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Origin and geochemistry of arsenic in surface and groundwaters of Los Pozuelos basin, Puna region, Central Andes, Argentina



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- There are at least three different geogenic sources of arsenic in the basin.
 Concentrations of As in waters increase
- to the center of the basin.
- A(V) is the dominant specie in all the water types.
- The presence of A(III) in the lagoon indicates reductive conditions.
- The closed basin effect, and high evaporation increase As in waters.



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ABSTRACT

Los Pozuelos is a closed basin in the Puna region of NW Argentina, Central Andes. This is a semi-arid region where closed basins are the most important feature for the hydrologic systems. The center of the basin is occupied by a fluctuating playa lake called Los Pozuelos lagoon, which constitutes a UNESCO Biosphere Reserve. This is one of the most populated closed basins in the Argentinian Puna and residents use groundwater for drinking and cooking. Lowest concentrations of As and dissolved solids are in the headwaters of the rivers (1.46–27 µg/L) and the highest concentrations are in the lagoon (43.7–200.3 µg/L). In groundwater, arsenic concentrations increase from the outer ring aquifer (3.82–29.7 µg/L) composed of alluvial-alluvial fan sediments to the inner lacustrine aquifer (10–113 µg/L) that surround the playa lake. Moreover, high concentrations of As during the dry season (90.2 and 113 µg/L), Na/K mass ratios (0.2 and 0.3), and formation of Na-rich efflorescent salts suggest that high evaporation rates increases As concentration, while rainwater dilutes the concentration during the wet season. As(V) is the dominant species in all the water types, except for the lagoon, where As(III) occasionally dominates because of organic matter buildup. There are at least three potential sources for As in water i) oxidation of As sulfides in Pan de Azúcar mine wastes, and acid mine drainage discharging into the basin; ii) weathering and erosion of mineralized shales; iii) weathering of volcanic eruptive non-mineralized rocks. Because it is a closed basin, the arsenic released from the natural and anthropogenic sources is transported in

* Corresponding author at: 9 de Julio, 14, Rosario de Lerma CP 4405, Argentina. *E-mail address:* murray.jesica@conicet.gov.ar (J. Murray). solution and in fluvial sediments and finally accumulates in the center of the basin where the concentration in water increases by evaporation with occasional enhancement by organic matter interaction in the lagoon. © 2019 Elsevier B.V. All rights reserved.

1. Introduction

Argentina was the first Latin American country where arsenic (As) occurrence in groundwater was reported and the first in the world to document As poisoning from natural sources (Bundschuh et al., 2012). Most of the studies in this country have been focused in the Chaco-Pampean plain region, which is known as one of the most extensive areas in the world with high As concentration in surface water and groundwater (Nicolli et al., 2012). However, in the Puna region of NW Argentina, the presence of As in groundwater above the limit for human consumption recommended by the World Health Organization $(10 \,\mu\text{g/L})$ was reported and related to the weathering of volcanic rocks (de Sastre et al., 1992; Farías et al., 2009). The Puna region, between 22° and 26° latitude south, forms the south-half portion of the Altiplano-Puna plateau in Central Andes which extends through parts of Argentina, Bolivia, Chile and Peru, between 3500 and 4500 m above sea level (see Tapia et al., 2019, this issue). It is the second highest plateau in the Earth after Tibet. Here, the altitude and widening of the Andes produces distinctive meteorological conditions making it a semi-arid region, with high temperatures fluctuations, intense solar irradiation, and high evaporation. More than 70% of the precipitation occurs in the austral summer decreasing westwards and southwards from 700 to <50 mm per year (Garreaud et al., 2003). In this region the Cenozoic volcanism and closed basin hydrology are the most important features. Drainages are not connected to the ocean and terminate in big lakes and salt flats in the center of the basins.

High levels of As have been detected in all the types of waters in the Altiplano-Puna (Tapia et al., 2019, this issue). However, only a few publications report arsenic speciation as well as a complete physicalchemical characterization of the waters that help to understand the mobility of arsenic in the closed basins (Tapia et al., 2019, this issue). Extensive studies related to the geogenic and anthropogenic origin of arsenic in the region are also scarce.

High concentration of As in urine and hair in woman and children in local Andean communities associated with arsenic-contaminated water were detected (Concha et al., 1998, 2010), especially in some areas with very high arsenic concentration like San Antonio de Los Cobres. This is an emblematic site situated in the Puna of Argentina where the As consumption in drinking water is $\approx 200 \ \mu g/L$. Here the arsenic source is associated with acid volcanic eruptive rocks, volcanic ash, and also hydrothermal activity (de Sastre et al., 1992; Farías et al., 2009; Hudson-Edwards and Archer, 2012). Recently, Schlebusch et al. (2015) identified the presence of the AS3MT gene in the local aboriginal community of San Antonio de Los Cobres, which have habited the region from >10,000 yrs. This is a major gene for arsenic metabolism in humans leading to human adaptation to arsenic-rich environments.

Los Pozuelos is one of the most populated closed basins in the Argentinian Puna with a total population of about 3500 (Cajal, 1998; INDEC, 2010). The local original communities are dispersed along the basin and groundwater is used as drinking and cooking water by most of the inhabitants. Previous studies indicate the presence of arsenic in surface and groundwater of the basin associated to different anthropogenic and geogenic sources (Murray et al., 2016).

The aim of this work is to understand the origin of As, its mobility, and cycling in surface and groundwater of Los Pozuelos basin. Arsenic from different anthropogenic and geogenic sources migrate downstream and converge in the center of the closed basin where evaporation may increase its concentration. To achieve our objective we analyzed and interpreted long term data (2011 to 2017) that includes arsenic concentration, arsenic redox speciation, and the geochemistry (major ions and physical-chemical parameters) of surface and groundwaters of the basin. Moreover, the effect of the geomorphological closed hydrologic system and semi-arid conditions on As mobility, concentration, and cycling are discussed. This work contributes to the larger framework of arsenic sources, mobility, and cycling in the closed basins of the Altiplano-Puna.

2. Setting of Los Pozuelos basin

2.1. Geology

Pozuelos is a closed NNE–SSW piggyback basin located in the Puna morphotectonic province from the Central Andes Altiplano-Puna Plateau (Allmendinger et al., 1997; Rubiolo et al., 1997). Tectonostratigraphic relationships indicate that Pozuelos basin formed in the late Oligocene – early Miocene between 28 and 16 Ma (Rubiolo et al., 1997). This basin is bounded by westward-verging thrust sheets. These sheets uplifted Ordovician marine shales (Fm. Acoite) forming the Rinconada Range in the west and Ordivician volcanic-sedimentary rocks (Cochinocha-Escaya Complex) in the east, forming the Cochinoca-Escaya Range (Rubiolo et al., 1997; Caffe et al., 2001) (Fig. 1 A). The basin has a surface area of 3800 km² (*ca* 110 km long and *ca* 25 km wide), it is located about 3650 m above sea-level and the relief between its bottom and the crests of the marginal mountain ranges exceeds 700 m.

The center of this depression is occupied by the Los Pozuelos lagoon, which is a large seasonally fluctuating playa lake (McGlue et al., 2012). The lagoon surface can exceed 135 km² during years with above average precipitation (Igarzábal, 1978). The lagoon constitutes one important refuge of aquatic habitat within a desert matrix in Central Andes and harbors protected bird species such as New World Flamingos (*Phoenicopterus jamesi, Phoenicopterus andinus, Phoenicopterus chilensis*) (Cendrero et al., 1993; Caziani et al., 2001). Due to its environmental importance the lagoon has been declared a National Natural Monument by the Argentinian government (National Parks Administration of Argentina), Ramsar Site (Ramsar Sites Information Service), and a site of importance for migratory shore birds (Western Hemisphere Shorebird Reserve Network). The whole basin constitutes a UNESCO Biosphere Reserves).

Intervals of prolonged drought commonly lead to desiccation of the playa lake. During this period, the exposure of lacustrine mud and the formation of some salts crust are common, but it does not form a saline deposit such as others in the Altiplano-Puna (Igarzábal, 1978, 1991). Santa Catalina and Cincel Rivers are the most important rivers in the basin with discharges in the lagoon (Igarzábal, 1978). In wet season, the lagoon level shows a rapid recovery of the water surface. When completely filled, the lagoon reaches a maximum depth near its center (<2 m) and progressively shoals towards its margins (Igarzábal, 1978; McGlue et al., 2012).

The lithology of the basin is diverse in composition and age (Coira and Zappettini, 2008). Ordovician marine shales are the most abundant rocks in the basin and contain many epithermal Au-Pb-Ag-Zn deposits and placer deposits (Rubiolo et al., 1997; Segal and Caffe, 1999; Caffe et al., 2001; Rodriguez et al., 2001; Rodríguez and Bierlein, 2002)

Fig. 1. (A) - Geological map of Los Pozuelos basin and sampling points of surface waters and groundwaters. (B) - Zoom of sampling area in the upstream area of Cincel River. (C) - Zoom of sampling are in the South-central area of the basin. (D) - Zoom of sampling are in the lagoon area.









(Fig. 1 A). Epithermal Au is hosted in small quartz veins, which also are rich in arsenopyrite and pyrite (Segal et al., 1997). The Au mineralization is structurally controlled and occurs typically along large anticline hinges. Geochemical data indicate that the hydrothermal systems are rich in Au-As and Sb together with subordinate quantities of base metals (Pb, Zn, Cu, and Mo; Rodriguez et al., 2001). The exploitation of these Au deposits along the whole Rinconada hill are known from previous colonial times, but are inactive at the present. Cretaceous continental sediments such as sandstones and conglomerates (Pirgua Subgroup) are present in the southern end of the basin (Rubiolo et al., 1997; Caffe et al., 2001) (Fig. 1 A). Miocene mixed continental sediments including volcanoclastic rocks, sandstones, conglomerates, and carbonates, crop out in the Cochinoca-Escaya Range as well as in the southern end of the basin (Fm. Moreta, Fm. Cara-Cara, Fm. Tiomayo; Rubiolo et al., 1997). Several Miocene dacitic volcanic centers domes (Pozuelos Volcanic Complex) contain Pb-Ag-Zn sulfide mineralized veins that were mined until the nineties (Pan de Azúcar, Cerro Redondo, and Chinchillas mines; Segal and Caffe, 1999). Miocene ignimbrite deposits also comprise some of the epithermal and placer deposits, which are common along the eastern flank and south border of the basin (Coranzulí Complex, Caffe et al., 2001) shown in Fig. 1 A. Conglomerates and alluvial fans were deposited at the foot of Rinconada Hills during the Pliocene.

