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

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Abstract

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

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

1. Introduction

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

The origin of As in these environments is linked to geogenic sources derived from Andean orogeny and volcanism, a large scale geological processes affecting in some level most of the Argentinian territory. Only in the Chaco-Pampian plain approximately 2 - 8 million inhabitants are potentially affected by As (Nicolli, 2012). Here, the origin of As (and fluorine) in the groundwater is related to the leaching of volcanic components present in the loess sediments with important quantities of volcanic glass, volcanic minerals and volcanic lithic fragments (Nicolli et al., 2012). Consequently, HACRE develops, sometimes associated with dental and/or skeletal fluorosis. In the Altiplano-Puna plateau, As is found in most of the water types of the region (i.e. groundwater, rivers, lakes, brines, salines, thermal waters, and acid mine drainage) indicating multiple natural (volcanic-mineralogical-geothermal) and anthropogenic origins for As (Murray et al., 2018). San Antonio de Los Cobres town (located 250 km to the west of the Lerma valley) is an emblematic case where As concentrations measured in drinking water are around 200 µg/L.

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

This study focuses on the Lerma valley the easternmost intermontane basin of the Cordillera Oriental geological province. The Cordillera Oriental is situated in northwestern Argentina, lying between the Altiplano-Puna plateau and the Chaco-Pampean plain (Fig. 1). The groundwater of the Lerma valley which is the main source of drinking water, has been qualified as good quality (Baudino 1996). The largest urban area corresponds to the city of Salta, located in the northern part of the valley with more than 600.000 inhabitants. It is the capital of the homonymous province and corresponds to the seventh most populated city in Argentine (Argentinian National Census, 2010). Smaller rural towns of the Lerma valley which also consume groundwater are Vaqueros, Rosario de Lerma, Campo Quijano, Cerrillos, La Viña (Fig. 1). The major threatsto groundwater quality are related to urban contamination (Rocha and Baudino, 2002), overexploitation of the aquifers, and in some areas (Arenales Aquifer) anthropogenic contamination with boron, with values that reach 3 mg/L (Bundschuh et al., 1994). Low As concentrations in the Lerma valley groundwaters are described by de Sastre et al. (1992). The authors highlighted the difference with the Puna and the Chaco-Salteña plain (North area of the Chaco-Pampian plain, Fig. 1) where high As concentration in groundwater can be found. In the As-risk map published by the Secretariat of Water Resources of Salta province (Secretaría de Recursos Hídricos), low As concentrations for the Lerma valley are also observed (Hoyos, 2013). Moreover, a study of metabolism of inorganic As in children comparing the villages of San Antonio de los Cobres (Altiplano-Puna plateau), Taco Pozo (Chaco-Pampean plain) and Rosario de Lerma (Lerma valley), highlight the difference in As concentrations and health effects among the regions (Concha et al., 1998). The group of children from Rosario de Lerma was selected as a reference group due to their low As intake (0.65 µg/L of As in drinking water), while children form San Antonio de los Cobres, and Taco Pozo (>200 µg As/L in drinking water), had the highest concentration of As in blood and urine ever recorded for children (on average 9 µg/L for blood, and 380 µg/L for urine) (Concha et al., 1998).

The aim of this study is to analyze possible geological, structural, sedimentary, hydrological and geochemical, processes that favor low As concentrations in the Lerma valley in a regional context of high As. n order to attain that goal, local and regional factors and processes are analyzed. Among them, the existing data related to the aquifer composition, the origin of the sediments, the geological and structural evolution of the valley, the hydraulics of the aquifer, and the geochemical characteristics of groundwaters. A map of As concentrations in the Lerma valley with data provided by different government offices and from our own sampling work is also presented. In the world-wide context of increasing population, and demand of water resources, this work highlights the importance of a better understanding of the natural processes that create conditions and reservoirs where good quality of groundwater can be found. This is of high importance in territories such as Argentina with extended regions of high arsenic in groundwater.

2. Geological setting

2.1. Stratigraphy of the Lerma valley

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

2.2. Location and formation of the Lerma valley

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

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

2.3. Aquifer systems in the Lerma valley

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

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

3. Methodology

3.1. Data compilation

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

3.1.1 Aguas del Norte company

This company (public and private capital) is the provider of the drinking water and sanitation service of the Salta province. The data obtained correspond to twenty-two (22) well samples of the period 2016 (Table 1). The chemical analyses for As, K, and Na were performed in their own laboratories with ICP-OES (Inductively coupled plasma - optic emission spectroscopy). The detection limits for As were variable according to the calibration curves between <0.015 and <0.035 mg/L. For these samples, Ca, Mg, and HCO_3 were not analyzed.

