



Hydrogeochemical contrasts in the shallow aquifer systems of the Lower Katari Basin and Southern Poopó Basin, Bolivian Altiplano

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ABSTRACT

Drinking water sources in the southeastern part of Lake Titicaca (Lower Katari Basin: LKB) and the southern part of Lake Poopó (Southern Poopó Basin: SPB) have high concentrations of arsenic (As), >10 µg/L compared to the WHO and NB-512 guideline value. These regions belong to the Bolivian Altiplano and are characterized by a semiarid climate, slow hydrological flow, with geological formations of volcanic origin, in addition to brines and other mineral deposits. The present study is focused on comparing the geochemical processes of As in relation to the sources and mobilization in groundwater (GW) in LKB and SPB. Groundwater (GW), surface water (SW) and sediment samples were collected from both basins. The As (LKB: 0.8–288 µg/L and SPB: 2.6–207 µg/L), boron (B) (LKB: 96–2473 µg/L and SPB: 507–4359 µg/L), manganese (Mn) (LKB: 0.6–7259 µg/L) and salinity (LKB: 125–11740 µS/cm) were found to be higher than the WHO guideline values, which is a serious concern about the GW quality for human consumption. The dissolution and exchange of bases are the processes that govern the mineralization of GW. Load of solids and liquids of anthropogenic origin in surface water (LKB) represents an environmental problem for communities on river banks. The spatial distribution of As was attributed to the geology of both the basins and the heterogeneously distributed evaporites in the sediments. The highest As concentrations are found in alluvial sediments of the northern region of LKB and “PACK belt” (an approximately 25 km long belt stretching along the southern shores of the Lake Poopó, between the villages of Pampa Aullagas and Condo K) in SPB. Sequential extraction of sediment and mineral saturation indices indicate that iron (Fe) and aluminum (Al) oxides as well as hydroxides are the most predominant mineral phases as potential sorbents of As.

1. Introduction

The water pollution due to natural and anthropogenic sources is considered as a matter of global environmental and social concern. The worldwide threat comes from geogenic and anthropogenic arsenic (As) due to its toxicity to biotic life (Bhattacharya et al., 1997, 2002a,b, 2006, 2007; Bhattacharya et al., 2011; Nriagu et al., 2007; Polya and Charlet,

2009; Quintanilla et al., 2009; Ormachea Muñoz et al., 2013, 2015, 2016; Maity et al., 2011a, 2011b, 2011c, 2012, 2017, 2019; Quino Lima et al., 2019, 2020; Aullón Alcaine et al., 2020; Mukherjee et al., 2008a,b, 2009, 2019; Samal et al., 2013; Ravenscroft et al., 2009; Bundschuh et al., 2010a, 2012, 2013; Islam et al., 2013; Bundschuh and Maity, 2015; Herath et al., 2016; Kar et al., 2011a, 2011b, 2010; Liu et al., 2009, 2011, 2012, 2013). Numerous regions around the world have

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elevated levels of As in drinking water, with the potential to cause cancer and other adverse effects on human health (Kapaj et al., 2006; Smith et al., 2000; Chen et al., 2010; Maity et al., 2012; Khan et al., 2020; Ahmad et al., 2020). New data on the As-exposed populations in different Latin American countries (Khan et al., 2020) indicate effects of As exposure, genetic susceptibility and genotoxicity, and present risk assessment to further characterize the health effects to the exposed populations and appropriate adaptive mitigation strategies (Bundschuh et al., 2010b; Ormachea et al., 2012; Litter et al., 2019b). Although the WHO guideline limit for As in drinking water is currently set at 10 µg/L, recent studies indicate that As can also have negative effects on human health at concentrations much lower than that (Ahmad et al., 2020; Ahmad and Bhattacharya, 2019).

Elevated concentrations of As are found in groundwater (GW) worldwide, especially in Argentina, Chile, Mexico, China, USA, Taiwan and Hungary (Smedley et al., 2002; Bhattacharya et al., 2002, 2006; Mukherjee et al., 2009; Maity et al., 2011b); as well as in the state of West Bengal in India, Bangladesh and Vietnam (Bhattacharya et al., 1997, 2002a,b, 2007; Berg et al., 2001; Nriagu et al., 2007; Bundschuh et al., 2009; Mukherjee et al., 2008a,b, 2019; Samal et al., 2013; Maity et al., 2011c, 2012, 2019). Approximately 150 million people are affected by As worldwide (Ravenscroft et al., 2009; Bundschuh et al., 2012).

In Latin America, many regions (e.g. Argentina, Bolivia, Chile) are known to have high levels of As in GW (Aullón Alcaine et al., 2020; Bundschuh et al., 2009; Bundschuh et al., 2010b; Litter et al., 2019a,b; Sosa et al., 2019; Tapia et al., 2019; Mariño et al., 2020). The contamination is due to the release of As from sulphide-rich minerals formed due to extensive magmatic and hydrothermal activities, and the extensive volcanism along the Andean mountains (Bundschuh et al., 2009, 2017; Coomar et al., 2019; Raychowdhury et al., 2014; Maity et al., 2017).

Studies focused on contamination of drinking water by combined release of As, boron (B) and other trace elements (TEs) in drinking water have been carried out in few Latin American countries (García, 2006; Cortes et al., 2011; Concha et al., 2010; Ramos Ramos et al., 2012, 2014; Ormachea Muñoz et al., 2013, 2014, 2016). In Bolivia, Banks et al. (2004) revealed the presence of high concentrations of As and B in the surface waters (SW) of the catchment areas of the salt plains. In GW, elevated concentrations of As and B were reported by Ormachea Muñoz et al. (2013, 2016) and Ramos Ramos et al. (2012, 2014). There are also recent studies on the occurrence and natural distribution of As in the Bolivian Altiplano (Coomar et al., 2019; Tapia et al., 2019, 2020; Quino Lima et al., 2019, 2020). Studies carried out in the area have reported elevated concentrations of naturally occurring As in areas not affected by mining activities, located in the southern and western parts of the Lake Poopó Basin (PPO, 1996a; Van Damme, 2002; Hermansson and Karlsson, 2004; Van Den Bergh et al., 2010; Ramos Ramos et al., 2012; Ormachea Muñoz et al., 2013, 2016), as well as in the area southeast of Lake Titicaca (IIS, 2013; Espinoza et al., 2016; Quino Lima et al., 2019, 2020).

The objective of the present work is to investigate the geochemical processes of As mobilization and other TEs, geochemical characterization of GW, along with surface and subsurface water quality in the Lower Katari Basin (LKB) and Southern Poopó Basin (SPB) in the Lake Titicaca and Lake Poopó regions respectively of the Bolivian Altiplano. The use of GW in these two study areas are mainly human consumption and irrigation. These basins are located near the northern and southern limits of the TDPS system (Lake Titicaca – Desaguadero River – Lake Poopó – Salt Flat of Coipasa). Furthermore, the present investigation aims to enhance our scientific understanding of the GW and SW quality of both the basins, in order to improve the efficiency of drinking water management from GW sources in an extreme environment in addition to the mitigation of water pollution.

2. Study area

2.1. General description

The TDPS system (Fig. 1) is a closed basin between the Peruvian and Bolivian Altiplano, comprising of the watersheds of Lake Titicaca (39%), Desaguadero River and Lake Poopó (38%) and Coipasa Salt Flat (23%) (CMPRALT, 2014). The TDPS system is located between the Eastern and Western Andes Cordillera from 3600 to 4500 m a.s.l. (ORSTOM, 1991).

The LKB (Fig. 1b) is located in the southeastern part of Lake Titicaca, with an elevation ranging between 3800 and 4200 m a.s.l., and includes part of Cohana Bay. Upstream of the LKB is the Eastern Andes Cordillera, where there are local mining activities (Milluni) (Archundia et al., 2017) and the cities of El Alto and Viacha, which include discharges from urban centers and many small manufacturers and industries located along the banks of the tributaries of the Katari River (Seque, Seco and Pallina rivers) (UNEP, 2008; UNEP, 2011; Ribera Arismendi, 2010; Archundia et al., 2017). Finally, the Katari River ends in Cohana Bay, is located on Lake Titicaca.

The SPB (Fig. 1c) is located in the Department of Oruro to the east of the Bolivian Altiplano. It covers an area of 1400 km² with an elevation ranging between 3700 and 3900 m a.s.l. (IGM, 1966; Ormachea Muñoz et al., 2013). The area is essentially a flat basin enclosed to the north by Lake Poopó, to the east by the Eastern Andes Cordillera mountain range, to the west by the Marqués River and to the south by the volcanic plateau of Los Frailes. The climate is semi-arid (Ormachea Muñoz et al., 2013) with a mean annual precipitation of 510 mm in LKB and 300–400 mm in SPB.

2.2. Geology and hydrogeology

LKB and SPB are recognized along the Eastern Andes Cordillera (Eastern Andes range) in the Bolivian Altiplano (Fig. 1a). The predominant geological formations in the SPB, specifically in the eastern part, are the sediments of the plain, which includes Quaternary alluvial and evaporite deposits. Outcrops of rhyolitic volcanic rocks occur within the mounds of the plain (Fig. 2). Pleistocene fluvial and lacustrine sediments form sequences of gravel, sand, silt, clay, limestone and evaporites that cover the eastern part of the plain, while Holocene alluvial deposits (unconsolidated sediments) are more common in the western part (Almendras et al., 2002; Ormachea Muñoz et al., 2013).

On the other hand, LKB is formed by scattered hills related to Devonian sandstones, lutites and siltstones (Devonian rocks are present in the Eastern Andes Cordillera), and Neogene conglomerates, sandstones, argillites, marlstones, with volcanic rocks, such as tuff, interspersed lava and diapirs. Surface geology is dominated by Quaternary alluvial, fluvial lacustrine, fluvio-glacial, colluvial, lacustrine, moraine and dune deposits (MMAyA, 2010).