In the central area of the basin, Late Pleistocene-Holocene lacustrine deposits surround the actual lagoon as a product of ancient fluctuations of the playa lake (Igarzábal, 1978; Camacho and Kulemeyer, 2017). The thickness of these sediments is variable and are composed of silts with minor clay fraction and fine sand with abundant quartz (Igarzábal, 1978). Calcareous levels, gypsum-halite, ostracods, algae, diatoms, and gyttja are present in these sediments (Igarzábal, 1978; Camacho and Kulemeyer, 2017). Moreover, efflorescent salts precipitate in the surface as a result of capillary forces induced by strong evaporation (Igarzábal, 1978). The lacustrine sediments intercalate progressively with Pleistocene-Holocene alluvial and alluvial fan deposits situated at the foot of Rinconada and Cochinoca-Escaya hills (Igarzábal, 1978; Camacho and Kulemeyer, 2017). Finally, thin riverbed and floodplain deposits of Cincel and Santa Catalina rivers overly the lacustrine sediments and central parts of the basin occupied by the meandering rivers. They are composed of sand, silt as well as salt precipitation (Igarzábal, 1978; Camacho and Kulemeyer, 2017) (Fig. 1 A).

The lacustrine and alluvial-alluvial fan sediments comprise the unconfined aquifer that hosts groundwater in Los Pozuelos basin (Igarzábal, 1978; Alcalde, 2008). Previous studies indicate that the water table is shallow, the piezometric surface is North-South elongated, and the drainage goes to the central area of the basin (Alcalde, 2008).

2.2. Weather and vegetation

Available meteorological data in Los Pozuelos basin from the middle 1970s to middle 1990s can be found in the Instituto Nacional de Tecnologia Agropecuaria (INTA) database (Bianchi and Yañez, 1992). Data from the town of Rinconada, from 1972 to 1996 located in the mid-west area of the basin (Fig. 1) indicates that this is a semi-arid region with an annual precipitation of 486 mm occurring mainly in the Austral summer between December and March (Fig. 2). The annual potential evapotranspiration is higher (530 mm) than the annual precipitation and the deficit increases from April to November (Fig. 2). The lowest temperatures occur in winter with a mean value of 1.7 °C for July, while the highest temperatures occur in summer with a mean value of 9.4 °C for January and February.

The vegetation of the basin is composed of plant assemblages that generally follow topographic and soil-moisture gradients. The dominant plants are the shrubs *hemicryptophytes* and *nanophanerophytes* (Bonaventura et al., 1995). Some lead zinc analysis from vegetation sampled at different distances from the Pan de Azúcar mine, indicate that most plants contain zinc in their biomasses as a necessary nutrient,



Fig. 2. Water balance of Los Pozuelos basin. P = precipitation; P-Evp = potential evapotranspiration; R-Evp = real evapotranspiration.

while plants growing closer to the mine contain lead providing evidence of contamination from the mine (Plaza Cazón et al., 2013).

3. Methods

3.1. Sample collection, preservation, and analysis

3.1.1. Water samples collection

A total of 120 water samples were obtained from rivers (n = 32), lagoon (n = 6) and groundwater (n = 28), which were sampled during 6 field campaigns between 2011 and 2017 (Table ST1). The sampling design attempted to cover the whole basin from the higher areas to the center of the basin (Fig. 1). In rivers the sampling sites were located at the head waters of the main rivers, at intermediate distances, and at the discharge point in the lagoon. In the lagoon the samples were taking from the North and the South borders. The wells were selected in order to cover the two different aquifers in the basin, this campaign was mainly possible in the south area of the basin due to higher amount of existing wells. Before sampling, 10 buckets of water from the bottom of the well were taken out, after that, another bucket from the bottom was taken to get the water sample. Only at W9 site it was possible to pump the well for 10 min before taking the sample. Not all the sites were accessible during wet season due to flood conditions, for that reason not only the field campaigns but the number of samples obtained is lower than during the dry season (Table ST1).

Measurements of conductivity, temperature, dissolved oxygen, and pH were performed on site with multi-parametric Hanna equipment (Codes HI991300N and HI9142). All samples were filtered with 0.2 μ m pore size HV (Millex) filtration units by using a syringe in some cases and with polyethersulfone (GVS) 0.2 and 0.45 μ m membrane filters using a filter holder (Thermo Scientific) and manual pump. The samples were stored in a cooler at 4 °C in polyethylene tubes and bottles precleaned with deionized water for anions and 5% HNO₃ for cations, rinsed three times with deionized water after treatment. The samples for cation analyses were acidified to pH < 2 with ultrapure HNO₃ and the samples for anions were only filtered.

3.1.1.1. Major and trace elements analyses. Samples from 2011, 2012, and 2013 periods were analyzed at ActLabs laboratories (Canada). Cations were determined by inductively coupled plasma – optical emission spectrometry (ICP-OES) and by inductively coupled plasma – mass spectrometry (ICP-MS) to obtain the concentration of those elements below detection limits by ICP-OES. Anion concentrations were determined by ion chromatography (IC) at ActLabs laboratories for 2011 and 2012 samples and at University of Brasilia for 2013 samples. Alkalinity was measured on site by titration with bromophenol blue and 0.03 N HCl.

Samples from 2015, 2016, and 2017 periods were analyzed at the U.S. Geological Survey (USGS, Boulder, Colorado, USA) laboratories by

| Table 1 | |
|--------------------------------|--|
| Surface water samples, field j | parameters data and major ions analyses. |