3.1.2. Secretariat of Water Resources

The Secretariat of Water Resources is the water resources control agency in Salta Province. The company Merco Aguas, performs the well drilling service. The chemical analyses obtained from this source comprises twenty-eight (28) water samples taken between the periods 2008 to 2017 from the wells (Table 1). Data of the wells (depth, static level of well, granulometry of the productive layers) was also compliled (Table 1 and 3). Each performed well has between 4 and 11 screens. The screens were mainly situated in the coarse sediments layers of the multilayered aquifer that were qualitative described during drilling (Table 3). The transmissivity (T) of the wells (Table 3) were calculated in this study with the information of the technical reports of each well using the Jacob method (Cooper and Jacob, 1953). At each well, the chemical analyses correspond to the mix of waters from the different productive layers where the screens were situated (Table 1 and 2). The water analyses were performed in different external laboratories. The method used for As analysis was spectrophotometry with a detection limit of 0.05 mg/L. This detection limit could be considered high, since the recommended value by the WHO is 0.01 mg/L (WHO, 2017). However, it is in the range for local analyses since the permitted value for drinking water in Argentina is 0.05 mg/L (CAA, 2012). Major ions were measured with AAS (Atomic Adsorption Spectrometry) for Na and K with detection limits of 0.5 mg/L. For Ca, Mg, HCO_3, and Cl the method was titration with detection limits of 0.1 mg/L for Ca and Mg, 3 mg/L for bicarbonates and 2 mg/L for chlorine. Finally, SO_4 was determined with turbidimetry with a detection limit of 0.5 mg/L.

3.2. Water sampling (this study)

Fifteen (15) water samples were collected during 2010 from groundwater and surface water in the northernmost Lerma valley (north of the Vaqueros river) (Fig. 2), and are presented in Table1. The samples were taken *in situ*, the wells were pumped 10 minutes before taken the sample. The samples were filtered with Millex-HV-Durapore-PVDF type of 0.45µm pore size. The samples were acidified with HNO_3, and preserved at 4 °C until being analyzed at ActLabs laboratories (Canada). The analytical method was ICP-MS (Inductively coupled plasma - mass spectroscopy) for and As. The detection limit for As was 0.03 µg/L. Cations and anions were determined by titration according to the standards methods described in Eaton et al., (1998).

4. Results

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

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

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

Regarding to the geochemistry of major ions, most of the waters samples are HCO_3-Ca-Mg type with a normal evolution to HCO_3-Na-K (Table 2, Fig. 4). A sample in the North of the valley has SO_4-Ca as dominant ions (sample 82), which is attributed to dissolution of secondary gypsum present in the sediments of the Orán Group (Hoyos, 2005; Lopez, 2017). The sample 63 which has high SO_4 can also interpreted as more evolved since it is located in the central part of the valley. Baudino (1996) associates the presence of SO_4-Cl type groundwaters in La Viña aquifer

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

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

5. Discussion

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

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

5.1.1.Puna

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

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

In the Lerma valley there is a lack of Cenozoic volcanism as known in the Puna. Despite the Neogene volcanism had episodes of expansion with volcanic manifestations that reached the eastern edge of the Puna including the Cordillera Oriental geological province (Hongn et al., 2018), the lack of volcanic rocks is observed in the stratigraphy of the Lerma valley (section 2.1). During the middle to upper Miocene, the Lerma valley was included in the fragmented foreland basin after the exhumation of the Mojotoro and Pascha mountain ranges and between 12 and 8 Ma the fluvial dynamics in the valley was very energetic (conglomerates in the Guanaco and Piquete Formations) (Gallardo et al., 1996, Monaldi et al., 1996; González Bonorino and Abascal, 2012; Pearson et al., 2013) (Fig. 5). The synorogenic Neogene sediments in the Lerma valley are composed of reddish sandstones and mudstones, and brownish conglomerates interbedded with mudstones of the Guanaco and Piquete formations, respectively (Gebhard et al., 1974) with a general lack of volcanic components. The distinctive geomorphology of the Puna with closed and endorreic basin systems make the Puna an isolated geological province where there is a lack of transference of sediments and chemical components such as As outside of the system. This natural characteristic of the Puna preserves the surrounding areas such as the Lerma valley out of the direct transference of As. Instead, in the Puna region, the closed basin and its high evaporation rates produces an enrichment in the depocenter of the basins reflected in high concentration of As in brines, salines, and lakes (Tapia et al., 2019, this issue).

Another important geogenic source of arsenic in the Puna are sulfide mines (Tapia et al., 2019, this issue). Sulfide mines (Pb, Zn, Cu, Au, Ag, Sn) in the Puna are in many cases related to the Cenozoic volcanism (Allmendinger et al., 1997; Richards et al., 2006; Caffe and Coira, 2008). These mineral deposits contain As in gangue minerals as well as in ore minerals. Arsenic is present in pyrite, arsenopyrite, and other rich As mineral accessories. Rich As-pyrite and arsenopyrite is also present in epithermal and alluvial rich gold mineralization hosted in marine shales from the Ordovician period (Rodriguez et al., 2010). The natural weathering of these sulfide deposits releases As into the surrounding environment in the Pozuelos basin (Murray et al., 2019, this issue). Arsenic is also present in the mining wastes of sulfide mining sites that were exploited between the 70’ and 90’ decades, as well as in the acid mine drainage (AMD) generated by oxidation of the wastes. Examples of inactive mines and AMD generation in the Puna are La Poma treatment plant, La Concordia, and Pan de Azúcar mines, which affect the basins of San Antonio, Tajamar, and Cincel rivers, respectively (Kirschbaum et al., 2012; Murray et al., 2014; Murray et al., 2019 this issue).