The general GW flow (6.65 L/s) (Blanco, 2016) pattern towards Lake Poopó (Figs. 1 and 2) is slow (mean GW velocity: 0.00045 m/d in silt layer and 0.03 m/d in silty sand layer) (Blanco, 2016), due to low hydraulic gradient (plain slope 1.1%) (GITEC, 2014). This is primarily due to low permeability of the sediments, which are predominantly of lacustrine and alluvial origin with high proportions of silt and clay fractions. Shallow aquifers in the plain generally have low productivity and greater exploitation during the dry season. Sand dunes and riverbed sediments in the plain can represent important productive aquifers (Huaranca Olivera and Neumann-Redlin, 2000; Ormachea Muñoz et al., 2013). In the southeastern area of Lake Titicaca, the GW flow that reaches the SW system is limited due to the low transmissivity and low gradient (mean slope of 3.8%). Aquifers in general represent a very limited part of the total basin; but in rainy season, there is a significant transfer of SW to GW aquifers (Desaguadero River) (Martínez et al., 2007).

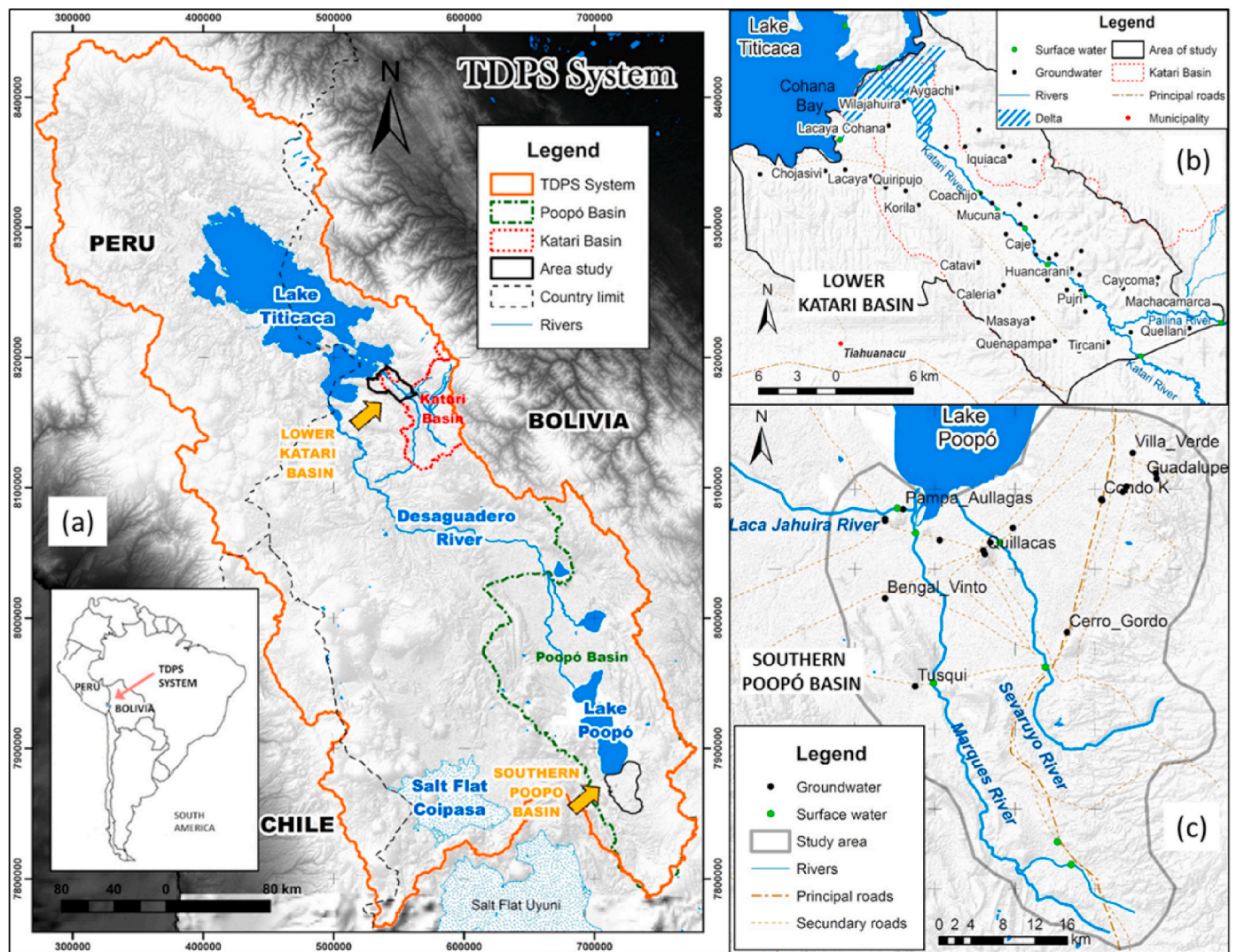


Fig. 1. TDPS system (Lake Titicaca – Desaguadero River – Lake Poopó – Salt flat of Coipasa) (a), Lower Katari Basin (b) and Southern Poopó Basin (c).

3. Material and methods

3.1. Field investigations

In both the LKB and SPB, the sampling campaign was carried out during the dry season in August 2017 and November 2009, respectively. The pH, temperature (T), electrical conductivity (EC), redox potential (Eh) and total dissolved solids (TDS) were measured in the field with a multiparameter portable meter HANNA-HI 9828 in LKB and with a OAKTON 11 pH meter – HACH conductivity-TDS meter in SPB. The Eh value was corrected with respect to standard hydrogen electrode (Appelo and Postma, 2005). The portable instruments were calibrated daily and the electrodes were rinsed with deionized water (three times). Alkalinity (quoted as HCO_3^-) was determined on-site by titration with sulfuric acid (H_2SO_4), using a microdosimeter (portable titrator West Systems Hi Tech Devices RGD) in LKB and with hydrochloric acid (HCl) at the end of each sampling day in SPB. Geographical coordinates were recorded at each site using a handheld GPS (GARMIN GPS12™). Samples were filtered using Sartorius 0.45 μm filters and water samples were collected in three replicates from each site: 80 mL in LKB and 30 mL in SPB for anions, cations (TEs) and As speciation. The As speciation was performed with disposable cartridges (Metal Soft Center, USA). The samples were passed through the cartridge that retains all As(V) following the methodology described by Meng et al. (2001). The

samples for the TEs analysis and As speciation were acidified using 1% v/v HNO_3 and all the samples were stored in a refrigerator at 4 °C until laboratory analyses.

3.1.1. Piezometer installation

Nineteen monitoring wells (piezometers) were installed in the central flat area (10 km) along the Katari River (LKB), including the villages of Pujri, Masaya, Caleria, Catavi, Chacalleta, Huancarminto, Cajé and Mucuna (Table 1). The Katari River overflows many times in this region seasonally, due to its natural slow flow rate. In addition, eleven community wells close to the piezometers were monitored (Fig. 3a). The piezometers were manually installed with prefabricated augers of 2 and 3 inches in diameter, the depth of the profiles was 3–4.5 m.

Two locations were chosen for sampling with a hand-held auger (Fig. 3b) in the SPB. The first borehole was drilled close to Condo K (GW9) at up to a depth of 7.5 m because of the occurrence of high As concentrations in an adjoining well (Ormachea et al., 2009; Ramos et al., 2012). The second borehole was drilled 3 km northwest of Quillacas, near the road to Pampa Aullagas up to a depth of 5 m.

3.2. Water sampling and analysis

3.2.1. Groundwater samples

The GW samples were taken with a bucket or pump, depending on

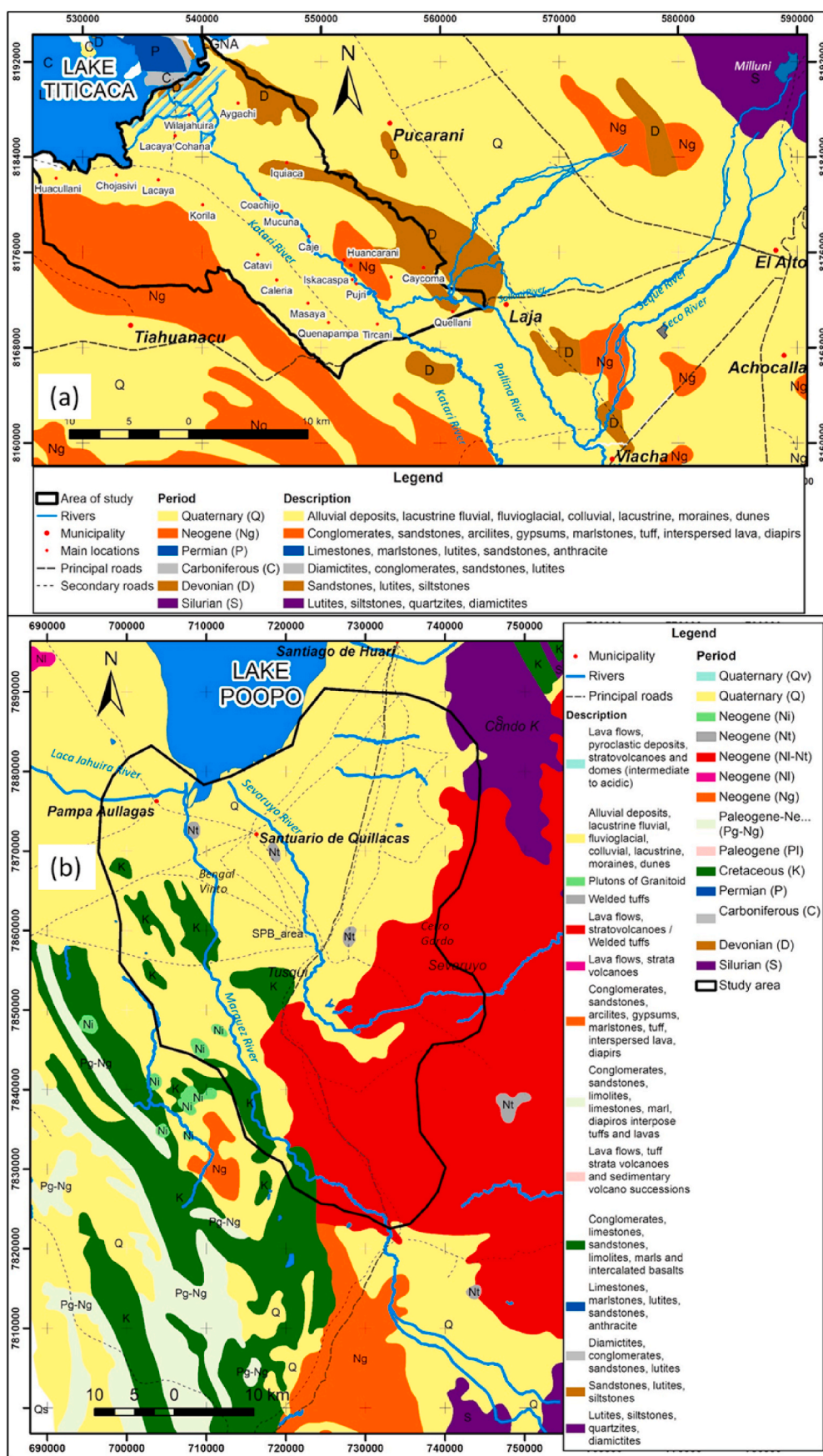


Fig. 2. Geological map of Lower Katari Basin (a) and Southern Poopó Basin (b).