| Sample | Sampling date | Lat | Long | pН | Т | Conductivity | TDS | DO | Discharge | Na | К | Ca | Mg | SO4 | Cl | HCO3 | NO3 | PO4 | F | Water-Type |
|---------------|------------------------|-------------|------------------------|------|------|--------------|------------|----------|---------------------|-------|-------|-----------|-------|--------|--------|--------------|-------------|--------|-------------|------------|
| | | | | | °C | μS/cm | ppm | mg/L | m ³ /seg | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | |
| Cincel River | | | | | | | | | | | | | | | | | | | | |
| CR-1-DS | 6/13/2013 | 22 40 58.5 | 66 08 11 | 6.99 | 5.8 | 152.8 | n.d. | 2.3 | 0.52 | 13.7 | 1.81 | 10.9 | 2.9 | 10.92 | 4.34 | 80.52 | < 0.08 | <0.2 | < 0.08 | HCO3-Na |
| CR-1-DS | 5/1/2015 | 22 40 58.5 | 66 08 11 | 9.15 | 17.7 | 139.7 | 53.5 | n.d. | 0.20 | 14.4 | 2.61 | 9.86 | 2.77 | 14.3 | 5.5 | 56.0 | < 0.05 | < 0.04 | < 0.05 | HCO3-Na |
| CR-1-DS | 5/8/2017 | 22 40 56 | 66 08 12.1 | 8.23 | 12.7 | 165 | 87 | 8.1 | 0.13 | 16.7 | 2.90 | 11.8 | 3.16 | 21.3 | 7.08 | 63.7 | 0.01 | < 0.04 | 0.09 | HCO3-Na |
| CR-2-DS | 6/13/2013 | 22 40 53.9 | 66 07 52.9 | 7.19 | 9 | 311.0 | n.d. | n.d. | 0.53 | 15.6 | 1.93 | 12.4 | 3.11 | 12.21 | 7.1 | 73.2 | <0.08 | <0.2 | <0.08 | HCO3-Na |
| CR-2-DS | 5/1/2015 | 22 40 53.9 | 66 07 52.9 | 8.94 | 13.6 | 163 | 61.5 | n.d. | 0.27 | 16.4 | 2.82 | 12.1 | 3.14 | 15.6 | 6.7 | 62.3 | < 0.05 | 0.14 | < 0.05 | HCO3-Na |
| CR-2-DS | 5/8/2017 | 22 40 51.3 | 66 07 53.6 | 8.40 | 10.2 | 181 | 95 | 8.4 | 0.14 | 17.9 | 2.92 | 12.9 | 3.34 | 21.5 | 7.82 | 67.2 | 0.02 | <0.04 | 0.12 | HCO3-Na |
| CR-3-DS | 6/13/2013 | 22 31 44.4 | 65 58 47.8 | 6.94 | 10.0 | 416.6 | n.d. | n.d. | 0.06 | 21.2 | 2.89 | 16.9 | 4.06 | 16.83 | /.82 | 106.14 | <0.08 | 1./ | <0.08 | HCO3-Na |
| CR-3-DS | 5/11/2017 2/21/2011 | 22 31 44.4 | 65 58 47.8 | 8.07 | 10.8 | 315 | 168 n.d | 9.2 o | Almost U | 23.0 | 4.83 | 31.3 | 0.05 | 32.0 | 12.8 | 140 76 25 | 0.01 p.d | <0.04 | 0.12 n.d | HCO3-Ca Na |
| CR 5 W/S | 2/21/2011 | 22 30 30.1 | 65 50 40 22 | 7.50 | 16.5 | 160.7 | n.d. | 68 | n.u. | 12.06 | 2.59 | 0.4 | 2.01 | 0 | 5 | 70.23 | n.d. | n d | n d | HCO3 No |
| CR-5-DS | 6/14/2013 | 22 28 24.18 | 65 59 40 22 | 9.03 | 12.8 | 3166 | n d | n.d | 0.25 | 27.7 | 5.09 | 5.4 27 | 6.37 | 40.91 | 15.08 | 113 521 | 1 16 | <0.2 | <0.08 | HCO3-Na |
| CR-5-DS | 5/4/2015 | 22 28 24 18 | 65 59 40 22 | 8.52 | 5.8 | 290.3 | 110 | n d | 0.12 | 24.8 | 4 2 9 | 25.2 | 6.12 | 39.9 | 13.00 | 923 | 2.96 | <0.2 | <0.00 | HCO3-Ca-Na |
| CR-5-DS | 12/6/2016 | 22 28 24.18 | 65 59 40 22 | 9.20 | 25.4 | 253 | 133 | 8.8 | Almost 0 | 23.2 | 5.13 | 20.2 | 4 5 3 | 28.5 | 10.3 | 92.6 | 1.08 | <0.04 | 0.05 | HCO3-Na |
| CR-5-DS | 5/12/2017 | 22 28 24.18 | 65 59 40.22 | 8.26 | 9.1 | 210 | 110 | 7.9 | 0.08 | 23.1 | 4.76 | 20.5 | 4.64 | 30.1 | 12.8 | 92.9 | 2.57 | < 0.04 | 0.18 | HCO3-Na |
| CR-6-DS | 6/14/2013 | 22 26 11.7 | 65 58 46.9 | 8.57 | 12.4 | 338.3 | n.d. | n.d. | 0.26 | 29.4 | 5.33 | 28.6 | 6.9 | 41.63 | 15.69 | 124.44 | 1.21 | 1.43 | 0.23 | HCO3-Na-Ca |
| CR-7-DS | 6/14/2013 | 22 24 46.1 | 65 58 35.85 | 8.67 | 8.2 | 352.4 | n.d. | n.d. | n.d. | 30.3 | 5.73 | 29.5 | 7.31 | 45.05 | 17.92 | 126.08 | 0.57 | 1.98 | < 0.08 | HCO3-Na-Ca |
| CR-7-DS | 12/5/2016 | 22 24 43.1 | 65 58 39.7 | 9.52 | 28.6 | 267 | 140 | n.d. | n.d. | 23.9 | 6.03 | 21.0 | 4.57 | 29.9 | 11.1 | 97.9 | < 0.05 | < 0.04 | 0.19 | HCO3-Na |
| CR-7-DS | 5/9/2017 | 22 24 44 | 65 58 42.5 | 8.05 | 14.4 | 255 | 135 | 9.2 | 0.00 | 22.6 | 4.81 | 21.6 | 4.84 | 31.2 | 12.7 | 96.7 | 2.55 | < 0.04 | 0.19 | HCO3-Na |
| C 1 1 D | | | | | | | | | | | | | | | | | | | | |
| Candado Rive | 2F | 22 41 04 75 | 66.00.12 | 0.70 | 10.4 | 2277 | | | 0.10 | 24.0 | 2.20 | 17.0 | 2.00 | 20.15 | 12.00 | 04.001 | 0.21 | 0.04 | .0.00 | LICO2 No |
| Cak-1-DS | 6/13/2013 | 22 41 04.75 | 66 08 12 | 8.72 | 10.4 | 237.7 | n.a. | n.a. | 0.16 | 24.9 | 2.28 | 17.9 | 3.80 | 20.15 | 13.80 | 94.001 | 0.21 | 0.84 | <0.08 | HCO3-Na |
| CaR-1-DS | 5/1/2015 | 22 41 04.75 | 66 08 12 66 08 14 F | 8.54 | 17.3 | 233.1 | 93 | n.a. | 0.10 | 23.5 | 3.00 | 18.8 | 4.33 | 21.1 | 12.8 | 85.5 | <0.05 | 0.27 | < 0.05 | HCO3-Na |
| Car-1-DS | 5/8/2017 | 22 41 02.4 | 00 08 14.5 | 8.70 | 12.5 | 249 | 151 | 9.1 | 0.02 | 24.0 | 5.25 | 21.5 | 4.57 | 24.0 | 10.5 | 101 | 0.02 | <0.04 | 0.14 | HCO3-Na |
| Santa Catalin | a River | | | | | | | | | | | | | | | | | | | |
| SCatR-1-DS | 5/10/2017 | 21 57 22.7 | 66 03 21.6 | 7.24 | 10 | 227 | 120 | 9.6 | 0.10 | 16.1 | 2.48 | 16.7 | 7.38 | 48.6 | 14.7 | 48.1 | 0.02 | < 0.04 | 0.12 | SO4-Ca-Na |
| SCatR-2-DS | 5/10/2017 | 21 55 50.7 | 66 03 10.8 | 8.42 | 13.8 | 227 | 115 | 10.6 | 0.21 | 16.1 | 2.43 | 15.8 | 6.69 | 47.3 | 14.4 | 45.3 | 0.01 | < 0.04 | 0.13 | SO4-Na-Ca |
| SCatR-3-DS | 12/6/2016 | 22 17 25.4 | 65 59 15 | 8.40 | 21.9 | 412 | 218 | 6 | Almost 0 | 25.1 | 4.88 | 31.7 | 10.0 | 101 | 21.5 | 47.4 | 5.53 | 0.22 | 0.16 | SO4-Ca |
| SCatR-3-DS | 5/12/2017 | 22 17 25.4 | 65 59 15 | 7.65 | 8.9 | 448 | 236 | 9.8 | 0.00 | 47.6 | 6.13 | 40.7 | 14.2 | 83.2 | 49.7 | 142 | 0.02 | < 0.04 | 0.27 | HCO3-Na |
| Colmavito st | ream | | | | | | | | | | | | | | | | | | | |
| CoStr-DS | 5/8/2017 | 22 39 58 1 | 66 11 19 6 | 8 14 | 69 | 280 | 146 | 8 | x | 177 | 4 63 | 25.4 | 5 71 | 574 | 11 5 | 66.9 | 0.03 | <0.04 | 0.15 | HCO3-Ca |
| 00011 20 | 0,0,2011 | 22 30 5011 | 00111010 | 0111 | 0.0 | 200 | 1.10 | 0 | | | 1105 | 2011 | 5171 | 5711 | 1110 | 0010 | 0.05 | 010 1 | 0110 | nees ea |
| Chajarahuaic | o River | | | | | | | | | | | | | | | | | | | |
| ChR-DS | 5/8/2017 | 22 40 28.2 | 66 11 10.8 | 7.25 | 14.8 | 139 | 73 | 8.6 | 0.13 | 15.9 | 2.37 | 9.22 | 2.63 | 12.1 | 5.64 | 64.1 | 0.01 | < 0.04 | 0.07 | HCO3-Na |
| Lopiara River | | | | | | | | | | | | | | | | | | | | |
| LopR-DS | 5/8/2017 | 22 40 17.1 | 66 10 40.4 | 7.53 | 16.4 | 208 | 110 | 8.6 | 0.04 | 17.7 | 3.20 | 15.2 | 4.88 | 44.2 | 7.84 | 51.9 | 0.21 | < 0.04 | 0.14 | HCO3-Na |
| | -,-, | | | | | | | | | | | | | | | | | | | |
| Colquimayo I | River | | | | | | | | | | | | | | | | | | | |
| ColR-DS | 5/11/2017 | 22 31 40.8 | 66 12 7.5 | 8.23 | 12.3 | 271 | 143 | 10.2 | 0.05 | 33.6 | 2.98 | 16.7 | 6.97 | 40.1 | 16 | 123 | 0.01 | < 0.04 | 0.17 | HCO3-Na |
| Guavatavoc F | River | | | | | | | | | | | | | | | | | | | |
| G-DS | 5/12/2017 | 22 16 06.7 | 66 02 01.0 | 7.61 | 7.5 | 242 | 127 | 10.6 | 0.10 | 15.9 | 1.68 | 15.9 | 14.0 | 90.7 | 12.7 | 28.0 | 0.01 | < 0.04 | 0.16 | SO4-Ca-Na |
| | | | | | | | | | | | | | | | | | | | | |
| Peñas Blanca | s River | | | | | | | | | | | | | | | | | | | |
| PBR-1-WS | 3/27/2012 | 22 35 32.3 | 66 03 30.8 | 8.71 | 21.3 | 325.5 | n.d. | 7.5 | n.d. | 29.2 | 6.07 | 22.2 | 4.71 | 27.2 | 28.9 | 124.44 | < 0.01 | 0.1 | 0.22 | HCO3-Na |
| PBR-2-WS | 3/27/2012 | 22 35 25.65 | 66 3 24.31 | 8.36 | 15.5 | 297.1 | n.d. | n.d. | n.d. | 32.3 | 6.32 | 24 | 5.29 | 29.7 | 31.9 | 120 | < 0.01 | 0.1 | 0.15 | HCO3-Na |
| Los Pozuelos | Lagoon | | | | | | | | | | | | | | | | | | | |
| PL-1-DS | 6/14/2013 | 22 24 49.4 | 65 58 48.1 | 7.03 | 15 | 1589.7 | n.d. | n.d. | х | 236 | 24.8 | 54 | 17 | 145.37 | 308.09 | 175.68 | < 0.08 | <0.2 | < 0.08 | Cl-Na |
| PL-1-DS | 12/14/2016 | 22 23 55.6 | 65 59 54.5 | 7.98 | 25.2 | 365 | 190 | 8.2 | х | 33.5 | 8.63 | 24.9 | 5.41 | 40.9 | 19.3 | 116 | < 0.05 | 0.22 | 0.19 | HCO3-Na |
| PL-1-DS | 5/9/2017 | 22 24 53.4 | 65 59 37.4 | 9.74 | 14.4 | 344 | 182 | 10.1 | х | 40.9 | 9.30 | 23.0 | 2.84 | 70.0 | 24.1 | 74.1 | 0.07 | < 0.04 | 0.38 | HCO3-Na |
| PL-2-DS | 5/3/2015 | 22 24 49.4 | 65 58 48.1 | 8.68 | 15.5 | 5660 | n.d. | n.d. | х | 990 | 97.2 | 113 | 53.4 | 594.8 | 1353.1 | 337.8 | < 0.05 | 2.13 | 4.0 | Cl-Na |
| PL-2-DS | 12/5/2016 | 22 24 56.3 | 65 59 20.6 | 9.69 | 18.9 | 288 | 150 | n.d. | х | 29.1 | 7.25 | 21.8 | 3.69 | 35.7 | 14.5 | 96 | < 0.05 | 0.22 | 0.21 | HCO3-Na |
| PL-3-DS | 5/3/2015 | 22 24 40.5 | 66 00 57.1 | 8.71 | 15.7 | 5460 | n.d. | n.d. | х | 988 | 95 | 112 | 52.9 | 536.7 | 1346.0 | 311.7 | < 0.05 | 1.28 | 4.2 | Cl-Na |

TDS = total dissolved solids.DO = dissolved oxygen.



Fig. 3. Piper diagram for surface waters and groundwater in Los Pozuelos basin.

ICP-OES (PerkinElmer 7300 DV) for cations and IC (Dionex DX 600) for anions. Alkalinity was determined in the laboratory by automated titration (Thermo, 940-960 autotitrator) using standardized 0.01 N $\rm H_2SO_4$.

3.1.1.2. Fe and As redox speciation (collection, preservation and analysis). The samples from 2011, 2012, and 2013 were only analyzed for Fe (T) and As(T) by ICP-MS as described in Section 3.1.1.1, while samples for iron and arsenic redox species (Fe(T), Fe(II), As(T), As(III)) were sampled in the sampling campaign of 2015, 2016 and 2017. These samples were filtered with 0.2 μ m HV (Millex) filtration units by using a syringe in some cases and with polyethersulfone (GVS) 0.2 and 0.45 μ m membrane filters using a filter holder (Thermo Scientific) and manual pump. Preservation of arsenic species was made by adding 1% (ν/ν) 6 M HCl to the sample preserved in opaque polyethylene bottles (125-mL) which were previously soaked in 5% HCl and rinsed 3 times with deionized water. The samples were immediately stored in a cooler at 4 °C after sampling and in refrigerator until analysis.

Iron and arsenic redox species were determined at the U.S. Geological Survey (Boulder, Colorado) laboratories. Total dissolved iron (Fe(T)) and ferrous iron (Fe(II)) concentrations were measured by the colorimetric FerroZine method (To et al., 1999) with a Hewlett Packard 8453 diode array UV/VIS spectrophotometer. Total dissolved arsenic (As(T)) and dissolved arsenite (As(III)) concentrations were determined with a Perkin Elmer (FIAS 100) hydride generation atomic absorption spectrometry system (HG-AAS) using the method described by McCleskey et al. (2003).