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

The Puna region is also characterized by the presence of numerous hot springs (Pesce and Miranda, 2003). Thermal waters are also natural sources of arsenic (Nordstrom 2002; Smedley and Kinniburgh 2002; Bowell et al., 2014). Despite only few studies measured As in the thermal waters, some examples can be mentioned in the Argentinian Puna such as the hot springs near San Antonio de Los Cobres (9,490 µg/L) (Hudson-Edwards and Archer, 2012) and in Vilama (6,170 µg/L) (Peralta Arnold et al., 2017). El Tatio geothermal site in the Chilenian Puna is also well known by the high arsenic concentrations (45,000 – 50,000 µg/L) (Webster and Nordstrom 2003). There are no hot spring sites registered for the Lerma valley (Pesce and Miranda 2003).

5.1.2. Chaco-Pampian plain

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

The beginning of the loessoid sedimentation cycle has been related to a phase of Late Miocene (~10 Ma) orogeny of the Andes resulting in the elevation of the Cordillera, which acted as a barrier to moisture-laden Pacific winds (Zarate, 2003). According to Ramos (1999), accumulations of synorogenic sediments several hundred meters thick, derived from erosion of the uplifted Cordillera were deposited during the Late Miocene and the Pliocene. Loess deposition was furthermore related to a multistage transport mechanism, involving fluvial and aeolian processes with westerly and southwesterly wind directions, as dominant carriers of the aeolian deposits (Zarate 2003). However, westerly tropospheric winds and northerly winds were also important (Iriondo, 1990, 1997)

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

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

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

The Lerma valley is characterized by a meso-thermal and sub-humid climate with dry season and little annual change in temperature (Burgos and Vidal, 1951). The wet season occurs during the austral summer from November to March. In contrast with the Chaco-Pampian plain and the Puna regions with arid or semiarid regimes and a low annual rainfall and a high evaporation (Nicolli et al., 2012; Tapia et al., 2019) The Lerma valley has an average annual precipitation between 700-800 mm (Romero Orué et al., 2017). Most of the recharge of the exploited aquifers occurs due to infiltration of rainfall (Baudino, 1996). The infiltration of rainwater measured in La Caldera aquifer in the North of the valley (where samples with < 0.01 mg/L of As were obtained) is high > 60% and contribute to fresh water recharge (López, 2017). In The Chaco-Pampian plain and the Puna, climate plays an important role, affecting dissolved As through evaporation during the dry season (Nicolli et al., 2012; Tapia et al., 2019 this issue; Murray et al., 2019 this issue). Moreover, in those regions, poorly drained flat plains, lowlands and closed depressions that concentrate shallow unconfined groundwater, of form salars depressions, are affected by a slow drainage and a delayed runoff, or closed systems making them preferential landforms for As-accumulation (Nicolli et al., 2012, Tapia et al., 2019 this issue; Murray et al., 2019 this issue). The conductivities of the groundwater (350 – 850 µs/cm), the pH (5.5 – 7.8), and the composition of major ions (HCO_3-Ca-Mg with normal evolution to HCO_3-Na) (Table 1, Fig. 4) indicates that these groundwaters are little evolved as well as indicated by Baudino (1996) who also suggest a little time of circulation and/or circulation by inert materials. In the Lerma valley, the most productive levels of the multilayered aquifer are placed in Quaternary layers composed of fine gravels and sands to fine sands Baudino (1996). The grain size favor high porosity, permeability and circulation of the groundwater with medium to high transmissivity values which implies low residence times (Table 3).

Another important fact for lowe As in groundwaters is that the aquifer sediments in the Lerma valley have an origin in the erosion of the early to middle Cambrian basement composed of low grade metamorphic rocks of the Puncoviscana Formation, the Cretaceous-Paleogene continental strata with conglomerates, sandstones, mudstones and the limestones of the Salta Group rift with a lack of geogenic arsenic sources (sections 5.1.1 and 5.1.2). An example of similar free arsenic conditions can be observed in the Chaco-Pampean plain in some specific environments where low As concentration in groundwater can be found. These natural free arsenic conditions are created by the presence of fluvial sediments layers interbed in the aeolian loess deposits. The fluvial sediments do not contain arsenic and contribute to higher porosity and permeability and circulation of the groundwater. In the paleo-channels of the Cuarto river located in Córdoba Province, Giacobone et al. (2018) describe a scarcely evolved groundwater of HCO_3-Ca to HCO_3-Na type. These waters result from high velocities flows that circulate in coarse fluvial sediments composed of inert mineralogy with low interaction time resulting in a low As (1 – 10 µg/L) concentrations in groundwater. In the south of Córdoba province, Becher Quinodoz and Blarasin (2014) described fresh HCO_3-type groundwater in active dunes sediments that conform a fluvial-aeolian environment linked to local flows with current precipitation recharge. In this case, As concentrations are still above the limits for human consumption, but with lower values than in the surrounding loessoid environments, where high concentrations of As are related to brackish-salty groundwater (SO_4-Cl type), as the result of long existing regional flows and long interaction time with the loess.

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

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

Finally, the characteristics of the wells construction with several screens situated in the coarse sediments layers can also favor to low As concentration in the Lerma valley. That is the case in multilayered glacial aquifers where construction practices such as exploiting a thick, coarse aquifer and installing a long well screen yield good water quantity for public water system wells (Erickson and Barnes, 2005). Moreover, in that environment wells with long screens set at a distance from an upper confining unit are at lower risk of exposure to geochemical conditions conducive to arsenic mobilization via reductive mechanisms such as reductive dissolution of metal hydroxides and reductive desorption of arsenic. Exploiting the coarse sediments in the Lerma valley seems to ensures extraction of the good quality groundwaters. However, the wells with higher As values of 0.01 and 0.02 mg/L (wells 25 and 68) could indicate that may exist groundwater with higher As content (released either by local higher pH or reductive conditions). Therefore, a better understanding of the redox conditions, mineralogy and geochemistry of the sediments (i.e. the loess present in the Lerma valley) and a better correlation between the wells characteristics and the exploited levels will be necessary to understand the processes that increase As concentrations in the mentioned wells.