Table 1

Location and main characteristics of sampling sites in Lower Katari Basin (LKB) and Southern Poopó Basin (SPB).

Lower Katari Basin (LKB)				Southern Poopó Basin (SPB)			
Groundwater (GW)				Groundwater (GW)			
Code	Location	Type	Water level (m)	Code	Location	Type	Water level (m)
AYP1	Aygachi	Excavated	1.4	HUNP1	Huancarani	Excavated	2.5
CAGP1	Caje	Excavated	2.2	IQGP2	Iquiaca	Excavated	3.8
CAGP2	Caje	Excavated	1.7	IQGP4	Iquiaca	Excavated	3.3
CALCHP1	Calachaca	Excavated	0.9	IQUP1	Iquiaca	Excavated	5.0
CALEP2	Caleria	Excavated	5.9	ISKP2	Iskacaspa	Excavated	2.4
CALEP3	Caleria	Drilled	ND	KOP1	Korila	Excavated	1.4
CAVP1	Catavi	Excavated	7.6	KOP2	Korila	Excavated	0.4
CAVP2	Catavi	Excavated	2.3	LACP1	Lacaya	Excavated	0.2
CAVP3	Catavi	Excavated	2.5	LACP2	Lacaya Cohana	Excavated	0.6
CCJP1	Coachijo	Excavated	1.4	LACP3	Lacaya Cohana	Excavated	ND
CCJP2	Coachijo	Excavated	2.3	MASP1	Masaya	Excavated	2.8
CCJP3	Coachijo	Excavated	2.3	MCHP2	Machacamarca	Drilled	ND
CCJP4	Coachijo	Excavated	4.6	MCHP4	Machacamarca	Excavated	3.4
CHCP1	Chacalleta	Excavated	3.0	MUCP3	Mucuña	Excavated	4.6
CHCP2	Chacalleta	Excavated	2.3	PK1	Iskacaspa	Drilled	2.1
CHCP3	Chacalleta	Excavated	2.7	PK10	Caleria	Drilled	2.0
CHJP1	Chojasivi	Excavated	0.5	PK11	Catavi	Drilled	2.1
CUAP1	Coachijo	Excavated	1.8	PK12	Chacalleta	Drilled	3.6
CYCP2	Caycoma	Excavated	2.1	PK14	Caje	Drilled	1.8
CYCP3	Caycoma	Excavated	5.5	PK15	Caje	Drilled	2.1
HUAP1	Huacullani	Drilled	ND	PK18	Coachijo	Drilled	2.0
HUAP2	Huacullani	Drilled	ND	PK19	Chacalleta	Drilled	2.4
Groundwater (GW)				Groundwater (GW)			
Code	Location	Type	Water level (m)	Code	Location	Type	Water level (m)
PK2	Iskacaspa	Drilled	2.0	GW1	Pampa Aullagas North	Excavated	0.7
PK4	Masaya	Drilled	2.3	GW2	Pampa Aullagas Plaza	Excavated	5.7
PK8	Caleria	Drilled	1.6	GW3	Pampa Aullagas Lower	Excavated	1.5
PUJP1	Pujri	Excavated	3.1	GW4	Plain 3 km SE Pampa Aullagas	Excavated	5.2
QLLP1	Quellani	Excavated	5.5	GW5	Quillacas Village South	Excavated	4.1
QLLP2	Quellani	Excavated	5.9	GW6	Quillacas Village North	Excavated	ND
QLLP3	Quellani	Excavated	9.0	GW7	Quillacas Main Well	Excavated	2.9
QLLP4	Quellani	Excavated	2.4	GW8	Bengal Vinto	Excavated	3.0
QUAP1	Quenapampa	Excavated	4.8	GW9	Condo K Yard	Excavated	1.8
QUIRP1	Quiripujo	Excavated	2.0	GW10	Condo K Plaza	Drilled	Closed
TIRP1	Tircani	Excavated	1.4	GW11	Plain NE Quillacas	Excavated	2.7
TIRP3	Tircani	Excavated	2.2	GW12	Tusqui	Excavated	8.2
TIRP4	Tircani	Excavated	5.1	GW13	Caraynacha	Excavated	Closed
WIP1	Wilajahuira	Excavated	1.1	GW14	Guadalupe	Excavated	Closed
Surface water (SW)				GW15	Cerro Gordo North	Excavated	Closed
River/sediment	Location	Type	Flow (m3/s)	CONP2	Condo K Centre	Excavated	1.7
COL1	Cascachi	Titicaca Lake	ND	CARP1	Caraynacha South	Excavated	4.4
COR1	Cohana	Katari River	ND	VIVP1	Villa Verde	Excavated	4.7
COR2/COS2	Lacaya	Katari River	0.09	JIP1	Guadalupe	Excavated	8.3
COR3/COS3	Calachaca	Katari River	0.09	Surface Water		Flow (m3/s)	
KAR1/KAS1	Quellani	Katari River	0.02	MAR3	Marquez/Estacion	River	ND
KAR2/KAS2	Pujri	Katari River	0.14	LAR1	Lacajahuira	River	ND
KAR3/KAS3	Catavi	Katari River	0.18	MAR1	Marquez/Pampa Aullagas road	River	ND
KAR4/KAS4	Chacalleta	Katari River	0.07	MAR2	Marquez/Tusqui	River	ND
KAR5/KAS5	Catavi	Katari River	0.09	MAR3	Marquez/Estacion M.	River	ND
KAR6/KAS6	Caleria	Katari River	0.19	SEVR1	Sevaruyo/Condo K road	River	ND
PARI/PAS1	Laja	Pallina River	0.21	SEVR2	Sevaruyo/Sevaruyo	River	ND

ND: not determined.

the type of well. The sampling bottles were rinsed three times with well water before samples were taken. In the wells, the depth to water table was measured with a water level meter (Solinst 101). Fifty-eight samples were collected in August 2017 from LKB and nineteen water samples were taken in November 2009 and March 2010 at selected well sites from SPB.

3.2.2. Surface water samples

In August 2017, eleven water samples were collected in LKB along the Pallina and Katari rivers to Cohana Bay. In SPB (November 2009),

one river sample was obtained from Marques River (Marques Train Station) (Figs. 1–3), whereas other river sites for sampling were dry. In March 2010, five water samples were collected along the Sevaruyo and Marques Rivers. All samples (LKB and SPB) were taken from the middle of the river channel, with a plastic bucket rinsed three times with river water, following the same procedure as for groundwater.

3.2.3. Chemical analysis of water

Major anions such as chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-) and phosphate (PO_4^{3-}) were measured by ion chromatograph (Dionex -

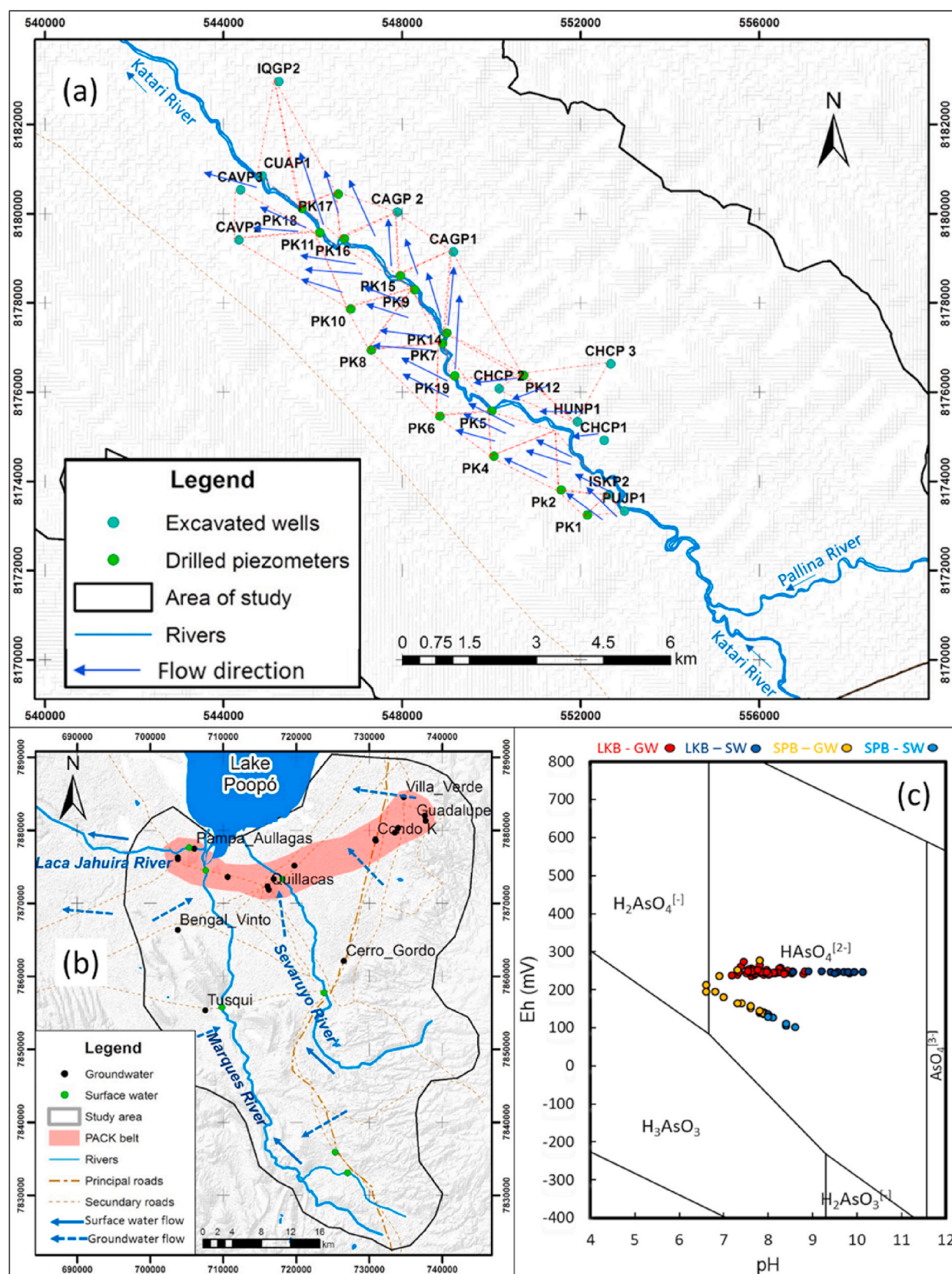


Fig. 3. Geographical location of piezometers and wells in LKB (a) and SPB (b) with their GW flow direction. pH and Eh values plotted in the Eh-pH diagram and the stability of the various inorganic As species in water at 25 °C and 1 atm for the systems As–O–H (modified from Panagiotaras et al., 2012; Ticona, 2018) for SW (blue) and GW (red) samples in LKB and SW (light blue) and GW (yellow) in SPB (c). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