3.1.1.3. Geochemical modeling and statistical treatment of the data. Saturation indices for water samples were calculated with PHREEQC.v3 (Parkhurst and Appelo, 2013). The statistical analysis of the data consisted in calculations of mean, maximum, minimum, and range values. Ions rates (Na/K) were also calculated. 3.1.2. Lacustrine sediments and secondary minerals samples

One sediment sample (LS-1) of 1 kg weight was taken in the south area of the Los Pozuelos lagoon in the dry season of 2013 next to the lagoon water sampling site (PL-1-2013) (Fig. 1 D). The sediments were preserved in a cooler at 4 °C after sampling and immediately dried at room temperature and fractioned for analysis. In the laboratory USGS (Boulder, Colorado) the sediments were completely digested and total arsenic was analyzed by HG-AAS with a Perkin Elmer (FIAS 100). Three different certified standard reference materials (SRM-Mess-1 (Canadian), SRM-2702-Marine sediments (NIST), and SRM-8704 Buffalo river sediment (NIST)) were used. The detection limit for As was 0.25 mg/kg.

In the dry season of 2015 200 g samples of fine fluvial sediments with abundant secondary iron precipitates were taken from SM-1 and SM-2 sites in Peñas Blancas River flood plain (Fig. 1 C). The samples were preserved in a cooler at 4 °C after sampling and immediately dried at room temperature and fractioned for analysis. These samples were digested and analyzed for total As with the same procedure described above for the lacustrine sediments. These samples were also analyzed by quantitative XRD at USGS Boulder laboratories with a Siemens D500 X-ray diffractometer from 5° to 65° 20 using Cu K α (λ = 1.54056 Å) X-ray radiation with a step size of 0.02° and a dwell time of 2 s per step. Quantitative mineralogy was calculated using the USGS software, RockJock (Eberl, 2003), which fits XRD intensities of individual mineral standards to the measured diffraction pattern.

Moreover, samples of efflorescent salts were taken in Peñas Blancas River (SM-3) and in the surface of soils in the vicinity of W8 well (SM-4) (Fig. 1 C). The samples were taken with plastic spoons and preserved in sealed polyethylene tubes in a refrigerator under dark conditions to prevent changes by oxidation and/or dehydration. These samples were analyzed by qualitative XRD at USGS Boulder laboratories with a Siemens D500 X-ray diffractometer from 5° to 65° 20 using Cu K α (λ = 1.54056 Å) X-ray radiation with a step size of 0.02° and a dwell time of 2 s per step. The mineralogy was identified using Jade software (MDI, version

| Та | bl | le | 2 | |
|----|----|----|---|--|
| | | | | |

Surface water samples, arsenic and iron content and speciation.

| Sample Date | As(T) | As(III) | As(V) | Fe(T) | Fe(II) | Fe(III) |
|-------------------------|-------------------|-----------|-------------------|----------------------|------------------|------------------|
| | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L |
| Cincel River | | | | | | |
| CR-1-DS 6/13/2013 | 4.57 | n.d. | n.d. | <100 | n.d. | n.d. |
| CR-1-DS 5/1/2015 | 3.5 | <1 | 3.5 | 9.5 | 7.8 | 1.7 |
| CR-1-DS 5/8/2017 | 7.33 | 1.9 | 5.43 | 10 | 8 | 2 |
| CR-2-DS 6/13/2013 | <mark>5.55</mark> | n.d. | n.d. | <mark><100</mark> | n.d. | n.d. |
| CR-2-DS 5/1/2015 | <mark>4.8</mark> | <1 | <mark>4.8</mark> | <mark>6.9</mark> | <mark>6.5</mark> | 0.4 |
| CR-2-DS 5/8/2017 | <mark>7.58</mark> | 0.5 | <mark>7.08</mark> | 6 | <mark>6</mark> | 0 |
| CR-3-DS 6/13/2013 | 7.49 | n.d. | n.d. | <100 | n.d. | n.d. |
| CR-3-DS 5/11/2017 | 12.1 | 0.3 | 11.8 | 11 | 11 | <mark>0</mark> . |
| CR-4-WS 2/21/2011 | 5.13 | n.d. | n.d. | 30 | n.d. | n.d. |
| CR-5-DS 6/14/2013 | 13.9 | n.d. | n.d. | <100 | n.d. | n.d. |
| CR-5-WS 2/21/2011 | 7.03 | n.a. | n.a. | 10 | n.a. | n.a. |
| CR-5-DS 5/12/2017 | 20.2 | 0 | 10 2 | 10 | 10 | 0 |
| $CR_{-5}-DS = 5/4/2015$ | 1.8 | 0.9 <1 | 19.5 | 07 | 03 | 05 |
| CR-6-DS = 6/14/2013 | 1.0 | n d | n.d | <100 | n.d | n d |
| CR-7-DS 6/14/2013 | 17.8 | n d | n d | <100 | n d | n d |
| CR-7-DS 5/9/2017 | 18.5 | 0.5 | 18 | 9 | 7 | 2 |
| CR-7-DS 12/5/2016 | 20.3 | 1.3 | 19 | 32 | 31 | 1 |
| | | | | | | |
| Candado River | 11.0 | | 1 | 100 | | |
| CaR-1-DS 6/13/2013 | 11.3 | n.d. | n.d. | <100 | n.d. | n.d. |
| CaR-1-DS 5/1/2015 | 7.9 | 7.9 | 10.0 | 7.4 | 7.1 | 0.4 |
| CdR-1-DS 5/8/2017 | 17 | 0.3 | 10.7 | Э | Э | 0 |
| Santa Catalina River | | | | | | |
| SCatR-1-DS 5/10/2017 | 1.81 | <0.3 | 1.81 | 19 | 19 | 0 |
| SCatR-2-DS 5/10/2017 | 1.46 | <0.3 | 1.46 | 23 | <2 | 23 |
| SCatR-3-DS 12/6/2016 | <1 | n.d. | n.d. | 117 | 0 | 117 |
| SCatR-3-DS 5/12/2017 | 2.09 | 1.9 | 0.19 | 10 | 10 | 0 |
| Colmayito Stream | | | | | | |
| CoStr-DS 5/8/2017 | 5.03 | 0.6 | 4.43 | 23 | 19 | 4 |
| Chajarahuaico Pivor | | | | | | |
| ChR-DS 5/8/2017 | 621 | 03 | 5 91 | 15 | 15 | 0 |
| 0,0,2017 | 0121 | 0.0 | 0.01 | 10 | 10 | U |
| Lopiara River | | | | | | |
| LopR-DS 5/8/2017 | 4.29 | <0.3 | 4.29 | 12 | 12 | 0 |
| Colquimayo River | | | | | | |
| ColR-DS 5/11/2017 | 6.47 | <0.3 | 6.47 | 13 | 13 | 0 |
| Cuertana Diner | | | | | | |
| CR_DS 5/12/2017 | 1.61 | <03 | 1.61 | 94 | 53 | /11 |
| GR-D3 J/12/2017 | 1.01 | <0.5 | 1.01 | 54 | 55 | 41 |
| Peñas Blancas River | | | | | | |
| PBR-1-WS 3/27/2012 | 22.8 | n.d. | n.d. | 210 | n.d. | n.d. |
| PBR-2-WS 3/27/2012 | 27 | n.d. | n.d. | 90 | n.d. | n.d. |
| Los Pozuelos Lagoon | | | | | | |
| PL-1-DS 6/14/2013 | 47.5 | n.d. | n.d. | <100 | n.d. | n.d. |
| PL-1-DS 12/14/2016 | 45.2 | 1.9 | 43.3 | 26 | 26 | 0 |
| PL-1-DS 5/9/2017 | 56.5 | 3.7 | 52.8 | 21 | 21 | 0 |
| PL-2-DS 5/3/2015 | 200.3 | 89.5 | 110.8 | 111.8 | 109.6 | 2.2 |
| PL-2-DS 12/5/2016 | 43.7 | 2.2 | 41.5 | 215 | 210 | 5 |
| PL-3-DS 5/3/2015 | 149.4 | 133.7 | 15.7 | 133.9 | 128.7 | <mark>5.2</mark> |

n.d. = not determined.

9) and the International Centre for Diffraction Data (ICDD) 2003 database.

4. Results and discussion

4.1. Hydrogeological and geochemical characterization of surface waters and groundwater in Pozuelos basin

4.1.1. Rivers

Cincel and Santa Catalina are the most important rivers in Pozuelos basin, their headwaters are in the south and northwest areas of the basin, respectively, discharging their waters into Los Pozuelos lagoon (Fig. 1). The Cincel River is the main source of surface water to the lagoon. The discharge of the rivers was mainly measured in the dry season when the field conditions permit access to most of the sites. In the headwaters of the Cincel River the discharge is permanent and vary between 0.13 and 0.52 m^3/s , but in the mid areas of the basin there is infiltration with very low to no discharge (Table 1). The runoff increases again in the vicinity of the lagoon with values between 0.08 and 0.26 m^3/s . In the headwaters of Santa Catalina River, the discharge was measured before and after the town of Santa Catalina with values of 0.10 and 0.21 m³/s respectively. In the mid areas of the basin there is also infiltration and its runoff increases again at the lagoon discharge with extremely low flow velocity. During the wet season, runoff increases all along the rivers. The discharge values for Santa Catalina and Cincel Rivers were measured previously between 1992 and 1996 by Paoli et al. (2011). Similar values were determined in the headwaters of Santa Catalina River for dry season (0.3 m³/s) while a strong increment was measured for wet season (0.9 m³/s). In Cincel River the discharge measurements were made in the proximity of Pan de Azúcar mine showing also low values for dry season (0.1 m^3/s) and higher values in wet season $(0.5 \text{ m}^3/\text{s})$ (Paoli et al., 2011).

The pH values observed in rivers have a mean value of 8.16. In general, the tendency is that the pH increases from the headwater of the rivers to its discharge in the lagoon. This trend is likely caused by calcite dissolution with some enhancement from evaporation. The mean value for calcite saturation indices in rivers is -0.89. For sites CR-5, CR-6, and CR-7 in the Cincel River, close to the discharge to the lagoon, the mean of calcite saturation indices is 0.21. The conductivity increases from the headwaters of the rivers to the center of the basin. The headwaters of the Cincel and Santa Catalina Rivers show the lowest conductivity values of 139.7 and 227 µS/cm respectively, which increase in the discharge to the lagoon to a maximum of 352 and 448 µS/cm respectively (Table 1).

The Piper diagram for river waters can be seen in Fig. 3. The water type of most of the rivers is mainly Na-HCO₃ with increments in Ca in some cases (Table 1). Sodium is the dominant cation, with concentrations from 13.7 to 47.6 mg/L (Table 1). This water type is common during weathering of crystalline bedrock in arid environments. In general, $HCO_3 > SO_4 > Cl > F > NO_3 > PO_4$ and Na > Ca > Mg > K. However, Santa Catalina River has a composition which is mainly Ca-Na-SO₄ as well as Guayatayoc River (GR-DS) (Table 1). Total iron concentration in rivers is low and varies between 5 and 210 µg/L, when measured, the concentration of ferrous iron (Fe(II)) is higher than ferric iron (Fe (III)), except for Santa Catalina River (SCatR-2-DS; SCatR-3-DS) (Table 2). Guayatayoc and Peñas Blancas Rivers, show some of the highest iron concentrations in the basin (94 µg/L and 90-210 µg/L respectively), probably related to oxidizing sulfide sources. In Guayatayoc River sulfide (i.e. pyrite) mineralized shales were observed in the fluvial sediments during the sampling campaigns.