5.3. Other similar intermountain valleys in Northwest Argentina

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

6. Conclusion

The concentrations of As in Lerma valley are within the recommended values for drinking water in Argentina (0.05 mg/L) and are remarkably lower in comparison to the Puna and the Chaco-Pampian plain surrounding regions. Low As concentration in the groundwater of the Lerma valley can be attributed to a combination of natural processes related to the geochemistry of groundwater (mainly HCO_3-Ca type, near neutral pH, and most probably oxidative conditions), the absence of the typical geogenic sources (Cenozoic volcanism, sulfide deposits, thermal water sources, and the rich-As volcanic ash Miocene loess), high fresh rain water infiltration rates, low residence times, and the characteristics of the wells construction (with screens settled in coarse inert sediments layers). The absence of the Mio-Pliocene loess was favored by the high-energy sedimentary environments that characterized this region during that time. However, a better understanding of the redox conditions, mineralogy, and geochemistry of the sediments (i.e. the loess present in the Lerma valley) with a better correlation between the wells characteristics will be necessary to understand the wells with the higher As values (0.01 and 0.02 mg/L). The geological, geochemical, and tectonic characteristics of the Lerma valley could be extrapolated to other similar valleys in NW of Argentina such as the Cordillera Oriental and Subandinas geological provinces. In the context of increasing population, and demand of water resources, a better understanding of the natural processes that create reservoirs for groundwater of good quality can be useful as an exploration tool. This is of high importance in territories with high As concentration in groundwater such as Argentina.

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Author Contributions

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

Conflict of Interest

The authors declare no conflicts of interest

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Figure captions

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

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

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

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

Fig. 5. Schematic overview of the tectonic evolution and sedimentation dynamics

from the Miocene to the Quaternary in the Lerma valley. Adapted from Hain et al. (2011).

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
				decimal degrees	decimal degrees	mbgs
Aguas del Norte	1	well	2016	248,053	654,367	-
	2	well	2016	248,553	654,451	-
	4	well	2016	248,469	654,517	-
	5	well	2016	248,138	654,231	-
	6	well	2016	248,363	654,881	-
	7	well	2016	248,482	654,622	-
	8	well	2016	248,626	654,645	-
	11	well	2016	248,949	655,445	-
	14	well	2016	247,201	654,088	-
	15	well	2016	247,251	654,073	-
	16	well	2016	247,413	654,054	-
	17	well	2016	247,876	654,020	-
	18	well	2016	247,920	653,694	-
	19	well	2016	247,955	653,665	-
	20	well	2016	247,960	653,704	-
	21	well	2016	247,963	654,286	-
	25	well	2016	248,213	653,897	-
	26	well	2016	248,130	653,962	-
	28	well	2016	248,375	653,897	-
	30	well	2016	248,318	653,884	-
	39	well	2016	249,641	655,902	-
	40	well	2016	249,590	655,987	-
Secretariat of Water Resources	41	well	2008	248,613	653,999	22
	42	well	2009	248,722	654,511	56
	43	well	2009	248,091	654,432	32
	44	well	2009	248,185	653,858	22
	45	well	2010	248,543	656,046	11
	46	well	2010	249,793	654,900	60
	47	well	2015	248,222	654,953	12
	48	well	2010	250,468	654,538	49

	49	well	2017	248,894	655,996	85
	50	well	2011	249,795	655,972	114
	51	well	2011	248,543	655,237	37
	52	well	2011	248,094	654,619	46
	53	well	2011	249,092	654,870	30
	54	well	2011	248,972	653,908	10
	55	well	2012	249,469	654,244	15
	56	well	2012	248,096	654,706	73
	58	well	2012	249,312	654,887	41
	59	well	2013	250,097	655,405	52
	60	well	2013	247,117	654,009	42
	62	well	2013	248,191	654,068	31
	63	well	2013	247,990	654,758	56
	64	well	2014	250,160	654,474	34
	65	well	2015	248,340	654,240	33
	66	well	2015	248,222	654,953	12
	67	well	2017	248,895	655,996	85
	68	well	2011	248,922	654,870	26
	69	well	2011	248,342	654,502	43
	70	well	2012	248,528	654,675	58
This study	71	well	2010	245,719	653,723	8.9*
	72	well	2010	245,770	653,681	9.0*
	73	well	2010	245,944	653,768	9.0*
	74	well	2010	246,888	653,948	5.75*
	75	La Caldera river	2010	245,998	653,752	-
	76	well	2010	246,901	654,051	16.3*
	77	well	2010	246,868	654,245	11.0*
	78	well	2010	246,612	653,811	8.0*
	79	well	2010	246,404	653,866	8.8*
	80	La Caldera river (La Calderilla site)	2010	246,398	653,908	-
	81	un-named stream	2010	246,614	653,825	-
	82	well	2010	246,276	654,575	6.0*
	83	Wierna and La Caldera rivers confluence	2010	246,888	653,915	-
	84	Vaqueros river	2010	247,109	654,119	-
	85	La caldera and Vaqueros rivers confluence	2010	247,110	653,939	-