ICS 1100) at the Environmental Chemistry Laboratory of Universidad Mayor de San Andrés (UMSA) (La Paz, Bolivia) for the samples of LKB whereas the samples of SPB were analyzed by a Dionex DX-120 Ion Chromatograph (IC) at Department of Land and Water Resources Engineering at KTH in Stockholm, Sweden. Major cations (Ca^{2+} , Mg^{2+} , Na^{+} , and K^{+}) and TEs (Si, As, Al, B, Cd, Cu, Fe, Li, Mn, Pb, Sr, Cr, Ba and Zn) for both the cases (LKB and SPB) were determined by inductively coupled optical emission spectrometry (ICP-OES; Varian Instruments, model Varian Vista Pro Ax) at the Department of Geological Sciences, Stockholm University in Sweden. The As-speciation samples gave the As (III) concentration; the amount of As (V) was obtained by subtracting As (III) from the total As.

The quality assurance of major ion analyses was ensured through the estimation of charge balance error (CBE), where most of the samples presented a CBE of less than $\pm 10\%$. Certified reference material (NIST SRM 1640a - Trace Elements in Natural Water) was used to check the accuracy of element concentrations. Replicate analyses were carried out to check the precision of the results (one replica for every 10 samples), accuracy and precision indicated variations within the range of $\pm 10\%$.

3.3. Sediment samples and analysis

Representative sediment samples of the saturated and unsaturated zones were collected for analysis in laboratory. Details are provided in the following sub-sections.

3.3.1. Core sediment sampling

Nineteen piezometers were installed and 54 sediment samples were taken from the profiles of all the piezometers in LKB, whereas 16 sediment samples were taken from two piezometers installed in SPB, with a handheld auger, and those were characterized by color, grain size and texture. Finally the sediment samples were stored in zip-lock bags for subsequent laboratory studies.

3.3.2. River sediment sampling

Nine sediment samples were collected in August 2017 from the Pallina and Katari rivers in LKB at the same sites where SW samples were taken (Table 1) to compare water and sediment chemistry (Fig. 1). Only one fluvial sediment sample was collected in November 2009 from the Marques River in SPB at the same site as the river water sample (Fig. 1). Approximately 1 kg of shallow sediment samples were taken from 1 m² areas of the riverbed in the middle of the stream using a shovel. Samples were recovered and stored in zip-lock bags until analysis.

3.3.3. Sediment analysis

The sediment samples (of rivers and piezometers) were dried at room temperature. Sediment color was determined on wet samples according to the Munsell color system (Munsell Soil Color Charts, 1994). A sediment profile was created based on the sample analysis data and observations from the auger drilling.

3.3.4. Pseudo total extraction of core sediments

Sixty three sediment samples (core sediments and river sediments) from LKB were digested using a digester (VELP DK-20, open digestion system) to quantify the total content of TEs by digesting 0.5 g of sample in a mixture of 3 mL of HNO_3 (65% m/v) and 3 mL of HCl (37% m/v), both purified by sub-boiling distillation. The sample was quantitatively transferred to a digestion tube (Kjeldahl digestion) with balls to prevent eruptive boiling, and was boiled in the digester. The extract was cooled and diluted to a total volume of 50 mL with deionized water, and then filtered through a filter paper (Whatman grade 44) and stored in plastic bottles.

For the samples of SPB, 2 g of sample were digested in 15 mL of 7 M HNO_3 (®Merck) in a conical flask and boiled on a sand bed for 2 h with glass balls to prevent eruptive boiling. The extract was cooled and then filtered through a 00K filter and diluted to a total volume of 50 mL with

de-ionized water (DIW) and stored in plastic bottles. All sediment extracts (LKB and SPB) were analyzed with an ICP-OES (Varian Instruments, model Varian Vista Pro Ax) at the Department of Geological Sciences, Stockholm University, Sweden.

3.3.5. Sequential extraction

The sequential extraction was performed on the 54 sediment core samples of the LKB using the BCR protocol (Community Bureau of Reference, superseded by the Standards, Measurements and Testing Programme of the European Community) (Ure et al., 1993). The procedure was adapted by varying the concentrations of chemical reagents ($\text{C}_2\text{H}_3\text{NaO}_2$; $(\text{NH}_4)_2\text{C}_2\text{O}_4$), pH and reagent volumes according to the procedure developed by Cáceres Choque et al. (2013). The BCR extraction procedure was developed considering the following steps: step one Fraction 1 (F1-exchangeable + acid soluble fraction), step two Fraction 2 (F2-reducible fraction), step three Fraction 3 (F3-oxidizable fraction), and step four Fraction 4 (F4-residual fraction).

In case of SPB, the sequential extraction was used to investigate the different phase associations and their potential for leaching of As, which were performed on a sediment core sample from Condo K and a sediment core sample from the lower terrain close to Quillacas. The extraction was performed in five steps using de-ionized water (DIW), 0.01 M sodium bicarbonate (NaHCO_3), 1 M sodium acetate ($\text{C}_2\text{H}_3\text{NaO}_2$), 0.2 M ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$) and finally 7 M HNO_3 following the methods described by Guo et al. (1997), Bhattacharya et al. (2006) and Claesson and Fagerberg (2003).

The sediment extracts from LKB were analyzed using an atomic absorption spectrometer with flame atomization (air/acetylene) for high element content and an electrothermal atomization in graphite furnace HGA 800 for lower concentrations at the Hydrochemistry Laboratory of the Universidad Mayor de San Andrés in La Paz, Bolivia. The extracts from SPB were analyzed using a Varian Vista Pro Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at the Department of Geological Sciences, Stockholm University, in Sweden.

3.4. Hydrochemical data analysis of water

To evaluate the water chemistry results and water type at the wells, Piper plots, Stiff diagrams and Box and Whisker plots were made using Aquachem software 4.0.264 (Waterloo Hydrogeologic Inc, 2003) and Diagrammes software 6.59 (Laboratoire d'Hydrogéologie d'Avignon, 1999). The aqueous speciation of As (saturation indices and distribution of species) in water samples was calculated using the PHREEQC software (Parkhurst and Appelo, 1999), using the MINTEQA database (minteq.dat) which includes a thermodynamic database for As.

4. Results and discussion

4.1. Groundwater and surface water chemistry

The depth of the GW level varies considerably between 0.2 and 9.0 m in LKB and 0.7–8.0 m in SPB (Table 1). The pH was slightly alkaline in both regions; the samples from wells located in the plain tend to have a higher pH than those located in the highlands in SPB. The Eh indicates oxidizing condition in LKB and a moderately reducing environment in aquifers of SPB (Table 2). All the GW samples plotted on the Eh–pH diagram indicate that H_2AsO_4^- and HAsO_4^{2-} are the dominant As species (Fig. 3c) and this was confirmed by PHREEQ C in both cases (LKB and SPB).

According to the EC results (Table 2), GW of both basins is strongly influenced by the water-sediment interactions, therefore the presence of lacustrine sediments originating from ancient lakes indicates that there is evaporation in flat areas, generating high salinity (Servant-Vildary and Mello e Sousa, 1993). This phenomenon usually occurs in regions with semi-arid climate (Ormachea Muñoz et al., 2013).

The major water type identified in the shallow GW from LKB is

Table 2

Statistical summary of groundwater (GW) chemical parameters in the studied wells in Lower Katari Basin (LKB) and Southern Poopó Basin (SPB).

