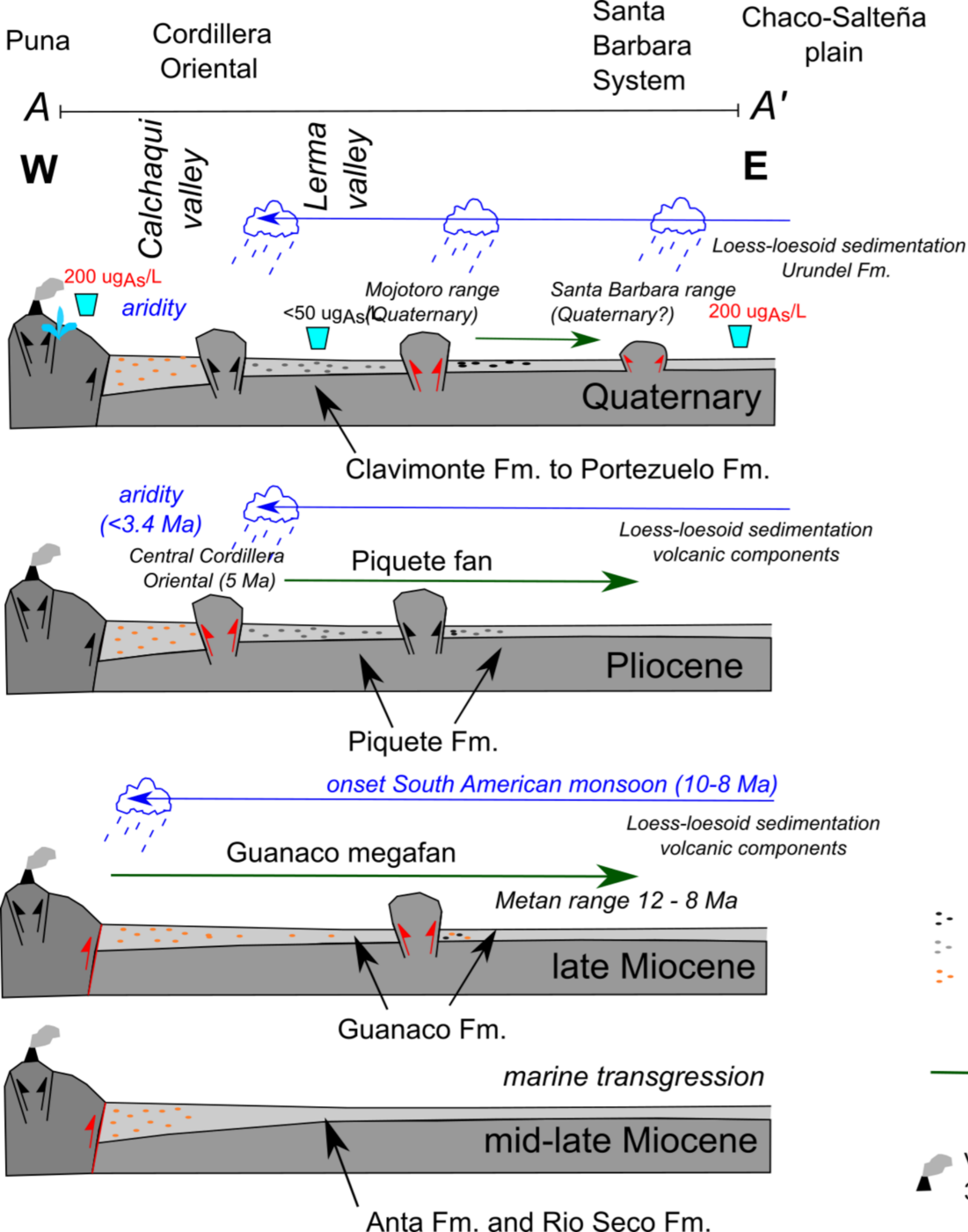
65°30'0"O

25°0'0"S

25°0'0"S

Piper diagram





- Source of conglomerates
- - Cordillera Oriental / Santa Barbara system
 - - Cordillera Oriental
 - - margin Puna
- alluvial / fluvial fan systems
- Hot springs (9,490 ug_{As}/L)
- <50 ug_{As}/L As content in drinking water
- ▲ Volcanism in the Puna
- 351 mg_{As}/kg in Miocene - Pliocene fluvial sediments (volcanic sources)

Table 1. List of water samples compiled and obtained in this study. Location, pH, conductivity and As concentrations.