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	K	Ca	Mg
			mg/L	mg/L	mg/L	mg/L
Aguas del Norte	1	well	33	2.2	-	-
	2	well	20	2.2	-	-
	4	well	20	0.9	-	-
	5	well	28	1.3	-	-
	6	well	19	1.2	-	-
	7	well	17	1.7	-	-
	8	well	12	2.5	-	-
	11	well	15	0.6	-	-
	14	well	13	2.2	-	-
	15	well	13	1.9	-	-
	16	well	33	1.6	-	-
	17	well	47	3.6	-	-
	18	well	74	7.1	-	-
	19	well	99	3.7	-	-
	20	well	111	6.4	-	-
	21	well	35	2.8	-	-
	25	well	22	2	-	-
	26	well	25	2.1	-	-
	28	well	21	1.1	-	-
	30	well	20	1.1	-	-
	39	well	23	2.7	-	-
	40	well	25	3	-	-
Secretariat of Water Resources	41	well	29.33	1	-	-
	42	well	15	1.9	29.6	7
	43	well	32.5	1.3	25.9	12.4
	44	well	85	4	-	-
	45	well	8	2	24	6
	46	well	14	4	49	15
	47	well	37	4.7	32	11
	48	well	5	0.37	56	14.55

	49	well	15	2.4	4.3	17
	50	well	19	4	48	12
	51	well	4.5	0.37	27	8.2
	52	well	18	4	24	6
	53	well	17	3	41	13
	54	well	4.8	0.21	28	7.14
	55	well	2.4	2.4	52	15.08
	56	well	104	2.8	12	9
	58	well	16.4	2.22	36	65.41
	59	well	15	2	63	21.7
	60	well	39	3.3	-	-
	62	well	20	1	-	-
	63	well	6.17	0.36	9	5
	64	well	24.8	2.6	51.8	11.8
	65	well	26.8	0.57	21.8	29.6
	66	well	37	4.7	32	11
	67	well	15	2.4	4.3	17
	68	well	12	2	41	11
	69	well	20	4	20	8
	70	well	17	1.5	31	9
This study	71	well	9.34	1.67	17.6	3.9
	72	well	11.5	3.76	35.2	7.81
	73	well	9.62	1.93	64	5.86
	74	well	7.75	1.66	35.2	10.74
	75	La Caldera river	5.68	1.34	35.2	6.83
	76	well	23.9	1.46	46.4	13.66
	77	well	10.6	4.64	36.8	4.88
	78	well	10.9	4.04	32	9.76
	79	well	5.61	1.71	32	7.81
	80	La Caldera river (La Calderilla site)	5.66	1.7	36.8	5.86
	81	un-named stream	9.7	2.46	25.6	6.83
	82	well	14.6	1.97	103	5.2
	83	Wierna and La Caldera rivers confluence	9.62	1.69	32	4.88
	84	Vaqueros river	4.69	0.81	9.6	6.83
	85	La caldera and Vaqueros rivers confluence	4.22	0.75	9.6	1.95

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	Lithology of the productive layers (in screen sites)	T
			mbgs		m^2/
Secretariat of Water Resources	41	well	255	fine-medium gravel, coarse sand	11
	42	well	255	coarse-medium sand, fine gravel	10
	43	well	186	-	50
	44	well	160	coarse gravel, medium-fine sand	23
	45	well	89	fine gravel with medium-coarse sand	2.
	46	well	150	medium-coarse sand	12
	47	well	71	coarse-medium sand, fine gravel	0.
	48	well	101	coarse gravel, medium-fine gravel, fine sand	10
	49	well	202	Gravel with sandy matrix	81
	50	well	205	conglomerate	96
	51	well	123	coarse-medium sand, interbed gravels	0.
	52	well	140	coarse-medium sand, fine gravel	16
	53	well	83	fine-medium gravel, coarse sand	20
	54	well	174	coarse gravel, medium-fine gravel	6
	55	well	90	fine gravel with medium-coarse sand	69
	56	well	195	coarse gravel, medium sand with fine gravel	7.
	58	well	115	coarse gravel	37
	59	well	143	medium-coarse gravel	36
	60	well	117	boulders, coarse gravel, coarse sand	3.
	62	well	242	boulders, coarse sand , medium sand	31
	63	well	120	boulders, medium sand, coarse gravel	1.
	64	well	196	Conglomerates, sand, coarse sand	14
	65	well	260	coarse gravel, fine gravel, boulders	18
	66	well	71	fine-medium gravel, sand gravel	0.
	67	well	202	gravel, sand	81
	68	well	143	fine-medium gravel, coarse sand	31
	69	well	183	-	38
	70	well	252	-	89

[a]Transmissivity of the well

mbgs = meters below ground surface

Graphical abstract

Highlights

- The concentration of arsenic in the Lerma valley groundwater is low
- In the Lerma valley there is a lack of geogenic sources of arsenic
- Tectonic, sedimentary evolution and climate favor low As
- Near neutral pH, redox, and geochemistry contributes to low arsenic
- Screens in coarse aquifer layers contributes to groundwater of quality