Parameter	Lower Katari Basin (LKB)				Southern Poopó Basin (SPB)			
	GW (n = 58)				GW (n = 19)			
	Min	Max	Median	Mean	Min	Max	Median	Mean
pH	7.2	8.8	7.8	7.9	6.6	7.9	7.6	7.4
EC ($\mu\text{S}/\text{cm}$)	125.0	11740.0	909.0	1773.4	340	2520	830	1035
Eh (mV)	235.4	274.0	246.4	247.2	135	278	158	175
T ($^{\circ}\text{C}$)	4.4	15.6	11.9	11.9	9.7	20.7	15.5	15.7
TDS (mg/L)	63.0	4363.0	455.0	797.1	180	1270	420	521
HCO_3^- (mg/L)	65.9	527.0	251.4	264.3	53	474	244	232
Cl^- (mg/L)	3.8	2568.0	70.6	268.9	17.7	542	90.5	154
SO_4^{2-} (mg/L)	7.4	2149.9	76.0	267.1	14.4	261	58.7	85.6
NO_3^- (mg/L)	0.1	228.2	4.5	18.4	0.1	109	9.7	19.1
PO_4^{3-} (mg/L)	0.01	4.1	0.01	0.2	0.1	12	0.7	2.2
Ca^{2+} (mg/L)	13.6	462.0	66.9	105.7	10.2	212	47.2	60
Mg^{2+} (mg/L)	2.4	153.7	19.3	30.8	2.3	43	5.5	9
Na^+ (mg/L)	4.5	1662.7	55.6	176.1	21.4	490	112	144
K^+ (mg/L)	2.7	42.7	9.9	13.2	6.2	40	11	15
Si (mg/L)	1.0	18.1	10.0	10.2	6.7	10.8	10.2	9.7
Al ($\mu\text{g}/\text{L}$)	5.3	4394.5	13.8	104.3	8.3	39	23	22
As ($\mu\text{g}/\text{L}$)	0.8	288.5	6.3	24.8	2.6	207	44	72
B ($\mu\text{g}/\text{L}$)	96.5	2472.9	288.6	452.6	507	4359	1761	1902
Ba ($\mu\text{g}/\text{L}$)	6.5	298.6	67.8	81.0	9.6	152	38.4	46.8
Cu ($\mu\text{g}/\text{L}$)	1.2	15.5	3.4	4.4	0.6	26	4	5.8
Fe ($\mu\text{g}/\text{L}$)	7.8	2444.8	23.5	150.8	4.2	260	13.7	28.5
Li ($\mu\text{g}/\text{L}$)	1.8	176.1	31.0	41.3	56	4372	241	731
Mn ($\mu\text{g}/\text{L}$)	0.6	7259.3	10.9	596.9	0.3	140	2.7	14.1
Sr ($\mu\text{g}/\text{L}$)	88.1	4746.3	715.2	1055.4	51.6	996.5	322.1	362.7
Ti ($\mu\text{g}/\text{L}$)	0.2	5.6	1.7	1.7	0.1	0.4	0.2	0.3
Zn ($\mu\text{g}/\text{L}$)	4.2	78.4	7.2	12.8	0.5	131	31	39
Cd ($\mu\text{g}/\text{L}$)	0.1	1.3	0.1	0.1	0.5	1.3	0.8	0.9
Cr ($\mu\text{g}/\text{L}$)	0.2	0.9	0.2	0.4	0.3	7.5	3.4	3.6
Ni ($\mu\text{g}/\text{L}$)	1.0	1.0	1.0	1.0	1.3	26	5.5	9
Pb ($\mu\text{g}/\text{L}$)	2.3	2.3	2.3	2.3	1	11	11	11
Rb ($\mu\text{g}/\text{L}$)	1.4	1.5	1.5	1.5	14.2	57.4	21.9	26.9
V ($\mu\text{g}/\text{L}$)	0.3	6.1	0.8	1.5	1	40	8.3	11

Ca-HCO_3 and to a lesser extent Na-Cl and Na-HCO_3 (Fig. 4a). Two major water types were identified in the shallow GW from SPB which correspond to the Na-Cl-HCO_3 type and Ca-Na-HCO_3 type (Fig. 4b).

Na^+ and Cl^- (Table 2) are the major cation and anion in LKB, which are positively correlated ($R^2 = 0.930$) (Fig. 4a), suggesting the dissolution of evaporitic minerals such as halite, that are common in semi-arid areas (Quintanilla et al., 1995; Banks et al., 2004; Ramos Ramos et al., 2012, 2014; Ormachea Muñoz et al., 2016) and this is also confirmed by geochemical modeling. Other predominant ions are noticed HCO_3^- , Ca^{2+} and SO_4^{2-} (Table 2). The correlation ($R^2 = 0.75$) between $\text{SO}_4^{2-} + \text{HCO}_3^-$ and $\text{Ca}^{2+} + \text{Mg}^{2+}$ is suggesting possible sources by weathering and/or dissolution of limestone (calcite), dolomite and gypsum (Ramos et al., 2012, 2014; Ormachea Muñoz et al., 2013; 2016), which is also confirmed by geochemical modeling. High concentrations of NO_3^- (Table 2) indicate anthropogenic sources, especially in some regions such as around the Pallina River, confluence between the Katari and Pallina rivers and near Lake Titicaca.

In SPB, the predominant anion is HCO_3^- (Table 2) (Fig. 4c), where the highest concentration levels are observed in the plain close to the sedimentary outcrops to the west, however high values are also occurring in Pampa Aullagas. The concentration of Cl^- varies significantly throughout the area. Na^+ is the predominant major cation (Table 2). Ca^{2+} concentrations are observed high in many samples (GW1: 81 mg/L; GW2: 122 mg/L; GW3: 92 mg/L; GW7: 67 mg/L; GW8: 67 mg/L; GW11: 83 mg/L; GW12: 212 mg/L; GW13: 56 mg/L), and the presence of ion Ca^{2+} can sometimes be linked to nearby calcareous rocks and sediments dissolution (Ormachea Muñoz et al., 2013).

The pH of the SW in LKB is observed to be more alkaline (mean: 9.5; range: 8.6–10.1), and the Eh indicates oxidizing conditions (mean: 247 mV; range: 244–249 mV). The range of EC was found to vary in between 970 and 2454 $\mu\text{S}/\text{cm}$ (mean: 1320 $\mu\text{S}/\text{cm}$). The highest EC values were observed in the southeast region of the Katari River (upstream) and in

the Cascachi region (near Lake Titicaca) (Fig. 2a). There is a dilution effect on the EC values in the SW, after the confluence of the Pallina River with the Katari River. In SPB, the pH of the SW is observed in the range of 7.9–8.5, which is higher than GW (Table 2). The EC and Eh are observed to be lower with average values of 616 $\mu\text{S}/\text{cm}$ and 120 mV, respectively. Major ions for SW samples of LKB have Ca-HCO_3 (69%) as major water type identified. There is a slight trend in geochemical evolution towards Na-HCO_3 . In the SPB, Na^+ is predominant, but none of the major ions exceeds the WHO guidelines.

In LKB, SW are not a safe source of drinking water and are not suitable for irrigation water, because the Pallina River initially and then the same Katari River carry a load of (liquid and solid) industrial and domestic sewage (El Alto, Viacha and Laja) (Duwig et al., 2014; Archundia et al., 2017). In the case of the SPB, SW are not a safe source of drinking water due to the high concentrations of As and B in the Sev-aruyo and Marques rivers (Ormachea Muñoz et al., 2013).

The wells with high concentration of As (WHO guideline limit: 10 $\mu\text{g}/\text{L}$) and B (NB - 512 guideline limit: 300 $\mu\text{g}/\text{L}$) in both regions are deemed to be unsafe for human consumption and irrigation. The high content of PO_4^{3-} (Table 2) in SPB and NO_3^- (Table 2) in both the basins could be a consequence of anthropogenic contamination by the discharge of wastewater, because the water table level of shallow wells is quite superficial (<10 m) in some places of LKB (Chacalleta) and SPB (Quillacas). The concentrations of silicon (Si) are elevated in GW samples in both basins (Table 2), and also elevated in SW (mean in LKB: 6 mg/L, range: 1–11 mg/L; mean in SPB: 6 mg/L, range: 4.6–9 mg/L).

4.2. Groundwater mineralization

The origin of the main processes controlling the mineralization of GW was determined in both the basins through the correlation between the main ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , SO_4^{2-} and NO_3^-) and

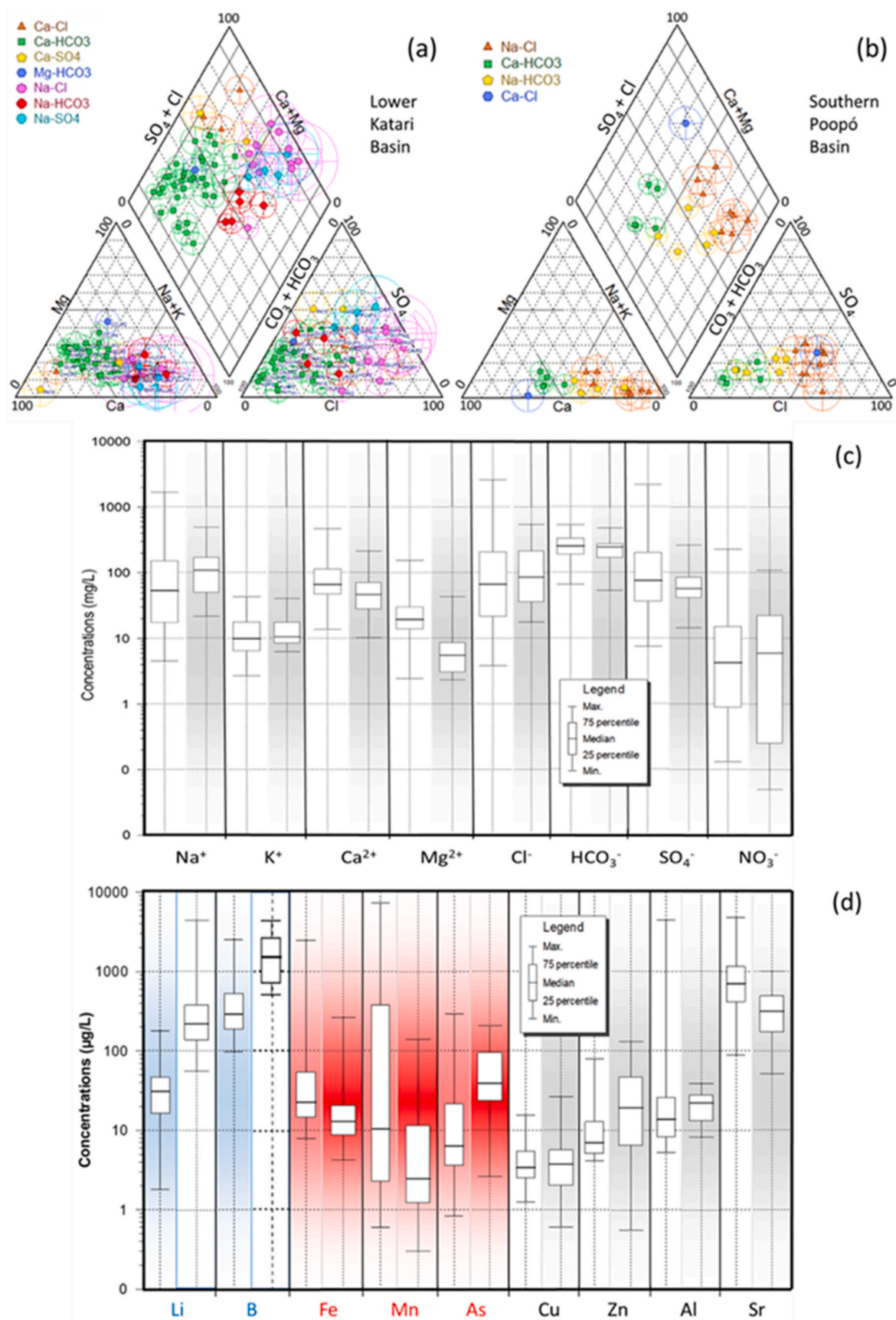


Fig. 4. Piper plot of groundwater samples in LKB (a) and SPB (b), Box and Whisker plot of major ions in groundwater samples in LKB (left side) and SPB (right side) (c) and Box and Whisker plot for each trace elements in groundwater samples in LKB (left side) and SPB (right side). Redox sensitive (red color) and evaporative (blue color) trace elements. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

total dissolved solids (TDS) (Fig. 5).