Origin of data	n	Type of sample	Date	Latitude (S)	Longitude (W)	Static level of well	pH	Conductivity	As
				decimal degrees	decimal degrees	mbgs		µs/cm	mg/L
<i>Aguas del Norte</i>	1	well	2016	248,053	654,367	-	7.15	298	<0.015
	2	well	2016	248,553	654,451	-	7.15	314	<0.015
	4	well	2016	248,469	654,517	-	7.21	309	<0.022
	5	well	2016	248,138	654,231	-	7.21	319	<0.022
	6	well	2016	248,363	654,881	-	7.32	324	<0.022
	7	well	2016	248,482	654,622	-	7.4	303	<0.015
	8	well	2016	248,626	654,645	-	7.25	351	<0.027
	11	well	2016	248,949	655,445	-	7.1	201	<0.022
	14	well	2016	247,201	654,088	-	7.36	280	<0.015
	15	well	2016	247,251	654,073	-	7.44	262	<0.015
	16	well	2016	247,413	654,054	-	7.5	265	<0.031
	17	well	2016	247,876	654,020	-	6.9	524	<0.035
	18	well	2016	247,920	653,694	-	7.29	668	<0.022
	19	well	2016	247,955	653,665	-	7.64	830	<0.031
	20	well	2016	247,960	653,704	-	7.38	679	<0.031
	21	well	2016	247,963	654,286	-	6.94	535	<0.028
	25	well	2016	248,213	653,897	-	7.15	331	0.022
	26	well	2016	248,130	653,962	-	7.04	253	<0.017
	28	well	2016	248,375	653,897	-	7.46	264	<0.022
	30	well	2016	248,318	653,884	-	7.2	258	<0.022
39	well	2016	249,641	655,902	-	7.9	304	<0.026	
40	well	2016	249,590	655,987	-	7.88	386	<0.015	
<i>Secretariat of Water Resources</i>	41	well	2008	248,613	653,999	22	7.34	265	<0.015
	42	well	2009	248,722	654,511	56	7.2	275	<0.01
	43	well	2009	248,091	654,432	32	6.5	310	<0.01
	44	well	2009	248,185	653,858	22	7.23	621	<0.015
	45	well	2010	248,543	656,046	11	6.82	186.5	<0.01
	46	well	2010	249,793	654,900	60	7.03	386	<0.01
	47	well	2015	248,222	654,953	12	7.3	495	<0.03
	48	well	2010	250,468	654,538	49	7.21	457	<0.002
	49	well	2017	248,894	655,996	85	7.2	350	<0.02
	50	well	2011	249,795	655,972	114	7.61	385	<0.01
	51	well	2011	248,543	655,237	37	7.38	281	<0.002
	52	well	2011	248,094	654,619	46	7.79	226.5	<0.01
	53	well	2011	249,092	654,870	30	7.15	343	<0.01
	54	well	2011	248,972	653,908	10	7.24	304	<0.002
	55	well	2012	249,469	654,244	15	7.32	304	<0.002
	56	well	2012	248,096	654,706	73	7.1	304	<0.002
	58	well	2012	249,312	654,887	41	7.81	-	<0.01
	59	well	2013	250,097	655,405	52	7.75	-	<0.02
	60	well	2013	247,117	654,009	42	7	314.7	<0.015
	62	well	2013	248,191	654,068	31	7.3	254	<0.015
63	well	2013	247,990	654,758	56	7.14	230	<0.002	
64	well	2014	250,160	654,474	34	6.4	386	<0.01	
65	well	2015	248,340	654,240	33	6.55	160	<0.01	
66	well	2015	248,222	654,953	12	7.3	495	<0.03	
67	well	2017	248,895	655,996	85	7.2	350	<0.02	
68	well	2011	248,922	654,870	26	-	310	0.01	
69	well	2011	248,342	654,502	43	6.61	229.5	<0.01	
70	well	2012	248,528	654,675	58	7.78	279	<0.002	
<i>This study</i>	71	well	2010	245,719	653,723	8.9*	6	147.5	0.002
	72	well	2010	245,770	653,681	9.0*	6.5	287	0.001
	73	well	2010	245,944	653,768	9.0*	7	376	0.001
	74	well	2010	246,888	653,948	5.75*	6	265	0.0001
	75	La Caldera river	2010	245,998	653,752	-	7	226	0.0004
	76	well	2010	246,901	654,051	16.3*	6.5	447	0.001
	77	well	2010	246,868	654,245	11.0*	6.5	258	0.003
	78	well	2010	246,612	653,811	8.0*	6	280	0.001
	79	well	2010	246,404	653,866	8.8*	7	223	0.001
	80	La Caldera river (La Calderilla site)	2010	246,398	653,908	-	7	193	0.001
	81	un-named stream	2010	246,614	653,825	-	5.5	233	0.004
	82	well	2010	246,276	654,575	6.0*	8.4	600	0.0004
	83	Wierna and La Caldera rivers confluence	2010	246,888	653,915	-	6.5	232	0.001
	84	Vaqueros river	2010	247,109	654,119	-	6	104.3	0.0004
	85	La caldera and Vaqueros rivers confluence	2010	247,110	653,939	-	6	105.2	0.001