4.1.2. Groundwater

The water table in the sampled wells varied between 1 and 7 m depth in the dry season, to 0.2–2.5 m depth in the wet season. The wells located in the upper to middle areas of the basin (W1, W2, W3, W4, W5, W7, W11, W12, W13, W15, W16) are situated on Pleistocene - Holocene coarse alluvial-alluvial fan deposits (Fig. 1). Wells located in the middle to lower area of the basin (W6, W8, W9, W14) are situated on the lacustrine lagoon deposits.

The pH of groundwater is circumneutral to basic with a mean value of 7.55. The conductivity ranges between 131 and 1355 μ S/cm increasing from the upstream wells to the lower area of the basin (Table 3). The composition of groundwater is mainly Ca-HCO₃ and Na-HCO₃ (Fig. 3). In general, HCO₃ > SO₄ > Cl > F > NO₃ > PO₄ and Ca > Na > Mg > K. However, some wells show a composition where SO₄ increases in some periods, like well W4. During the dry season of 2013 where the W4 composition is Ca-SO₄ suggesting dissolution of gypsum, the gypsum saturation index calculated is -1.59. For well W9, the composition changes from Na-HCO₃ to Na-SO₄ during the dry season of 2013 and 2015. The increase in SO₄, Na, and TDS from high to low basin reflects

 Table 3

 Groundwater samples, field parameters and major ions.

| Sample | Sampling date | Lat | Long | pН | Т | Cond. | TDS | DO | Depth | Na | К | Ca | Mg | S04 | Cl | HCO3 | NO3 | PO4 | F | Water-type | Aquifer facies |
|--------|---------------|------------|------------|------|------|-------|------|------|-------|-------|------|-------|------|-------|-------|-------|--------|--------|---------|------------|----------------|
| | | S | W | | °C | µS/cm | ppm | mg/L | m | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | | |
| W1-DS | 6/14/2013 | 22 40 04.4 | 66 08 19.8 | 6.98 | n.d. | 612 | n.d. | n.d. | 1.6 | 74.7 | 11.1 | 42.7 | 11.4 | 78.3 | 34.8 | 190.3 | 2.6 | 2.17 | < 0.08 | HCO3-Na | AD |
| W2-WS | 3/28/2012 | 22 37 59.6 | 66 03 01.1 | 6.94 | n.d. | 348 | 235 | 2.2 | 0.2 | 27.8 | 5.1 | 29.0 | 9.0 | 44.6 | 17.8 | 98.8 | 0.5 | 0.06 | 0.07 | HCO3-Ca | AD |
| W2-DS | 6/13/2013 | 22 37 59.6 | 66 03 01.1 | 7.81 | 7.1 | 310 | 248 | n.d. | 1.1 | 25.5 | 4.3 | 27.5 | 8.1 | 32.4 | 17.9 | 102.5 | < 0.08 | 2.59 | < 0.08 | HCO3-Ca | AD |
| W4-DS | 6/14/2013 | 22 33 53.2 | 66 01 18.9 | 8.38 | 10.7 | 631 | 316 | n.d. | 1.8 | 39.6 | 6.6 | 60.6 | 21.0 | 121.3 | 36.1 | 106.1 | 35.3 | 1.48 | < 0.08 | SO4-Ca | AD |
| W5-DS | 6/14/2013 | 22 33 32.0 | 66 1 30.49 | 6.89 | n.d. | 624 | n.d. | n.d. | 2.2 | 27.4 | 4.5 | 59.0 | 22.6 | 46.8 | 79.5 | 87.8 | 45.4 | 2.9 | 0.23 | HCO3-Ca | AD |
| W5-DS | 5/3/2015 | 22 33 32.0 | 66 1 30.49 | 6.7 | 13.4 | 510 | 255 | n.d. | 1.9 | 23.3 | 4.2 | 50.4 | 17.3 | 52.0 | 51.1 | 89.6 | 50.5 | 1.88 | 0.54 | HCO3-Ca | AD |
| W5-DS | 5/12/2017 | 22 33 32.0 | 66 1 30.49 | 7.58 | 12.7 | 744 | 393 | 4.2 | 3.0 | 29.0 | 5.9 | 70.9 | 25.7 | 66.6 | 97.4 | 87.2 | 98.9 | 1.16 | 0.28 | HCO3-Ca | AD |
| W7-DS | 6/16/2013 | 22 32 20.5 | 65 57 41.9 | 7.02 | n.d. | 233 | n.d. | n.d. | n.d. | 8.7 | 4.0 | 27.9 | 7.9 | 17.1 | 9.6 | 84.2 | 3.0 | 1.29 | < 0.08 | HCO3-Ca | AD |
| W12-DS | 5/12/2017 | 22 29 59.9 | 66 02 39.6 | 7.96 | 11.8 | 131 | 69 | 7.3 | 3.4 | 10.7 | 2.7 | 13.5 | 3.4 | 18.0 | 7.3 | 47.1 | 10.9 | < 0.04 | 0.23 | HCO3-Ca | AD |
| W13-DS | 12/6/2016 | 22 27 51.4 | 66 04 24.3 | 8.46 | 17.7 | 204 | 108 | n.d. | 7.5 | 12.2 | 1.7 | 18.5 | 5.2 | 26.9 | 9.8 | 56.3 | 10.1 | 0.20 | 0.06 | HCO3-Ca | AD |
| W13-DS | 5/9/2017 | 22 27 51.4 | 66 04 24.1 | 7.48 | 13.2 | 197 | 104 | 6.5 | 7.4 | 13.1 | 1.7 | 16.8 | 5.1 | 26.9 | 9.5 | 58.2 | 8.4 | 0.26 | 0.11 | HCO3-Ca | AD |
| W15-DS | 5/10/2017 | 22 17 46.4 | 65 54 59.3 | 7.26 | 12.3 | 645 | 343 | n.d. | n.d. | 58.8 | 5.3 | 57.5 | 14.9 | 142.0 | 26.8 | 185.0 | 8.0 | < 0.04 | 0.17 | HCO3-Ca | AD |
| W16-DS | 5/10/2017 | 22 02 56.9 | 65 55 04.3 | 7.7 | 14.2 | 156 | 84 | 6.9 | 2.5 | 9.6 | 2.3 | 12.5 | 5.0 | 19.9 | 6.2 | 49.9 | 7.0 | 0.31 | 0.09 | HCO3-Ca | AD |
| W6-WS | 2/21/2011 | 22 31 08.7 | 66 00 47.2 | 7.9 | 15.1 | 867 | 318 | 4.3 | 2.5 | 45.5 | 32.1 | 81.7 | 20.7 | 104.6 | 123.9 | 127.5 | n.d. | n.d. | < 0.3 | HCO3-Ca | LS |
| W6-DS | 6/14/2013 | 22 31 08.7 | 66 00 47.2 | 7.53 | n.d. | 737 | n.d. | n.d. | 2.1 | 35.3 | 18.0 | 83.4 | 17.3 | 102.4 | 63.7 | 157.4 | 22.4 | 0.93 | 0.21 | HCO3-Ca | LS |
| W6-DS | 5/3/2015 | 22 31 08.7 | 66 00 47.2 | 7.63 | 16.6 | 977 | 489 | n.d. | 2.2 | 49.6 | 50.9 | 93.4 | 21.1 | 83.3 | 75.3 | 234.1 | 119.5 | 1.89 | 0.15 | HCO3-Ca | LS |
| W8-WS | 2/21/2011 | 22 30 23.2 | 65 59 46.8 | 7.9 | 15.8 | 1141 | 584 | 2.9 | 2.0 | 62.1 | 70.6 | 101.6 | 26.1 | 114.4 | 163.5 | 178.0 | n.d. | n.d. | n.d. | HCO3-Ca | LS |
| W8-DS | 6/14/2013 | 22 30 23.2 | 65 59 46.8 | 6.84 | n.d. | 252 | n.d. | n.d. | 1.0 | 6.1 | 44.1 | 12.7 | 3.8 | 23.1 | 5.0 | 73.2 | 13.1 | 8.16 | < 0.08 | НСОЗ-К | LS |
| W8-DS | 5/3/2015 | 22 30 23.2 | 65 59 46.8 | 7.78 | 14.6 | 288 | 144 | n.d. | 1.5 | 7.3 | 48.9 | 12.7 | 4.2 | 23.9 | 5.1 | 78.6 | 25.1 | 10.88 | < 0.05 | HCO3-K | LS |
| W9-WS | 2/21/2011 | 22 28 23.2 | 65 59 37.4 | 7.3 | 13.9 | 969 | 438 | 2.7 | n.d. | 93.3 | 9.4 | 76.1 | 19.3 | 172.1 | 104.1 | 178.1 | n.d. | n.d. | < 0.3 | HCO3-Na | LS |
| W9-DS | 6/14/2013 | 22 28 23.2 | 65 59 37.4 | 7.45 | n.d. | 1355 | n.d. | n.d. | 1.9 | 112.0 | 11.8 | 144.0 | 29.4 | 399.5 | 119.5 | 120.8 | 3.6 | <0.2 | < 0.08 | SO4-Na | LS |
| W9-DS | 5/2/2015 | 22 28 23.2 | 65 59 37.4 | 7.12 | 12.9 | 843 | 422 | n.d. | n.d. | 81.7 | 9.6 | 78.2 | 16.0 | 223.7 | 40.2 | 171.2 | 5.8 | < 0.04 | < 0.05 | SO4-Na | LS |
| W9-DS | 12/6/2016 | 22 28 23.2 | 65 59 37.4 | 7.95 | 14.6 | 650 | 342 | n.d. | 2.0 | 61.4 | 7.0 | 42.5 | 8.5 | 128.0 | 19.4 | 147.0 | 6.8 | < 0.04 | 0.22 | HCO3-Na | LS |
| W9-DS | 5/11/2017 | 22 28 23.2 | 65 59 37.4 | 7.65 | 11.6 | 478 | 254 | 4.8 | 2.1 | 56.7 | 6.3 | 32.8 | 7.0 | 91.5 | 15.4 | 151.0 | 7.6 | < 0.04 | 0.32 | HCO3-Na | LS |
| W11-DS | 5/12/2017 | 22 30 12.6 | 66 01 49.1 | 7.79 | 10.1 | 213 | 113 | 5.4 | 1.8 | 12.6 | 4.1 | 23.5 | 4.4 | 20.3 | 8.7 | 91.0 | 4.0 | 0.93 | 0.24 | HCO3-Ca | LS |
| W14-DS | 12/14/2016 | 22 27 54.2 | 66 0 41.6 | 8.05 | 14.9 | 213 | 109 | 7.1 | 2.0 | 18.7 | 7.6 | 13.7 | 2.8 | 16.6 | 11.9 | 69.9 | 5.7 | 0.28 | 0.14 | HCO3-Na | LS |
| W14-DS | 5/9/2017 | 22 27 54.5 | 66 0 41.3 | 7.78 | 10.1 | 189 | 99 | 5.3 | 0.9 | 19.3 | 7.7 | 11.4 | 2.9 | 15.4 | 12.2 | 68.3 | 5.6 | < 0.04 | 0.22 | HCO3-Na | LS |
| W3-DS | 6/13/2013 | 22 36 17 | 66 04 10 | 7.61 | 11.8 | 251 | 191 | 3.4 | n.d. | 16.1 | 3.8 | 28.9 | 4.5 | 22.7 | 8.1 | 91.5 | 7.7 | <0.2 | < 0.08 | HCO3-Ca | VR |
| CAA | | | | | | | | | | | | | | 400 | 350 | | | | 0.9-1.7 | | |
| WHO | | | | | | | | | | | | | | 500 | | | | | 1.5 | | |

TDS = total dissolved solids.