In Fig. 5, the correlation plots show the evolution of the concentrations of the major ions as a function of TDS. It is observed that the mineralization of GW in both basins (LKB and SPB) is essentially controlled by the concentrations of Na^+ , Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} . The positive correlation (slope 1) between Na and Cl (Fig. 5i) indicates that

these two ions probably have the same origin. Most of the samples from both basins are scattered around the line with a positive slope, which indicates that there is a contribution of halite dissolution in GW. This statement is also supported by the negative saturation indexes of this mineral as a result of geochemical modeling in both basins. The samples (central, north, east and south plain in LKB; central, north and northeast

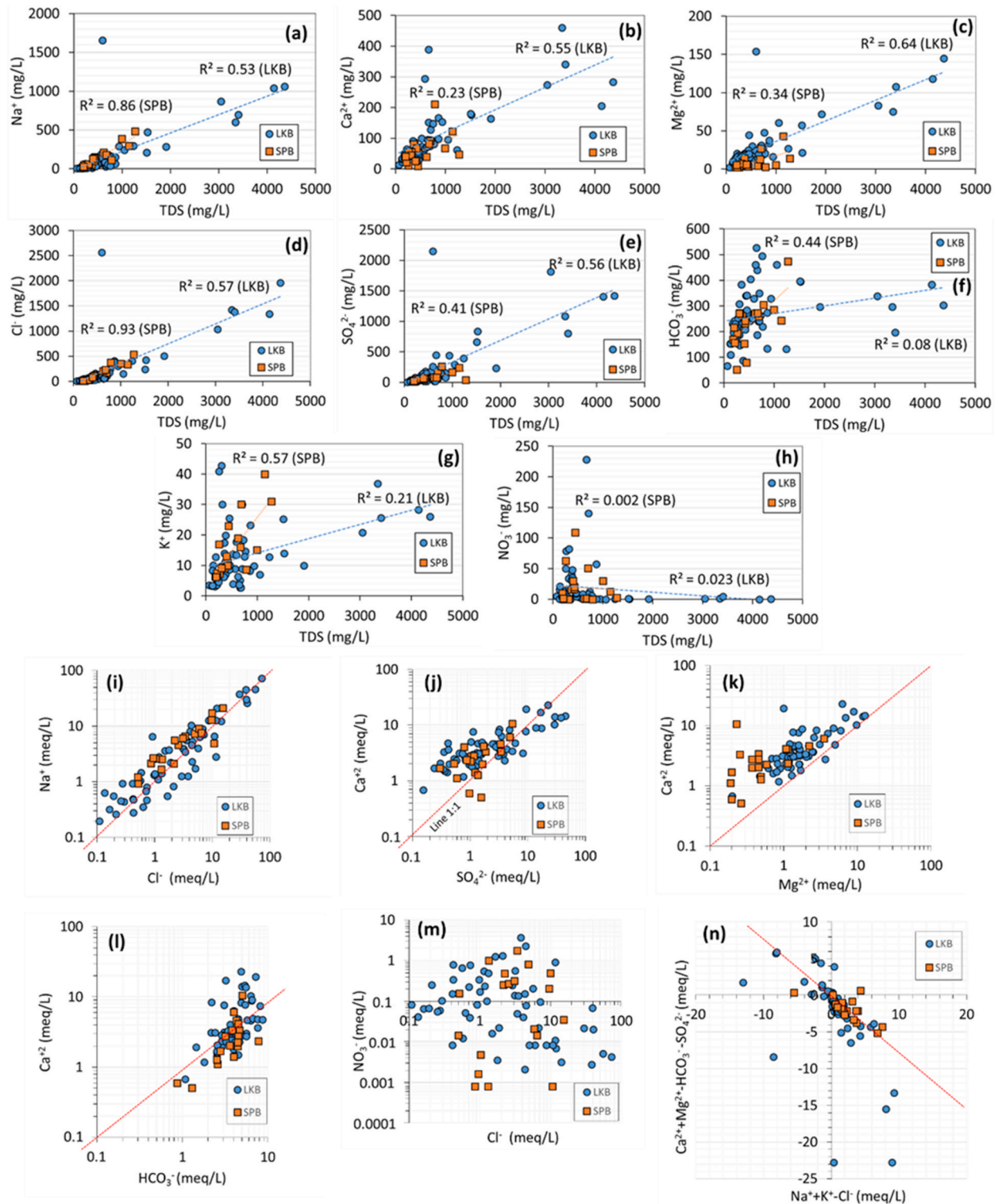


Fig. 5. Correlation plots between major ions (Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , K^+ , NO_3^-) and TDS (a to h) of groundwater samples of LKB and SPB. Correlation plots Na^+ vs Cl^- (i), Ca^{2+} vs SO_4^{2-} (j), Ca^{2+} vs Mg^{2+} (k), Ca^{2+} vs HCO_3^- (l), NO_3^- vs Cl^- (m) and $(\text{Ca} + \text{Mg} - \text{HCO}_3 - \text{SO}_4)$ vs $(\text{Na} + \text{K} - \text{Cl})$ (n), for groundwater of LKB and SPB.

plain in SPB) that have concentrations below the slope line 1 indicate that there would be an excess of Cl^- and a deficiency of Na^+ . This could be due to the fact that ion exchange processes take place where the Na^+ ions are released from the complex (halide minerals) and they are replaced by Ca^{2+} ions (Fig. 5n).

In Fig. 5k, it is observed that many samples are found around the slope line 1, which is indicating the contribution of the gypsum dissolution in the mineralization of GW in both basins. This phenomenon is also validated by negative values of the saturation index (SI) of this mineral. The values (concentration of Ca^{2+} with SO_4^{2-}) in Fig. 5j that are above slope line 1 are indicating an excess of Ca^{2+} in GW mineralization. In Fig. 5n, numerous values are aligned with the slope line -1 , which would be indicating that the excess Ca^{2+} is due to the phenomenon of inverse base exchange.

In Fig. 5k, some samples from both basins are aligned with slope line 1, which indicates the dissolution of dolomite. But most of the values are above the line, indicating an excess of Ca^{2+} , this phenomenon could be due to the ion exchange process (Fig. 5n). In Fig. 5l, it is observed that the Ca^{2+} and HCO_3^- ions do not have a significant correlation, and this phenomenon is also observed in the low correlation between HCO_3^- and TDS, both figures show the importance of this ion in groundwater mineralization.

4.3. Redox sensitive elements - spatial distribution

The concentration of redox sensitive elements (As, Mn, and Fe) in GW is shown in the box plots of Fig. 4d (red color), where they are compared one by one for LKB and SPB. In the LKB the GW showed elevated concentrations of As: 40% of wells samples have higher levels than the NB-512 (IBNORCA, 2004) and WHO guidelines values of 10 $\mu\text{g/L}$. In SPB, eighteen of the nineteen wells (95%) indicated higher levels of As ($>10 \mu\text{g/L}$).

The highest concentration of As was found in the wells of LKB with the shallowest phreatic level (0.8 m) within the north plain (flood delta) of Lacaya Cohana (LACP3) and Wilajahuira (WIP1) with 288.5 $\mu\text{g/L}$ and 233.3 $\mu\text{g/L}$ respectively (Fig. 6a). In SPB, the highest concentrations of As are found within the plain of the Pampa Aullagas, Quillacas and Condo K sites (PACK belt) (Fig. 6b). A well located in Condo K was drilled to a depth of 18 m and contained 14 $\mu\text{g/L}$, where shallow wells had As levels well above 100 $\mu\text{g/L}$. The highest value of As (207 $\mu\text{g/L}$) was found in the plain northeast of Quillacas (Table 2). High values tend to occur in lowland sedimentary deposits, as opposed to moderate values obtained at higher elevations (Fig. 6b). Arsenate is the predominant species due to relatively oxidizing conditions (Fig. 3c).

Both areas (LKB and SPB) are lowlands, with sediments of lacustrine origin, areas of low slope and with shallow water tables especially in LKB (0.6–0.8 m) (Fig. 2a and b). Other areas with minor concentration of As, but above the WHO guideline and Bolivian regulation (NB-512) for human consumption are located in slightly elevated areas around volcanic formations. This feature is present in Korila, Quiripujo, Chojasivi and Huacullani in LKB (mean: 22 $\mu\text{g/L}$) and the wells in high ground that are closer to the infiltration point with thicker soils in SPB (39 $\mu\text{g/L}$ mean).

In wells near the Katari River in the central plain of LKB, As concentrations are slightly elevated in Masaya (81–109 $\mu\text{g/L}$) and Tircani (86 $\mu\text{g/L}$), due to the presence of alluvial sediments with enriched organic matter (Bhattacharya et al., 2002a, 2002b). In some lowland wells (delta in LKB), there may be interchangeable fractions within sediments that can mobilize As to GW due to salinity (Ormachea Muñoz et al., 2013). In wells that are outside the northwest region in LKB and the PACK belt in SPB, the risk still persists for people who consume these waters, even though As concentrations are lower (mean: 21 $\mu\text{g/L}$ in LKB and 33 $\mu\text{g/L}$ in SPB).