mbgs = meters below ground surface

*Phreatic level in well

Table 2. Composition of major ions in groundwater and surface water of the Lerma valley.

Origin of data	n	Type of sample	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	Cl mg/L	HCO ₃ mg/L	SO ₄ mg/L	NO ₃ mg/L
<i>Aguas del Norte</i>	1	well	33	2.2	-	-	11	-	bdl	11.2
	2	well	20	2.2	-	-	15	-	bdl	13.2
	4	well	20	0.9	-	-	7	-	bdl	14.2
	5	well	28	1.3	-	-	17	-	36	15.1
	6	well	19	1.2	-	-	10	-	bdl	12.2
	7	well	17	1.7	-	-	5	-	bdl	9.7
	8	well	12	2.5	-	-	10	-	bdl	23.1
	11	well	15	0.6	-	-	4	-	bdl	5.8
	14	well	13	2.2	-	-	5	-	bdl	3.6
	15	well	13	1.9	-	-	3	-	bdl	2.7
	16	well	33	1.6	-	-	8	-	bdl	2.7
	17	well	47	3.6	-	-	25	-	bdl	28.4
	18	well	74	7.1	-	-	33	-	57	26.2
	19	well	99	3.7	-	-	38	-	44	34.6
	20	well	111	6.4	-	-	34	-	43	35.6
	21	well	35	2.8	-	-	32	-	bdl	24.1
	25	well	22	2	-	-	15	-	bdl	4.7
	26	well	25	2.1	-	-	10	-	bdl	9.8
	28	well	21	1.1	-	-	12	-	bdl	4.5
	30	well	20	1.1	-	-	11	-	bdl	3.9
39	well	23	2.7	-	-	15	-	bdl	6.3	
40	well	25	3	-	-	10	-	bdl	5	
<i>Secretariat of Water Resources</i>	41	well	29.33	1	-	-	5	-	23	bdl
	42	well	15	1.9	29.6	7	bdl	153	bdl	8.1
	43	well	32.5	1.3	25.9	12.4	-	168.36	26	bdl
	44	well	85	4	-	-	56	-	47	45.3
	45	well	8	2	24	6	5	109	11	bdl
	46	well	14	4	49	15	14	175	52	10
	47	well	37	4.7	32	11	3.5	-	11	bdl
	48	well	5	0.37	56	14.55	14.1	262	19.6	1.96
	49	well	15	2.4	4.3	17	15	160	15	bdl
	50	well	19	4	48	12	15	183	44	12
	51	well	4.5	0.37	27	8.2	3.5	95	31	1.35
	52	well	18	4	24	6	8	121	20	bdl
	53	well	17	3	41	13	11	170	38	bdl
	54	well	4.8	0.21	28	7.14	7.1	129	11.1	1.59
	55	well	2.4	2.4	52	15.08	31.8	90	10	1.35
	56	well	104	2.8	12	9	39	99	18	0.04
	58	well	16.4	2.22	36	65.41	30	13	59	bdl
	59	well	15	2	63	21.7	30	220	54.4	1.14
	60	well	39	3.3	-	-	15.7	-	35.7	3.1
	62	well	20	1	-	-	12	-	20	2.9
63	well	6.17	0.36	9	5	1.77	0.27	53.44	0.45	
64	well	24.8	2.6	51.8	11.8	10.3	-	21.3	5.9	
65	well	26.8	0.57	21.8	29.6	23	195	46	0.04	
66	well	37	4.7	32	11	3.5	-	11	1	
67	well	15	2.4	4.3	17	15	160	15	45	
68	well	12	2	41	11	10	179	17	bdl	
69	well	20	4	20	8	6	117	25	bdl	
70	well	17	1.5	31	9	12	145	27	0.04	
<i>This study</i>	71	well	9.34	1.67	17.6	3.9	1.33	82.96	3.73	nd
	72	well	11.5	3.76	35.2	7.81	2	156.16	5.94	4.23
	73	well	9.62	1.93	64	5.86	1.19	214.72	2.57	nd
	74	well	7.75	1.66	35.2	10.74	0.83	146.4	12.11	2.01
	75	La Caldera river	5.68	1.34	35.2	6.83	0.66	131.76	11.44	nd
	76	well	23.9	1.46	46.4	13.66	7.84	287.92	32.68	22.5
	77	well	10.6	4.64	36.8	4.88	1.39	141.52	1.95	nd
	78	well	10.9	4.04	32	9.76	1.42	141.52	13.92	6.13
	79	well	5.61	1.71	32	7.81	0.63	117.12	2.24	3.5
	80	La Caldera river (La Calderilla site)	5.66	1.7	36.8	5.86	0.82	117.12	1.94	nd
	81	un-named stream	9.7	2.46	25.6	6.83	1.27	102.48	13.87	5.23
	82	well	14.6	1.97	103	5.2	13	nd	93	3.1
	83	Wierna and La Caldera rivers confluence	9.62	1.69	32	4.88	1	165.92	19.83	nd
	84	Vaqueros river	4.69	0.81	9.6	6.83	0.68	58.56	9.13	4.75
	85	La caldera and Vaqueros rivers confluence	4.22	0.75	9.6	1.95	0.75	43.92	5	4.6