N
Brasil
Bolivia
Puna altiplano
Taco Pozo
Paraguay
Pilcomayo river
Chaco salteña plain
Paraguay river
San Antonio
de los Cobres
Salado river
Chile
Chaco Pampian plain
Paraná river
Uruguay
Argentina
References
Areas with high arsenic contents
Study area
Rivers

Figure 1

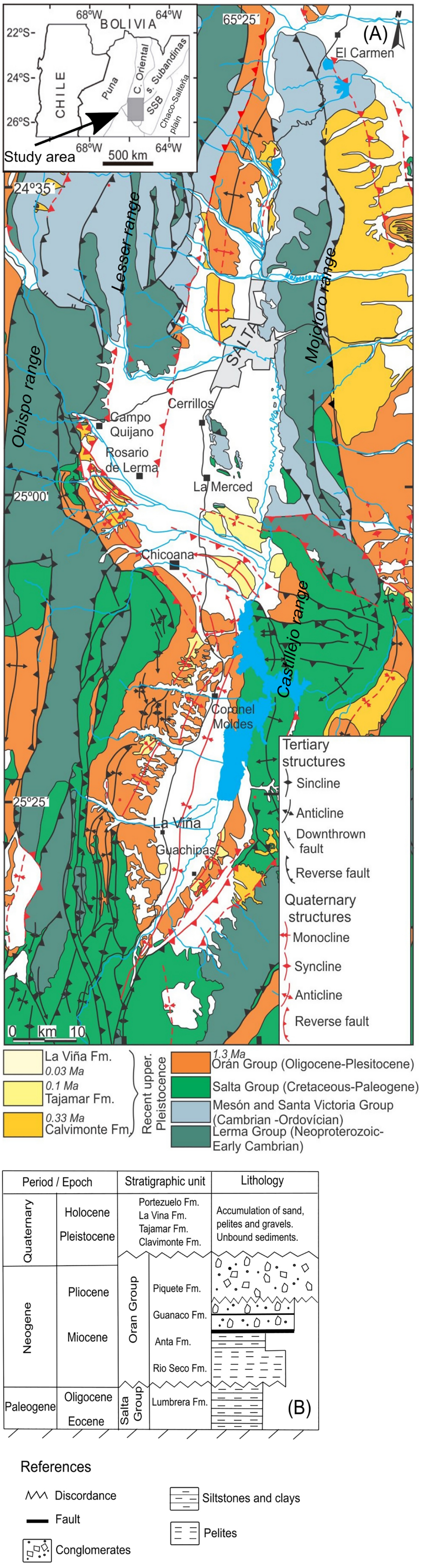
(A)
68ºW
64ºW
BOLIVIA
22ºS-
24ºS-
26ºS-
CHILE
Puna
C. Oriental
S. Subandinas
SSB
Chaco-Salteña plain
Study area
500 km
65º25´
El Carmen
24º35´
Lesser range
Mojotoro range
SALTA
Obispo range
Cerrillos
Campo Quijano
Rosario de Lerma
La Merced
25º00´
Chicoana
Castillejo range
Coronel Moldes
25º25´
La Viña
Guachipas
0 km 10
Tertiary structures
Sincline
Anticline
Downthrown fault
Reverse fault
Quaternary structures
Monocline
Syncline
Anticline
Reverse fault
La Viña Fm.
0.03 Ma
0.1 Ma
Tajamar Fm.
0.33 Ma
Calvimonte Fm.
Recent upper. Pleistocene
1.3 Ma
Orán Group (Oligocene-Plesitocene)
Salta Group (Cretaceous-Paleogene)
Mesón and Santa Victoria Group (Cambrian -Ordovícian)
Lerma Group (Neoproterozoic-Early Cambrian)
Period / Epoch
Stratigraphic unit
Lithology
Quaternary
Holocene
Pleistocene
Portezuelo Fm.
La Vina Fm.
Tajamar Fm.
Clavimonte Fm.
Accumulation of sand, pelites and gravels. Unbound sediments.
Neogene
Pliocene
Miocene
Oran Group
Piquete Fm.
Guanaco Fm.
Anta Fm.
Rio Seco Fm.
Paleogene
Oligocene
Eocene
Salta Group
Lumbrera Fm.
(B)
References
Discordance
Fault
Conglomerates
Siltstones and clays
Pelites