DO = dissolved oxygen.

AD = aluvial deposits.

LS = lacustrine sediments.

VR = volcanic rocks.

CAA = Código Alimetario Argentino, 2012.

WHO = World Health Organization, 2017.

n.d. = not determined.

Table 4Groundwater samples, arsenic and iron content.

| Sample | Sampling | As | As | As | Fe | Fe | Fe | Aquifer |
|--------|------------|------|-------|------|------|------|-------|---------|
| • | date | (T) | (III) | (V) | (T) | (II) | (III) | facies |
| | | | | | | | | |
| | | ug/I | ug/I | ug/I | ug/I | ug/I | ца/І | |
| | | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L | |
| W1-DS | 6/14/2013 | 16.1 | n.d. | n.d. | <100 | n.d. | n.d. | AD |
| W2-WS | 3/28/2012 | 10.8 | n.d. | n.d. | 100 | n.d. | n.d. | AD |
| W2-DS | 6/13/2013 | 8.9 | n.d. | n.d. | 110 | n.d. | n.d. | AD |
| W4-DS | 6/14/2013 | 21.4 | n.d. | n.d. | <100 | n.d. | n.d. | AD |
| W5-DS | 6/14/2013 | 29.7 | n.d. | n.d. | <100 | n.d. | n.d. | AD |
| W5-DS | 5/3/2015 | 18.4 | <1 | 18.4 | 3 | 2 | 1 | AD |
| W5-DS | 5/12/2017 | 23.1 | 0.5 | 22.6 | 2 | 2 | 0 | AD |
| W7-DS | 6/16/2013 | 14.1 | n.d. | n.d. | 240 | n.d. | n.d. | AD |
| W12-DS | 5/12/2017 | 8.21 | 2.5 | 5.71 | 9 | 9 | 0 | AD |
| W13-DS | 12/6/2016 | 5.2 | <0.8 | 5.2 | <2 | <2 | 0 | AD |
| W13-DS | 5/9/2017 | 6.33 | <0.3 | 6.33 | 12 | 7 | 5 | AD |
| W15-DS | 5/10/2017 | 5.67 | <0.3 | 5.67 | 13 | 2 | 11 | AD |
| W16-DS | 5/10/2017 | 3.82 | 0.4 | 3.42 | 32 | 15 | 17 | AD |
| W6-WS | 2/21/2011 | 55 | n.d. | n.d. | <10 | n.d. | n.d. | LS |
| W6-DS | 6/14/2013 | 54.7 | n.d. | n.d. | <100 | n.d. | n.d. | LS |
| W6-DS | 5/3/2015 | 69.0 | 0.9 | 68.0 | <2 | <2 | 0 | LS |
| W8-WS | 2/21/2011 | 74.3 | n.d. | n.d. | <10 | n.d. | n.d. | LS |
| W8-DS | 6/14/2013 | 113 | n.d. | n.d. | <100 | n.d. | n.d. | LS |
| W8-DS | 5/3/2015 | 90.2 | 1.1 | 89.1 | 1290 | 259 | 1031 | LS |
| W9-WS | 2/21/2011 | 19.9 | n.d. | n.d. | <10 | n.d. | n.d. | LS |
| W9-DS | 6/14/2013 | 16.1 | n.d. | n.d. | <100 | n.d. | n.d. | LS |
| W9-DS | 5/2/2015 | 10.0 | <1 | 10.0 | 8 | 7 | 1 | LS |
| W9-DS | 12/6/2016 | 19.1 | <0.8 | 19.1 | 3 | 2 | 1 | LS |
| W9-DS | 5/11/2017 | 19.6 | 0.6 | 19 | 13 | 9 | 4 | LS |
| W11-DS | 5/12/2017 | 33.6 | 0.7 | 32.9 | 5 | 5 | 0 | LS |
| W14-DS | 12/14/2016 | 12.4 | <0.8 | 12.4 | 2 | 2 | 0 | LS |
| W14-DS | 5/9/2017 | 12.3 | <0.3 | 12.3 | 5 | 5 | 0 | LS |
| W3-DS | 6/13/2013 | 8.2 | n.d. | n.d. | <100 | n.d. | n.d. | VR |
| CAA | ., ., | 50 | | | | | | |
| WHO | | 10 | | | | | | |

AD = aluvial deposits.

LS = lacustrine sediments.

VR = volcanic rocks.

CAA = Código Alimetario Argentino, 2012.

WHO = World Health Organization, 2017.

n.d. = not determined.

the normal evolution of groundwater in closed basins (Eugster and Jones, 1979; Deocampo and Jones, 2014). For well W8, the composition of the groundwater varies from Ca-HCO₃ in wet season to K-HCO₃ in dry season with Na/K rates of 0.2 and 0.3, which is well correlated with the precipitation of Na rich white salts in the surface of the soils in the vicinity of the well W8. These salts are composed of (in decreasing order of abundance) thenardite $(Na_2(SO_4))$ + halite (NaCl) + Eugsterite $(Na_4Ca(SO_4)3\cdot 2(H_2O))$ + scarce calcite $(CaCO_3)$ and gypsum (CaSO₄·H₂O). Efflorescent salts in the flood plain of Peñas Blancas river close to well W4 have a similar composition, in decreasing order of abundance these salts are compose of thenardite + halite + eugsterite + bloedite $(Na_2Mg(SO_4)_2 \cdot 4H_2O)$ + scarce gypsum. Total iron concentration is in general low (2-110 µg/L) except for well W8 where the concentration increases to 1290 µg/L (Table 4). When measured, Fe(II) is the dominant species, except for wells W8, W15, and W16 where the concentration of Fe(III) is higher (Table 4).

4.1.3. Los Pozuelos lagoon

The surface of the lagoon was different in the different sampling dates, with the highest extension in 2013 and 2015 and the lowest in 2016 and 2017 after five years of precipitation below the annual mean (Fig. 4 A, B). Analyzing satellite images of the surface area of the lagoon and the precipitation during the sampling period, surface areas not only vary between dry-wet season, but they strongly depend on the amount of precipitation during summer (Fig. 4 A, B). If the precipitation amount in summer was normal or close to the annual mean, the surface area of the lagoon will not decrease so much by evaporation. Whereas a complete dry out of the lagoon occurred after two or more consecutive

years of low precipitation. This phenomenon was also described by lgarzábal (1978).

Satellite and field observations indicate that during the driest periods, the waterbody of the lagoon depend on the discharge of the Cincel River, being the main source of water to the lagoon (Fig. 4 A).

Previous studies indicate that the salinity of the lagoon varies during the year and is influenced by the seasonal climate (Mirande and Tracanna, 2009; Rodríguez, 2012). Measurements made by Rodríguez (2012) during winter and summer of 2009 indicate alkaline pH (8–10.4), and a wide range of conductivity (219–1281 μ S/cm), the lowest values correspond to wet season and the highest values to dry season. McGlue et al. (2013) measured a high concentration of solutes in the lagoon during the dry season of 2007 with a relatively large surface area. They determined Na-Cl water types, oxygen saturated waters, and basic pH (mean of 8.7).

In this work, the highest conductivity values of 1589 and 5600 µS/cm were measured when the lagoon was completely full in the dry season of periods 2013 and 2015 respectively. At that moment, the dominant ions were Na-Cl and the pH varied between 7.03 and 8.71 (Fig. 4 A). In the periods 2016 and 2017 when the area of the lagoon was reduced and restricted to the proximity of the Cincel River discharge, the conductivity decreased to 288 and 344 µS/cm respectively, with a water type Na-HCO₃. At that time, the pH increased to values between 7.98 and 9.74 (Fig. 4 A). This pH behavior during extreme evaporation years is referred to as the pH divide (Drever, 1997). This phenomenon means that if the water in the lagoon has a pH > 7 ($OH^- > H^+$) and starts evaporating, the pH will steadily increase because the OH⁻ concentration keeps increasing from evaporation. If the initial pH is <7 (H⁺ $> OH^{-}$), the pH will steadily decrease with evaporation. In Fig. 4 C, a plot of Na, Mg, Cl, conductivity and As vs the lagoon surface area was made to evaluate the evaporation effect. It is observed that when the lagoon surface is small the composition of the lagoon is very similar to Cincel River and mainly influenced by the river discharge (see composition of Cincel River in CR-7; Table 1). However, when the surface area of the lagoon increases, as in the periods 2015 and 2013 the effect of evaporation is evident by increasing the concentration of Na, Cl, Mg, conductivity, as well as the pH values in May-2015.

With the present study, we observe that the variation in the physical-chemical parameters of the lagoon is not only related to the annual dry-wet seasonal variation, but also to a larger inter-annual scale process related to drier or wetter years affecting the total surface area of the lagoon and its physical-chemical parameters. In this sense, Magii and Navone (2009) indicate that the inter annual fluctuation of the surface area of the lagoon could be related to the El Niño-Southern Oscillation (ENSO). ENSO is a naturally occurring phenomenon involving fluctuating ocean temperatures in the central and eastern equatorial Pacific, coupled with changes in the atmosphere. This phenomenon has a major influence on climate patterns in various parts of the world and comprises three phases: El Niño (warm), La Niña (cold) and neutral. (World Meteorological Organization, 2014). Magii and Navone (2009), associated the retraction of the lagoon water body in the years 2002-2003 to dry periods during the El Niño 2002-2003. In the present study, the strong retraction of the lagoon observed between 2015 and 2016 (Fig. 4) could be also be related to a strong El Niño phase during 2015–2016 (Climate Prediction Center of United States).