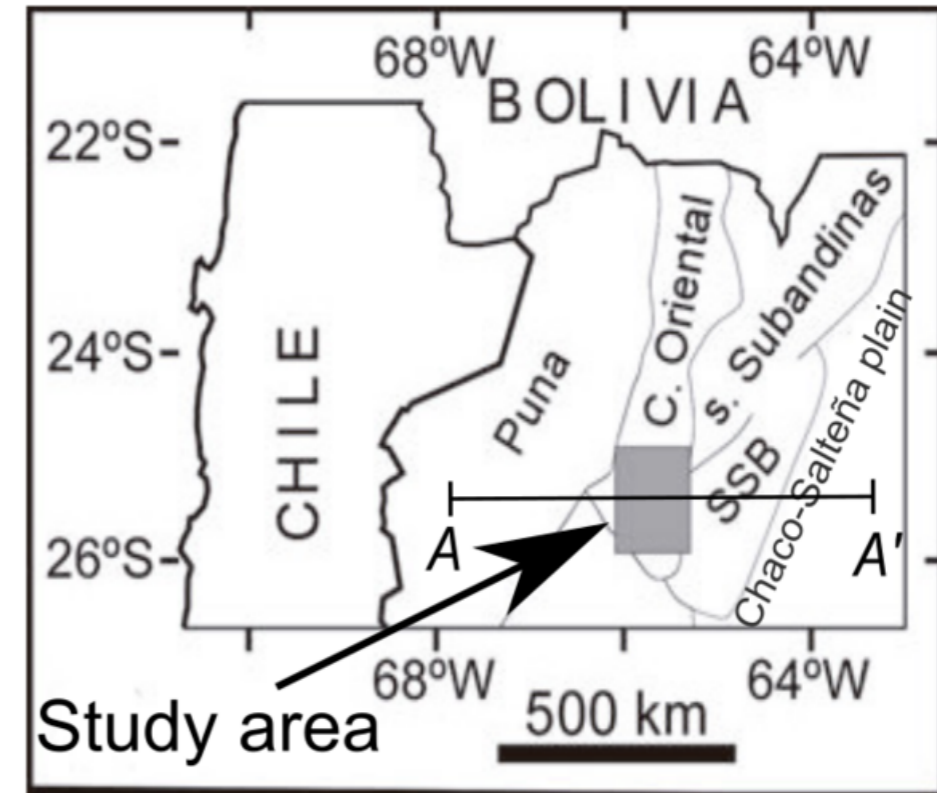
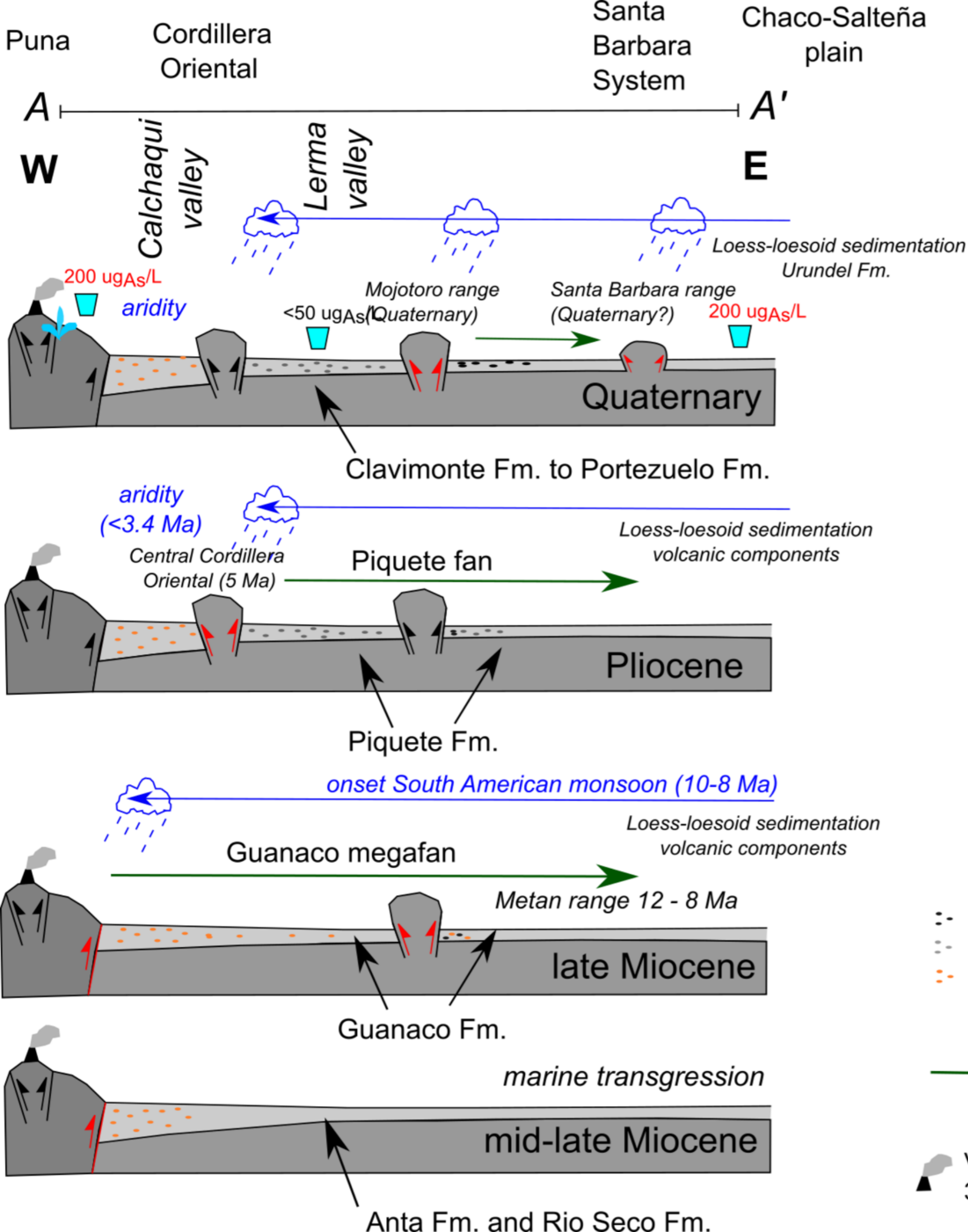
*nd = not determined**bdl = below detection limit*