Figure 2

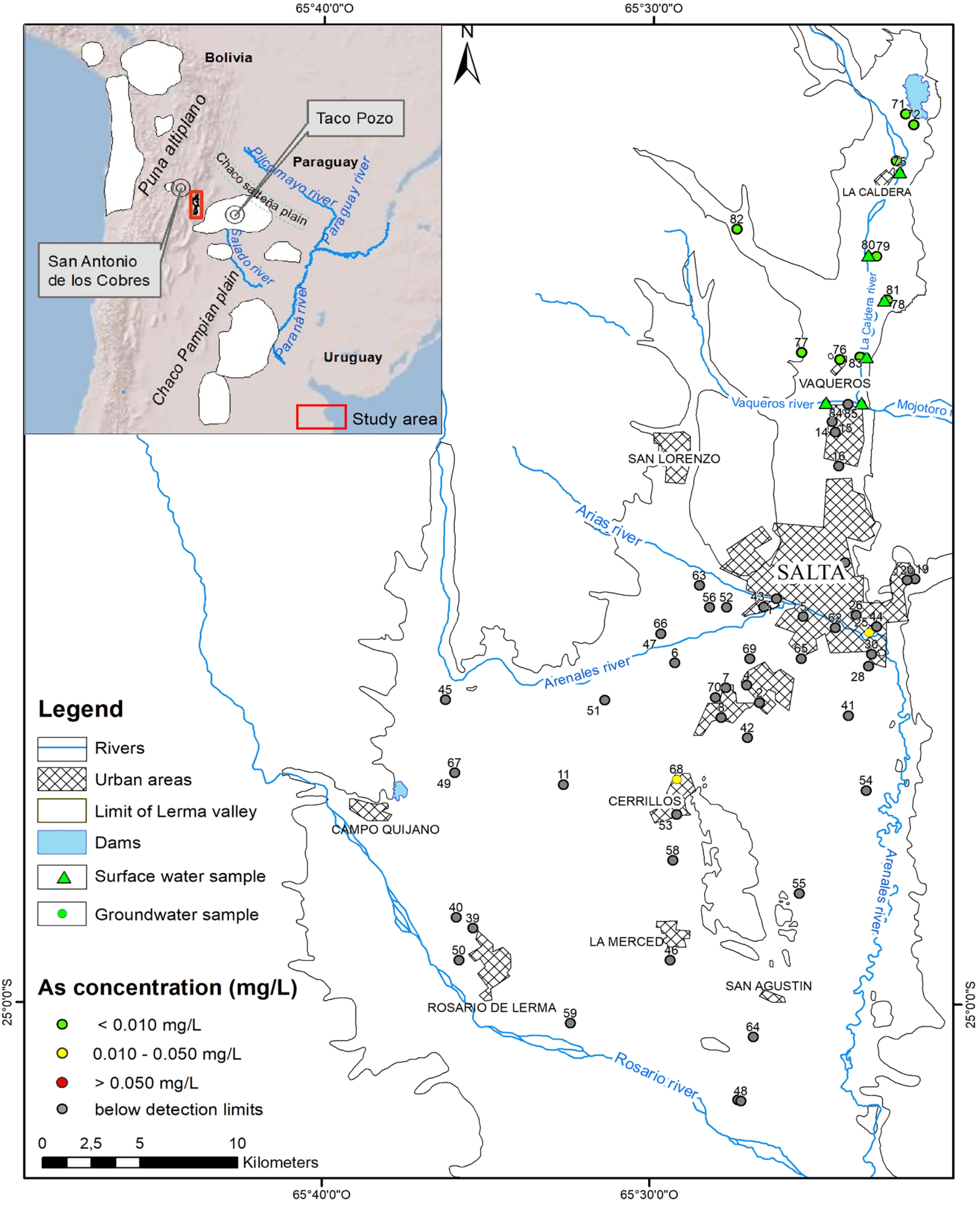
65°40'0"O
65°30'0"O
25°0'0"S
N
Bolivia
Paraguay
Uruguay
Puna altiplano
Taco Pozo
San Antonio de los Cobres
Chaco salteña plain
Chaco Pampian plain
Pilcomayo river
Paraguay river
Salado river
Paraná river
Study area
LA CALDERA
VAQUEROS
SAN LORENZO
SALTA
CAMPO QUIJANO
CERRILLOS
LA MERCED
SAN AGUSTIN
ROSARIO DE LERMA
La Caldera river
Vaqueros river
Mojotoro river
Arias river
Arenales river
Rosario river
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
0
2,5
5
10
Kilometers

Figure 3

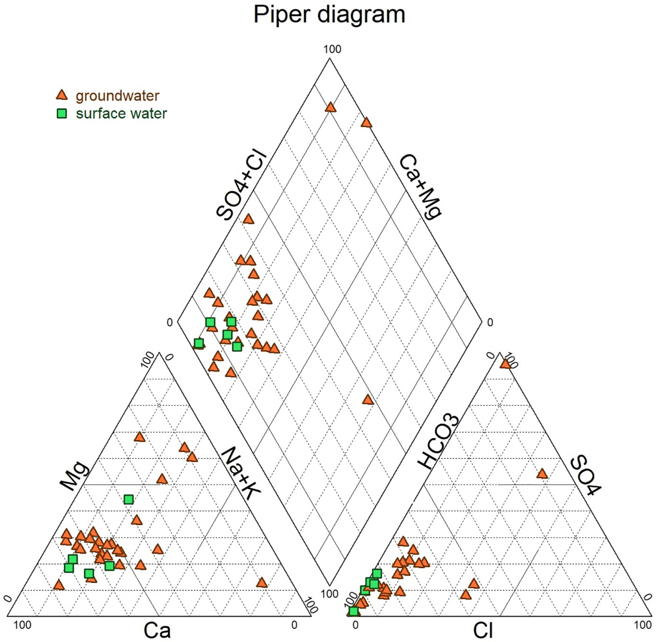
Piper diagram
groundwater
surface water
100
SO4+Cl
Ca+Mg
0
0
100
0
Mg
Na+K
0
100
HCO3
SO4
0
100
100
0
100
100
Ca
0
0
Cl
100