4.2. Total arsenic and arsenic speciation

4.2.1. Rivers

In rivers, the total arsenic concentrations vary in a range from 1.46 to 27 μ g/L (Table 1, Fig. 5 B). The concentration of As in rivers increased from the headwaters to the center of the basin. The lower values were found in the headwaters of the rivers such as in Santa Catalina River (1.46–1.81 μ g/L) and Cincel River (3.5–7.33 μ g/L). The highest values were observed in Peñas Blancas River after acid mine discharge (27 μ g/L) and in Cincel River in the discharge to the lagoon (17.8–20.3



Fig. 4. (A) - Variation in water surface, physical-chemical parameters, and total dissolved arsenic in Los Pozuelos Lagoon. Images from the Worldview NASA web site (World View, earth data, NASA, United States, n.d). (B) - Precipitation histogram of Rinconada town showing the mean value of precipitation and the sampling dates of the lagoon precipitation data obtained from satellite information provided by the IDE Visor (Agricultural and Industry Ministry, Argentina). (C) - Variation of Na, Cl, Mg, conductivity and As in the lagoon while increasing its surface area.



Fig. 5. Arsenic concentrations in waters of Los Pozuelos basin. (A) - Groundwater. (B) - Surface waters. The lagoon represented points correspond to the lowest (PL-2 (2016)) and highest (PL-2 (2015)) concentrations of As measured in the lagoon.

 μ g/L). Arsenate (As(V) \gg As(III)) is the dominant species in all river water samples (Table 1). Oxidation promotes higher As (V) concentration in rivers and also sorption in fluvial sediments.

Some sites like the Candado River (CaR-1), the Cincel River (CR-1, CR-5, CR-7), were sampled between 3 and 5 times. At each sampling site, the concentration of As varied with time, but the values remained in a similar range (Fig. 6).

4.2.2. Groundwater

Total dissolved As in groundwater ranges between 3.82 and $113 \mu g/L$ (Fig. 5 A). Regarding As speciation, As(V) (arsenate) is the dominant

species in groundwater (Table 4). The shallow unconfined aquifer conditions promote oxidation and higher As(V) concentrations.

According to the Argentinian Alimentary Code (CAA), total dissolved As concentration in wells W6 and W8 are above the limit for human consumption, which is 50 μ g/L. However, according to the World Health Organization, which recommended drinking water value is lower (10 μ g/L) most of the wells of the basin are not suitable for drinking purposes. Only wells W3, W12, W13, W15 and W16 have concentrations of arsenic lower than 10 μ g/L (Fig. 5 A).

A relation between the sedimentary facies of the aquifer and the concentration of arsenic is observed (Fig. 5 A). It is noteworthy that the wells located in the lacustrine sediments show higher concentration



Fig. 6. Concentration of total dissolved arsenic in sites sampled multiple times, bars represent individual samples in different sampling periods. (A) - Surface waters. (B) - Groundwater.

of As with a mean value of 44.6 µg/L, than wells located in nonlacustrine alluvial-and alluvial fan deposits with a mean value of 13.6 µg/L (Table 4, Fig. 5 A). This relation could be caused by the amount of water evaporation and, for that, water isotope analyses ($\delta^{18}O_{H2O}$, δD_{H2O}) are needed and planned for future research.

Some wells (W2, W5, W6, W8, W9, W14) were sampled between 2 and 5 times according to field accessibility, being W9 the most accessible and sampled site. For each site, the variation of total dissolved As with time are shown in Fig. 6. At each sampling site, the concentration of As varies, but the values remain in a similar range. A general tendency of increasing arsenic from the headwaters to the center of the basin can be observed (especially from wells W2 to W8). However, in wells W14 and W9, closer to the lagoon, the concentrations of As decrease. For well W8 lying in the lacustrine aguifer, the As concentration in the dry season (2013 and 2015 periods) were the highest (90.2 and 133 µg/L respectively). During the dry season, the composition of the groundwater was K-HCO3 with Na/K ratio of 0.2 and 0.3. The concentrations of As and K were found to increase towards the center of the basin and As follows a linear regression with K (R2 = 0.767). In closed basins, K concentrations generally increase towards the center of the basin, it is conserved in solution and it is eventually enriched over Na through the precipitation of Na-rich saline minerals (Eugster and Jones, 1979; Deocampo and Jones, 2014). The presence of Na-rich efflorescence salts near W8 well were described above in Section 4.1.2. The concentration of arsenic decreases in the wet season with respect to the dry season (Fig. 6). During the wet season the composition of the groundwater changed to Ca-HCO3 and the concentration of As decreased to 74.3 µg/L. This trend could indicate a tendency of decreasing arsenic by the effect of dilution by rainwater since the aquifer is very shallow, and increasing arsenic during the dry season by evaporation. However, this variation is not clearly observed in wells W9 and W2 because the value remains similar in both seasons.

4.2.3. Los Pozuelos lagoon

In the lagoon, the concentrations of total dissolved As vary between 43.7 and 200.3 μ g/L with As(V) the dominant species. The higher As concentration was observed during the dry season of May-2015 where the concentration increases up to 149.4 and 200.3 μ g/L with As (III) the dominant species (Table 2; Fig. 4 C).

The concentrations of As in the lagoon are the highest of all surface waters of the basin (Figs. 5 B and 6 A). In this sense, high evaporation and the closed system effect most probably favor high As concentrations in the lagoon. However, the abrupt increase of total dissolved As and the relative increase of As(III) during the 2015 period suggests another process that could be related to the biological activity in the lagoon-arrival of large numbers of flamingos (Fig. 4 C). Previous studies indicate that Los Pozuelos Lagoon is an important site for Andean Flamingo (Phoenicopterus andinus) and Puneño Flamingo (Phoenicopterus jamesi) during the austral winter when other lagoons in the Altiplano-Puna are frozen, or late in dry season when other lagoons are dry (Rodríguez, 2012). Data from the bird's census performed at the lagoon from 2006 to 2019, shows 2015 as a year of high abundance, especially for flamingos with >100,000 individuals by the end of the dry season (Sistema de Información de Biodiversidad, 2019). In this case, bird guano and organic matter reduction could favor reduction of As(V) to As(III) (Campbell and Nordstrom, 2014), especially in the sediment pore waters and therefore increase the concentration of As in the lagoon. The high iron concentration which is 45–90% reduced in the lagoon when the arsenic concentration was high, also supports the concept of reducing conditions from increased organic matter or diffusion of As(III) from sediment pore waters.

4.3. Comparison with arsenic content in water of other basins in the Altiplano-Puna region

According to Tapia et al. (2019, this issue) a compilation of data of different water types in the Altiplano-Puna plateau shows that the highest concentrations of As are found in acid mine waters (0.003–117 mg/L), followed by brines (0.008–88 mg/L), and saline water (0.0002–29 mg/L), whereas the lowest values are found in groundwater (0.0001–6 mg/L) and rivers and lakes exhibit variable concentrations of As (0.0001–32 mg/L). Accordingly, in Los Pozuelos basin, acid mine waters from historical mining activity show the highest As concentrations in the basin (0.7–44 mg/L, Murray et al., 2014). The next highest are the lagoon saline waters where the concentration goes up to 200 µg/L when the salinity of the lagoon increase, and to 43.7 µg/L when the salinity decrease during dry years and river water is the main source of water of the lagoon. Groundwater shows concentrations of As between 3.82 and 113 µg/L where the lowest values are in

alluvial-alluvial fan aquifer (3.82–29.7 µg/L) and the highest concentration are in the lacustrine aquifer that surround the lagoon (10–133 µg/L). Finally, rivers show variable concentrations of As (1.46–27 µg/L) increasing from the headwaters to the central area of the basin.

Only a few studies have undertaken As speciation in waters of the Altiplano-Puna region (Tapia et al., 2019, this issue). In San Antonio de Los Cobres, with circumneutral pH water (7.38), a majority of the As was in its oxidized form As(V) (tap and river water waters) and the average As concentration was 290 μ g/L (Hudson-Edwards and Archer, 2012). In the Bolivian Altiplano, oxidizing conditions were present in surface water and shallow groundwater, allowing As(V) species to be dominant over As(III) species (Ramos et al., 2012; Ormachea et al., 2015). In Pozuelos basin, As speciation measurements indicate that arsenate As(V) is the dominant species in all water types. Only during one sample period for the lagoon, As(III) was observed as dominant for a high water elevation of the lagoon and probably associated with reducing conditions promoted by high concentrations of organic matter.

4.4. Sources of As in Los Pozuelos basin waters

4.4.1. Pan de Azúcar mine (Pb-Ag-Zn)

Anthropogenic sources of As like mining, increase the availability and mobility of As by oxidative weathering of mine excavations, waste rocks and tailings (Bowell et al., 2014). Pan de Azúcar (Pb-Ag-Zn) is an inactive mine located in the south area of Pozuelos basin (Fig. 1 A, and SFig. 7 A). It constitutes an epithermal polymetallic deposit within adularia-quartz-sericite hydrothermal alteration hosted in a middle Miocene (12 ± 2 Ma) dacitic volcanic dome (Segal and Caffe, 1999). It was exploited since colonial times until 1990, when the operation ceased without setting any closure plan. About 70,000 m³ of sulfiderich tailings and waste surrounding the mine is undergoing sulfide oxidation and acid water generation (Murray et al., 2014). Nowadays it constitutes an anthropogenic source of arsenic to the surface waters and a potential source to groundwater in the basin as well.

Pyrite and marcasite are the most abundant sulfides in the mine tailings (9.5 wt%). Furthermore, arsenic sulfide phases such as arsenopyrite (FeAsS) and freibergite, $(Ag,Cu,Fe)_{12}$ (SbAs)₄S₁₃, are also present (Murray et al., 2014). In the primary zone of the tailings the As concentration is 623 mg/kg. After 25 years of oxidation, the amount of As in the oxidation zone of tailings ranges between 92 and 236 mg/kg and it is associated with jarosite ((Na, K, Pb)Fe₃(SO₄)₂(OH)₆) and schwertmannite (Murray et al., 2014), indicating As leaching.

Acid mine drainage with a pH = 2.1-4.06 and high As and metal concentrations (e.g. 0.7-44 mg/l As; 3.2-99.7 mg/L Cd; 0.4-1.7 mg/L Cr; 10–21.3 mg/L Cu; 1.3–47 mg/L Fe; 0.1–1.4 mg/L Pb; 388–8960 mg/L Zn) drains from the tailings and discharges mainly into Peñas Blancas River in the wet season (SFig. 7 B). During the wet season of 2012, it was possible to measure the AMD discharge in Peñas Blancas River with a pH = 4.06 and an As concentration of 3.2 µg/L. This low concentration of As in AMD discharge observed during wet season is related to a pH increase and As sorption in secondary iron precipitates (Murray, 2015). Upstream of the AMD discharge, the presence of As (22.8 μ g/L) with a high pH = 8.71 indicates a different geogenic source of As and the possibility of As to remain in solution due to the decreasing absorption capacity at basic pH (Campbell and Nordstrom, 2014). Moreover, downstream of AMD discharge, and because the relative runoff of AMD was lower than the Peñas Blancas River runoff, the pH of the river remains high (8.36) and the As concentration increases up to 27 µg/L, being the highest value of As measured in river waters of this study. The pH in the Peñas Blancas River remains high after AMD discharge and favors the solubility of As and its migration downstream in the basin.