Table 3. Depth of the drilled wells, lithology of the productive layers (in screen sites), and transmissivity of the wells.

Source of data	n	Type of sample	Depth of well mbgs	Lithology of the productive layers (in screen sites)	T ^a m ² /day
<i>Secretariat of Water Resources</i>	41	well	255	fine-medium gravel, coarse sand	110.9
	42	well	255	coarse-medium sand, fine gravel	108.6
	43	well	186	-	50.5
	44	well	160	coarse gravel, medium-fine sand	23.8
	45	well	89	fine gravel with medium-coarse sand	2.3
	46	well	150	medium-coarse sand	124.1
	47	well	71	coarse-medium sand, fine gravel	0.58
	48	well	101	coarse gravel, medium-fine gravel, fine sand	106.6
	49	well	202	Gravel with sandy matrix	81.4
	50	well	205	conglomerate	96.5
	51	well	123	coarse-medium sand, interbed gravels	0.2
	52	well	140	coarse-medium sand, fine gravel	16.2
	53	well	83	fine-medium gravel, coarse sand	200.8
	54	well	174	coarse gravel, medium-fine gravel	65
	55	well	90	fine gravel with medium-coarse sand	69.2
	56	well	195	coarse gravel, medium sand with fine gravel	7.4
	58	well	115	coarse gravel	371.5
	59	well	143	medium-coarse gravel	36.5
	60	well	117	boulders, coarse gravel, coarse sand	3.3
	62	well	242	boulders, coarse sand, medium sand	31.7
	63	well	120	boulders, medium sand, coarse gravel	1.7
	64	well	196	Conglomerates, sand, coarse sand	142
	65	well	260	coarse gravel, fine gravel, boulders	181.5
	66	well	71	fine-medium gravel, sand gravel	0.6
	67	well	202	gravel, sand	81.4
	68	well	143	fine-medium gravel, coarse sand	31.8
	69	well	183	-	38.1
	70	well	252	-	89.7

^a Transmissivity of the well

mbgs = meters below ground surface



- Source of conglomerates**
- - Cordillera Oriental / Santa Barbara system
 - - Cordillera Oriental
 - - margin Puna
- alluvial / fluvial fan systems**
- Hot springs ($9,490 \mu\text{gAs/L}$)**
- $50 \mu\text{gAs/L}$ As content in drinking water**
- Volcanism in the Puna**
 351 mgAs/kg in Miocene - Pliocene fluvial sediments (volcanic sources)