Figure 4

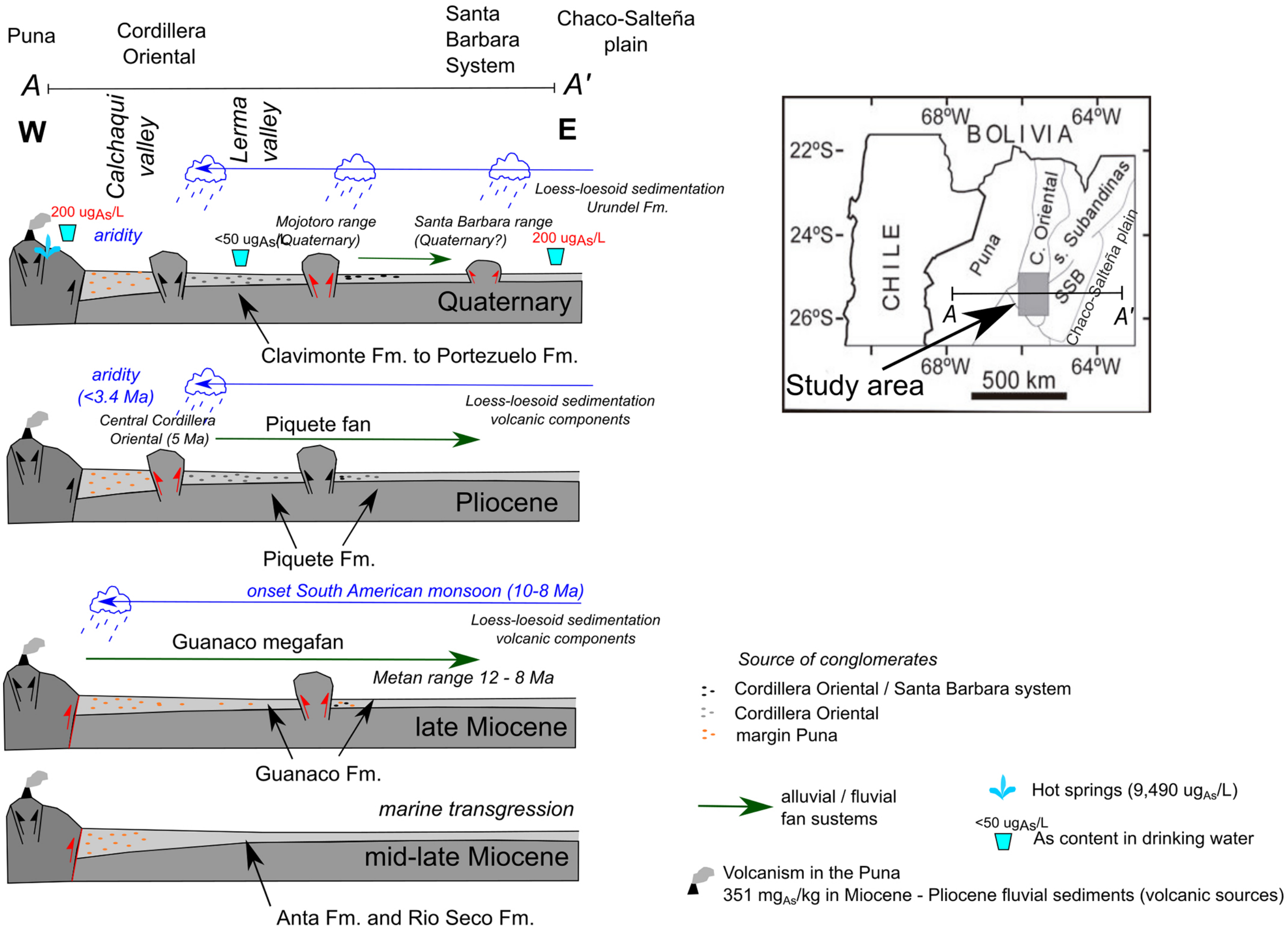
Puna
Cordillera Oriental
Santa Barbara System
Chaco-Salteña plain
A
A′
W
E
Calchaqui valley
Lerma valley
Loess-loesoid sedimentation
Urundel Fm.
200 ugAs/L
aridity
Mojotoro range
<50 ugAs/L
(Quaternary)
Santa Barbara range
(Quaternary?)
200 ugAs/L
Quaternary
Clavimonte Fm. to Portezuelo Fm.
aridity
(<3.4 Ma)
Loess-loesoid sedimentation
volcanic components
Central Cordillera Oriental (5 Ma)
Piquete fan
Pliocene
Piquete Fm.
onset South American monsoon (10-8 Ma)
Loess-loesoid sedimentation
volcanic components
Guanaco megafan
Metan range 12 - 8 Ma
late Miocene
Guanaco Fm.
marine transgression
mid-late Miocene
Anta Fm. and Rio Seco Fm.
68°W
64°W
BOLIVIA
22°S
24°S
26°S
CHILE
Puna
C. Oriental
S. Subandinas
SSB
Chaco-Salteña plain
A
A′
68°W
64°W
500 km
Study area
Source of conglomerates
Cordillera Oriental / Santa Barbara system
Cordillera Oriental
margin Puna
alluvial / fluvial fan sustems
Hot springs (9,490 ugAs/L)
<50 ugAs/L
As content in drinking water
Volcanism in the Puna
351 mgAs/kg in Miocene - Pliocene fluvial sediments (volcanic sources)

Figure 5