The X-ray diffraction analyses for sediments from the flood plains of the Peñas Blancas River at 6 km downstream of the mine (SM-1 and SM-2) indicate the presence of secondary iron minerals like schwertmannite and jarosite. The presence of these minerals indicates low pH (2–3.5) conditions related to the AMD discharge, probably at the beginning of the wet season. The amount of As determined in these sediments vary between 82 and 108 mg/kg of As. Because flood plains are potential aquifer recharge zones, they are potential sources of As to the groundwater.

Arsenic desorption from the surface of Al-, Fe- and Mnoxyhydroxides (coating lithic fragments) at high pH and mobilization as complex oxyanions (As and trace elements) in Na-HCO₃ type groundwaters is mentioned in the Chaco-Pampean plain by Nicolli et al., 2012 Moreover, reductive solubilization of As under water-saturated conditions by dissolution of As-bearing Fe(III)-oxyhydroxides is likely the main cause for high solubilization of As in mining impacted floodplains (Simmler et al., 2017). High concentrations of arsenic are found in groundwater downstream of the mine (W4 = 21.4 μ g/L; W8 = 113 µg/L), so it would be important to understand or identify potential processes of arsenic desorption from secondary iron minerals in the flood plains to the groundwater. Moreover, the major ion composition of groundwater in well W4 (SO₄-Ca) could indicate the influence of acid mine drainage by an increase of SO₄ in the groundwater. Analyses of environmental isotopes such as $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$ will be useful to better understand the transport and effect of As from the mine site to groundwater.

4.4.2. As-rich gold deposits in Rinconada Hill's shales

Ordovician marine shales with very low grade of metamorphism are the most abundant rocks in the basin and contain many epithermal and alluvial Au deposits (Fig. 1 A) (Rodriguez et al., 2001; Rodríguez and Bierlein, 2002). The origin of these deposits is linked to the main stage of deformation, which occurred in the upper Ordovician – lower Silurian (Rodriguez et al., 2001). Epithermal Au is hosted in small size quartz veins, which also are rich in pyrite and arsenopyrite. The Au mineralization is structurally controlled and occurs typically along large anticline hinges. Geochemical data indicate that these mineral deposits are rich in Au-As (Sb) and also contain subordinate quantities of basic metals (Pb, Zn, Cu, and Mo; Rodriguez et al., 2001). Arsenic is the main element that shows a strong correlation with hydrothermal gold mineralization (Nordstrom, 2012; Reich et al., 2005; Zhu et al., 2011; e.g. Minas Azulesmineralized area and Pasquiri), so this element may constitute a guide in the exploration of gold in the Puna (Rodriguez et al., 2001).

Sulfides are not stable under aerobic conditions and oxidize to hydrous iron oxides with the release of large amounts of sulfate, acidity, and associated trace constituents, including As (Bowell et al., 2014). The dominance of SO_4 over HCO_3 in the head of Santa Catalina River (SCatR-1 and SCatR-2) is related to the oxidation of sulfide in outcrops and alluvial deposits according to the following reaction (Dold, 2010; Nordstrom et al., 2015):

$$FeS_2(s) + 15/4O_2(l) + 7/2H_2O(l) \rightarrow Fe(OH)_3(s) + 2SO_4^{2-}(aq) + 4H^+(aq)$$

High concentrations of sulfate are also observed in Lopiara River and Gayatayoc River, where pyrite is observed on its fluvial sediments (SFig. 7 C). The oxidation of arsenopyrite and arsenic release can be expressed as follows (Mok and Wai, 1994):

FeAsS (s) + 7/2O₂ (l) + 4H₂O (l)
$$\rightarrow$$
 Fe(OH)₃ (s) + SO₄²⁻ (aq)

 $+H_2 \; AsO_4^{-} \; (aq) + 3H^+ \; (aq)$

During the oxidation of pyrite and arsenopyrite iron oxides are formed and can accumulate As up to concentrations of several weight per cent (Bowell et al., 2014). There is a tendency of As to be removed from the solution by co-precipitation in fluvial sediments especially when As(V) is the dominant species (Campbell and Nordstrom, 2014). Many iron oxide deposits were observed in the fluvial sediments or fluvial channels of Santa Catalina River and Lopiara River for example. The dominance of As(V) in the rivers could favor As adsorption to iron oxide deposits reducing the amount of dissolved As that reaches the lagoon.

4.4.3. Corranzulí volcanic complex ignimbrites

Another source for As is related to effusive volcanic rocks in the surrounding area of Pozuelos Basin, such as the Coranzulí ignimbrite volcanic rocks located in the headwaters of Candado River (SFig. 7 D). The concentration of As in Candado River is higher (7.9–17 µg/L) than in Cincel River (CR-1) in the confluence point (3.5–7.33 µg/L), indicating the contribution of As from the ignimbrites rocks. Data from the nearest area indicates arsenic concentrations in the range of 2.2-126 mg/Kg in these ignimbrites (Gorustovich et al., 1989). de Sastre et al. (1992) pointed out that in the Puna the Tertiary and Quaternary volcanic rocks are natural sources of arsenic in surface waters. Tapia et al. (2019, this issue) indicates that fluvial sediments originated from Neogene volcanic rocks (i.e. ignimbrites) exhibited the highest concentrations of As when compared to surficial sediments from other geologic periods and/or rock types. In addition, most sediments exhibited higher concentrations of As (107 mg/kg average) than the upper continental crust (5.7 mg/kg, Hu and Gao, 2008). It is unknown how As is hosted in the volcanic matrix of the ignimbrites.

According to Kay et al. (2010), the highest ⁸⁷Sr/⁸⁶Sr ratios at a given SiO₂ content in the most peraluminous ignimbrites fit with a shale-like component in the northeastern Puna Granada–Orosmayo–Cusi Cusi, Vilama, Panizos and Coranzulí magmas. Hence, because the shales are already enriched in As (Rodriguez et al., 2001; Rodríguez and Bierlein, 2002), the source of As of the ignimbrites could be derived from the shales.

4.4.4. Lacustrine deposits, and influence of semi-arid conditions

Because it is a closed basin, the As released from natural and anthropogenic sources is transported in solution, and precipitated in the fluvial sediments and transported downstream to be finally accumulated in the basin depocenter. As a consequence, higher concentrations of As are found in groundwaters located in the lacustrine aquifer as well as in the lagoon waters and the lagoon sediments. The concentration of As in the actual lagoon sediments is 24 mg/kg, four times higher than the upper continental crust (5.7 mg/kg; Hu and Gao, 2008). However, this value is lower than those found in other lake sediments in the Altiplano of Bolivia. Sediments of Lake Uru Uru and Cala Cala Lagoon show a value of 56 mg/kg of As (Tapia et al., 2012). According to these authors, this high value might be related to the metallogenic belts located in the Eastern Andes Range. In these sediments As was mainly associated with iron oxides and residual fractions (Tapia and Audry, 2013). In these lakes, the sediments act as a source of As in the dry and wet seasons, with increased mobility during the wet season (Tapia and Audry, 2013). The analysis of As in Los Pozuelos lagoon sediments was made in bulk samples and the mineralogy of the sediments was not identified, but high organic matter content was observed. As mentioned in Section 4.2.3, high evaporation could increase As concentrations in the lagoon, but the relative increase of As(III) during the 2015 period suggests biological reduction processes (Campbell and Nordstrom, 2014). McGlue et al. (2012, 2013) indicates high organic matter content in the sediments of the lagoon, with increasing values from the Cincel River delta to the center of the lagoon. Moreover, their mineralogical analyses in surface and core sediments of the lagoon indicates the presence of Fe-oxides and ungraded, massive, black pyrite-rich mud. Oxidation-reduction processes and the presence of organic matter in Los Pozuelos lagoon can influence the cycle of As by changes in the geochemistry of the water-sediment interphase, which can contribute to the variability in the concentration of As in the lagoon.

5. Conclusion

In Los Pozuelos basin the As concentrations increases from the upstream areas to the center of the basin in both surface and groundwater with the highest values observed in Los Pozuelos Lagoon. Total dissolved arsenic in rivers varies in a range from 1.46 to 27 µg/L. In the lagoon, the concentration of arsenic is highly variable $(43.7-200.3 \,\mu\text{g/L})$. High evaporation and the closed system effect most probably increases As concentrations in the lagoon. However, the abrupt increase of total dissolved As in May-2015 (up to values of 149.4; 200.3 µg/L), together with an increase in As(III) and Fe(II) species, suggests that a process related to migratory birds invasion that could increase the organic matter in the lagoon favoring arsenic reduction increasing its solubility and concentration. In groundwater, the main source of drinking water for the inhabitants of the basin, the arsenic concentrations vary between 8.22 and $113 \mu g/L$. The wells located in the external ring aquifer where alluvial-alluvial fan sediments are the dominant facies have lower As concentrations (13.6 μ g/L). The wells located in the internal ring aquifer where lacustrine sediments are the dominant facies show higher concentration of As (44.6 µg/L). According to the World Health Organization, 70% of the wells have arsenic concentrations above the recommended guideline (10 µg/L). According to the Argentinian Alimentary Code, only two wells are above the limit for human consumption (50 μ g/L).

Arsenate is the dominant species in all surface and groundwater, except for the lagoon where variations between As(V) and As(III) species were observed and associated with organic matter and reductive conditions in Los Pozuelos Lagoon.

There are at least three potential sources for As in surface and groundwater i) oxidation of As sulfides in Pan de Azúcar mine wastes, and acid mine drainage discharging into the basin; ii) weathering and erosion of mineralized shales; iii) weathering of volcanic eruptive non-mineralized rocks located in the headwater of some of the streams.

Because it is a closed basin, the arsenic released from the natural and anthropogenic sources is transported in solution, and in fluvial sediments, and finally accumulated in the center of the basin where the concentrations increase because streams and sediment coalesce, and because of evaporation. High evaporation rates that characterize a prolonged dry season in the basin most probably favor As concentration increase in groundwater and the lagoon. Moreover, a larger interannual scale process related to drier or rainy years most probably affects the total surface area of the lagoon, its physical-chemical parameters, and the biological activity causing variations in As concentration in the lagoon. Environmental isotopes ($\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, $\delta^{18}O_{H2O}$, δD_{H2O}) in combination with water geochemistry are needed to better understand multiple As sources, its mobility, and its behavior under semi-arid conditions. The data and interpretations of how different geological, climatological, geochemical, anthropological, and biological processes influence the presence and mobility of As in waters, as presented in this study, are transferable to other closed basins in Central Andes, Latin America, and beyond.

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Author contributions

JM, DKN, BD, and AK performed the sampling campaigns, laboratory work, and contributed to the interpretation, discussion of data, figures confectioning, and redaction of the manuscript. MRO contributed to the treatment of long term data and discussion. Blaine McCleskey is gratefully acknowledged for assistance and use of the USGS laboratory in Boulder, CO.

Declaration of competing interest

The authors declare no conflicts of interest.

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