In SW of LKB, the As concentrations are low upstream of the basin, but these levels increase downstream, in the northern plain (flood delta), in Cohana (COR1: 48 $\mu\text{g/L}$), Lacaya (COR2: 26 $\mu\text{g/L}$) and Calachaca

(COR3: 25 $\mu\text{g/L}$) (Fig. 6a). In SPB, the Marques and Sevaruyo rivers show high concentrations of As upstream of the basin due to the weathering of volcanic rocks (Ormachea Muñoz et al., 2013) and in the waters below the basin, the As concentrations also increase. The Marques River presents 67.8 $\mu\text{g/L}$ of As near the Marques Train Station (MAR3). The concentration of As in Marques and Sevaruyo rivers increases in the downstream direction of the basin. Arsenic concentrations in upper, middle and lower sections of the Marques River were observed as 38, 48 and 55 $\mu\text{g/L}$, respectively. In the Sevaruyo River, near the town of Sevaruyo, the As concentration was 71 $\mu\text{g/L}$ and near Quillacas it was 88 $\mu\text{g/L}$. In both cases (LKB and SPB) this downstream increase could be linked to concentrations by evaporation (Banks et al., 2004), which is corroborated by high salinity (Na^+ and Cl^-) in the same areas.

Manganese (Mn) occurs in high concentrations in some wells (PK4: 3781 $\mu\text{g/L}$; PK10: 7259 $\mu\text{g/L}$; PK11: 3974 $\mu\text{g/L}$; CCJP3: 4725 $\mu\text{g/L}$) in LKB (Fig. 4d), where 29% of the all wells exceed the NB-512 limit of 100 $\mu\text{g/L}$. The elevated concentrations of Mn occur predominantly in wells of the central flat area (mean: 1017 $\mu\text{g/L}$, range: 0.9–7259 $\mu\text{g/L}$) and close to the hills in the northeastern area (mean: 847 $\mu\text{g/L}$; range: 4–4725 $\mu\text{g/L}$) as well as in the north plain (flood delta) (mean: 782 $\mu\text{g/L}$; range: 199–1555 $\mu\text{g/L}$).

Fe concentration as major in GW was observed in the north plain (flood delta) (mean: 655 $\mu\text{g/L}$; range: 27–1251 $\mu\text{g/L}$) in LKB. The concentrations of dissolved Fe, aluminum (Al) and Mn in SPB are very low (Table 2) in comparison to LKB, except in one sample (CARP1) that has a Mn concentration of 139 $\mu\text{g/L}$ (Fig. 4d). All samples have levels below the WHO reference values for these elements (Table 2).

The content of Mn in SW is high in LKB (mean: 272 $\mu\text{g/L}$; range: 41–584 $\mu\text{g/L}$) and low in SPB (mean: 6 $\mu\text{g/L}$; range: 2–12 $\mu\text{g/L}$). The Fe concentration in SW in LKB (mean: 38 $\mu\text{g/L}$; range: 20–71 $\mu\text{g/L}$) and SPB (mean: 80 $\mu\text{g/L}$; range: 23–314 $\mu\text{g/L}$) are low.

In GW, a positive correlation was observed in between As and HCO_3^- (LKB: $R^2 = 0.97$ and SPB: $R^2 = 0.89$) and As and Na^+ (LKB: $R^2 = 0.61$ and SPB: $R^2 = 0.55$) in the northern region of both basins. Thus, it could be assumed from these results that As is associated with the Na– HCO_3^- system, related to the weathering/dissolution of carbonate minerals (limestone and dolomite), halite and plagioclase minerals which is in agreement with previous investigations (Ramos et al., 2012, 2014; Ormachea Muñoz et al., 2013; 2015). As a result of the dissolution of these minerals, Na^+ and HCO_3^- are incorporated in solution, with the consequent increase in pH and alkalinity; these are favorable conditions for the high mobility of As oxyanionic species (Bhattacharya et al., 2002a; Smedley and Kinniburgh, 2002; Sracek et al., 2004; Nriagu et al., 2007; Ormachea Muñoz et al., 2013; Mariño et al., 2020).

The As mobilization process appears to be controlled by the sorption/desorption of the ferric oxide surfaces in the GW in areas with oxidizing conditions, such as some areas of LKB and SPB, where the solubility of Fe and Mn oxides is low. This indicates the competitive adsorption of As and other oxyanions (Smedley et al., 2005). The oxyanions that compete with As could be HCO_3^- and SiO_4^{4-} that are related to alkaline pH (Ramos et al., 2014).

On the other hand, reductive dissolution of Fe oxides and As release could also be occurring, which could explain the high concentration of As in shallow aquifers (north region of LKB and SPB). In GW of both basins, pH values are slightly alkaline; therefore, the mobilization process could be related to the dissolution of Fe or Mn oxides by reduction to soluble Fe (II) and Mn (II), which could release the adsorbed As (Oscarson et al., 1981; Smedley and Kinniburgh, 2002; Ramos et al., 2014). This process could be occurring in the northern area of LKB and SPB (alluvial sediments). In turn, the process of immobilization of As can be influenced by adsorption to ferric oxide surfaces where GW has oxidizing conditions (Smedley et al., 2005; Ramos et al., 2014).

4.4. Evaporative elements - spatial distribution

The concentration of evaporative elements such as B and lithium (Li)

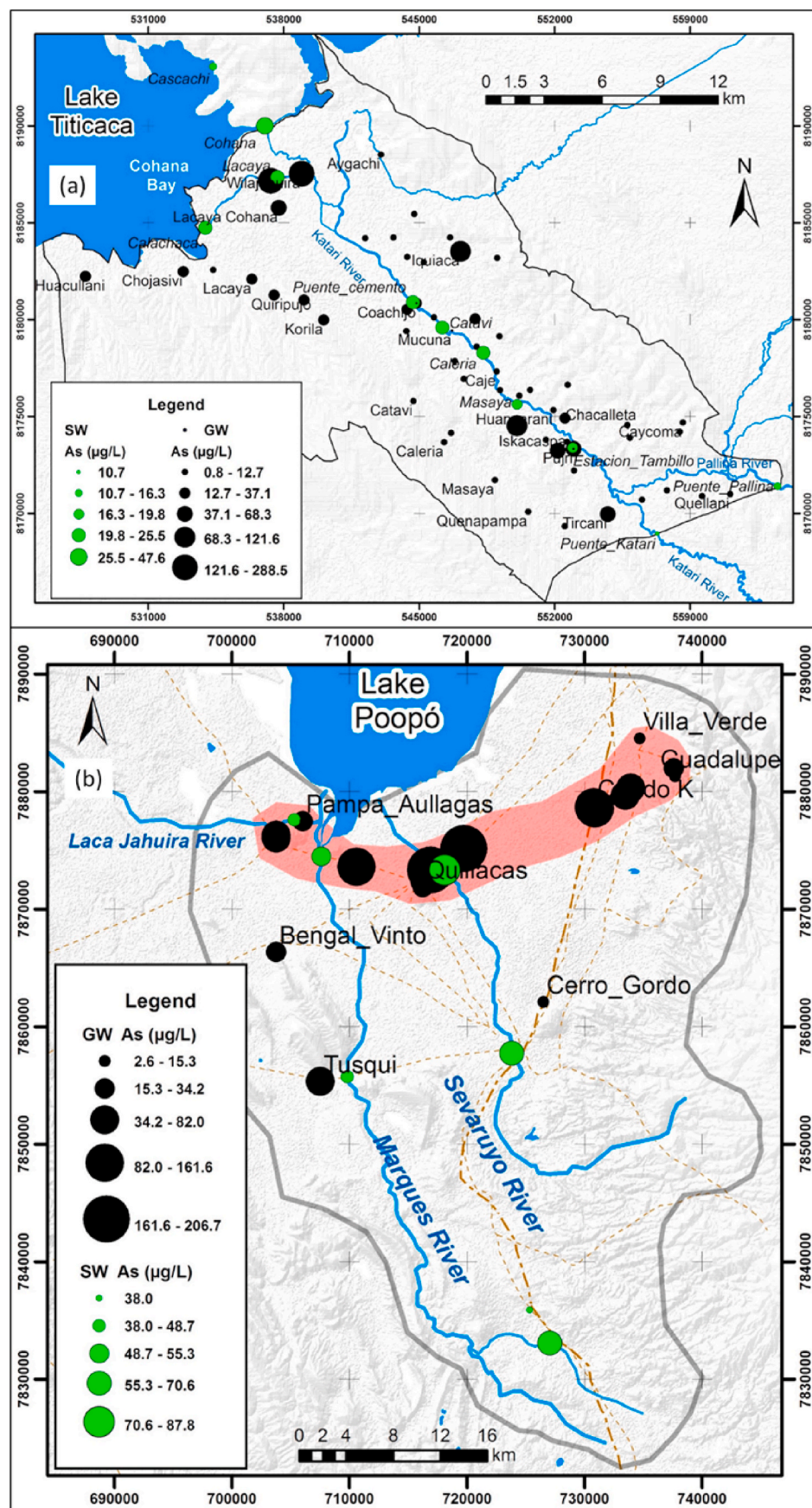


Fig. 6. Distribution of arsenic (As) concentrations in groundwater (GW) and surface water (SW) of LKB (a) and SPB (b).

in GW are shown in the box plots of Fig. 4d (blue color) where they are compared one by one for the LKB and SPB. The LKB has lower concentrations of Li in comparison to SPB; the maximum value was 4372 µg/L in SPB (Table 2 and Fig. 4d). The B concentrations in LKB exceed the NB-512 limit of 300 µg/L in 48% of the wells (n = 58). The B concentration values exceed the WHO limit of 500 µg/L in all wells of the SPB (Fig. 4d) (Table 2).

The B in LKB correlates with the ions HCO_3^- ($R^2 = 0.11$), Cl^- ($R^2 = 0.52$) and Na^+ ($R^2 = 0.70$). The B has higher concentrations in GW (Fig. 4d) in the southeastern portion of the study area at the confluence zone between Katari and Pallina rivers (mean: 573 µg/L; range: 284–1016 µg/L) and in the flat area (mean: 641 µg/L; range: 123–2473 µg/L). The B in SPB correlates with the cations HCO_3^- ($R^2 = 0.57$), Cl^- ($R^2 = 0.60$) and Na^+ ($R^2 = 0.66$). The Li in LKB correlates with the ions HCO_3^- ($R^2 = 0.14$), Cl^- ($R^2 = 0.71$), SO_4^{2-} ($R^2 = 0.67$) and Na^+ ($R^2 = 0.75$). The highest Li values occur predominantly in wells close to volcanic rock outcrops in SPB. The B concentration in SW has a mean of 237 µg/L and a range of 142–966 µg/L in LKB and are higher (mean:

959 µg/L; range: 270–2344 µg/L) in SPB.

In both basins, Li and B are correlated with the main ions that increase the salinity of GW, such as HCO_3^- , Cl^- and Na^+ (Fig. 5), which is suggesting that the weathering/dissolution of these TE is directly related to the salinity of the waters. An explanation for the presence of Li and B in high concentrations in some wells is linked to the origin of the sediments. Much of the material is likely to originate from the upstream volcanic formations in the southern part of both basins. The different alluvial processes in the paleolakes and the subsequent wind processes have redistributed the material throughout the Bolivian Altiplano, causing the sediments to be very heterogeneous as observed in the field.

Arsenic, Li and B are elements typically present in ignimbrites and correlate very well with the salinity (Na^+ , Cl^- and HCO_3^-) of GW (Ormachea Muñoz et al., 2013). These elements could remain in SW and accrue in GW. This process could be developed especially in wells located in lowlands of both basins. Part of exchangeable Li and B present in the sediments could be mobilized to the GW due to the increase in salinity caused by the arid climate and evaporation (Ormachea Muñoz

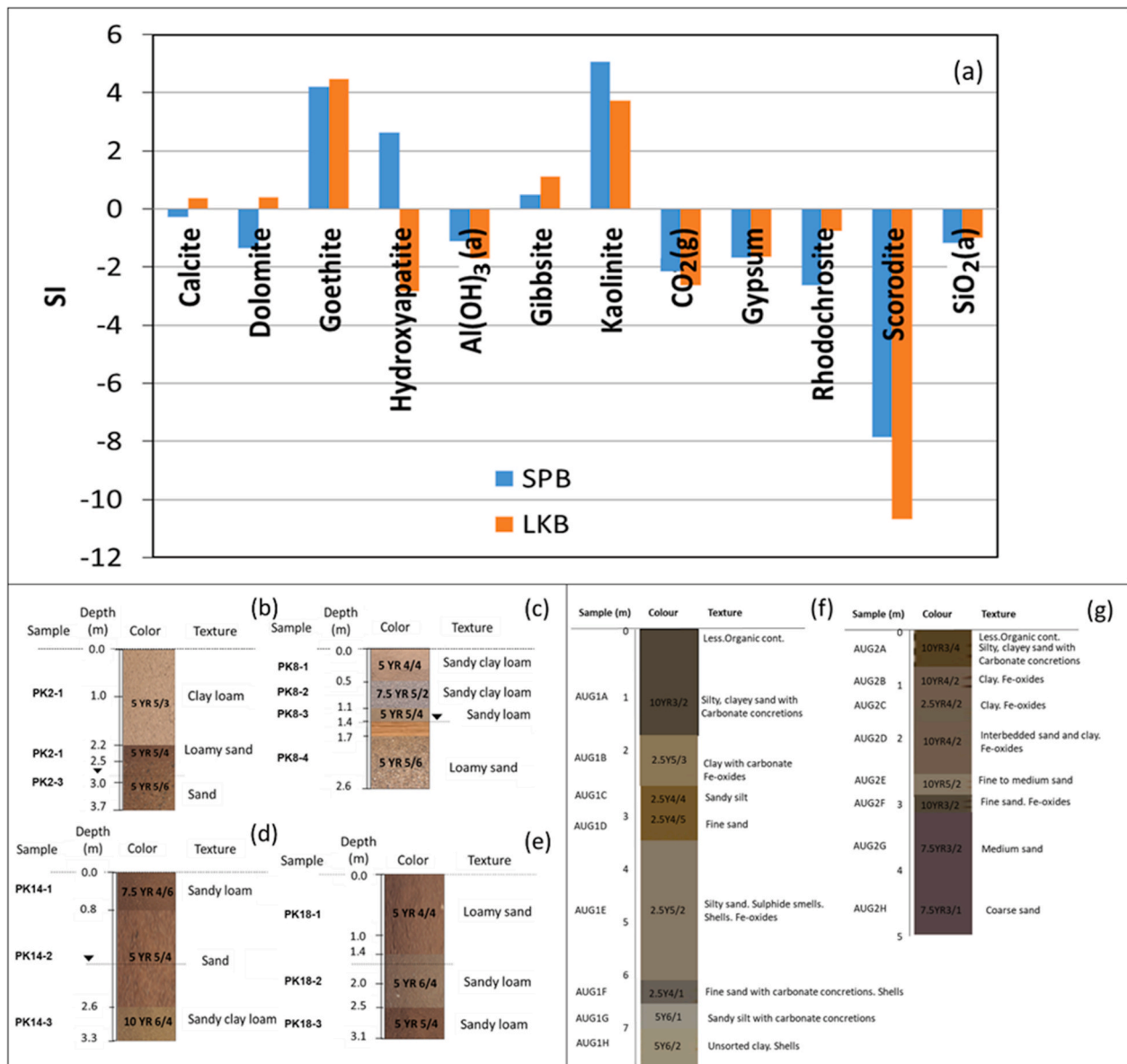


Fig. 7. Mean values of the saturation indices (SI) for selected minerals GW in LKB (orange) and SPB (blue) (a). Distribution for lithological profiles and color and texture of the sediments collected during the installation of the piezometers: PK2 (b), PK8 (c), PK14 (d) and PK18 (e) in Lower Katari Basin and AUG1 (f), AUG2 (g) in Southern Poopó Basin. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

et al., 2013).

4.5. Hydrogeochemical modeling

The saturation indices (SIs) obtained using the hydrochemical code PHREEQC applied to the data from LKB and SPB indicated that the GW is supersaturated with respect to the Fe-oxide/hydroxide minerals such as goethite [α -FeOOH], hematite [Fe_2O_3] and ferrihydrite [$\text{Fe}(\text{OH})_3$], and the Al-minerals such as gibbsite [$\text{Al}(\text{OH})_3$], K-mica [$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$], kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$], and boehmite [γ - $\text{AlO}(\text{OH})$]. These results are suggesting the precipitation of Fe(III) and Al(III) phases in GW. The SI for carbonate minerals, such as calcite [CaCO_3], dolomite [$\text{CaMg}(\text{CO}_3)_2$] and magnesite [MgCO_3], are more negative or at equilibrium, it could be suggesting that the chemistry of GW is controlled by precipitation and dissolution of carbonate minerals. The SI also revealed the dissolution of halite [NaCl] and gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$] minerals (Fig. 7a).

In both basins (LKB and SPB) the aqueous speciation data (based on hydrochemical modeling using PHREEQC code) indicates the As(V) as the predominant species (98.2% in LKB and 84.6% in SPB) with different degree of protonation such as HAsO_4^{2-} (54.6% in LKB and 51.2% in SPB) and H_2AsO_4^- (4.3% in LKB and 13.4% in SPB), as well as CaHAsO_4 (17.8% in LKB and 14.1% in SPB). The As(III) is the other species present (1.8% in LKB and 15.4% in SPB) in a very low proportion in both basins, with different degree of protonation such as H_3AsO_3 (1.7% in LKB and 15.2% in SPB) and H_2AsO_3^- (0.02% in LKB and 0.2% in SPB).

4.6. Solid – phase characterization

The northwest region (flood area) of the LKB, has highest As concentrations indicating that sediments are probably the most important sources of As. Similarly, in the SPB the tendency shows that higher concentrations of As are located in the wells of the central plain suggesting that sediments are an important source. The contents of As in sediments are high (84 mg/kg maximum value) compared to the estimated global mean 1–5 mg/kg (Bhattacharya et al., 2002a, 2002b; Ravenscroft et al., 2009; Ormachea Muñoz et al., 2013), which might be explained by the fact that alluvial sediments are favorable for the enrichment of As in many parts of the world (Bhattacharya et al., 2002a, 2002b). The high sediment contents in both basins (maximum values: 84 mg/kg in LKB and 50.6 mg/kg in SPB) indicate their importance in As anomalies.

4.6.1. Lithological characteristics

The drilling and sediment sampling of the piezometers revealed a high vertical variability in their characteristics (texture, color) and some differences between all sampling sites (19 piezometers in LKB and 2 piezometers in SPB). The LKB area has a recent Quaternary formation corresponding to deposits of riverine and lacustrine origin, according to the information of the sediments at different depths during drilling of the monitoring wells. These deposits of lacustrine origin would be formed by silty clay and other clay materials distributed in the extensive plain of the basin, with lacustrine processes of sedimentation. The fluvial deposits are associated with the rivers present in the area, and have varied sand granulometry starting with fine, medium to thick in the vicinity of the rivers, where a consolidated stratum 0.3 m–0.1 m conformed by silt and clay also is evidenced (Fig. 7b, c, 7d and 7e).

In the SPB, the sediment layers at Condo K (AUG1) are composed of finer fractions, viz. fine sand, silt and clay (Fig. 7f). The shells and grain size that were found in the profile indicate that sediments below 2 m have lacustrine origin. The most recent upper layer probably contains aeolian and alluvial sediments. Fe oxides abounded in many layers, indicating the existence of an oxidized environment. The water table was measured 1.51 m deep, similar to the GW9 well. The silty sand layer (AUG1E) has a reducing character with a strong sulphide smell (Fig. 7g). In both locations, the upper sedimentary layers are more colorful as red and brown (due to the presence of oxidized Fe), while the deeper layers

become more grayish (Fig. 7f and g) due to a seemingly reduced character. The sediments in Quillacas (AUG2) follow a pattern of alluvial sedimentation with thicker material at the bottom to gradually finer material near the surface (Fig. 7b–g). The upper layer of Quillacas comprises wind-blown sediments, however considerably thinner than in Condo K. On the contrary, the deeper sediments are thicker in Quillacas compared to those in Condo K with the presence of Fe oxides. Carbonate concretions are present on the water table that is in the upper layer in Condo K and Quillacas.

4.6.2. Geochemical characteristics

4.6.2.1. Elemental characteristics of core sediments of piezometers. In Table 3, the mean values of As in total extraction for each piezometer are presented for sediment samples of LKB in order of southeast to northwest (Fig. 3a). In a layer of the PK6 (Masaya) and PK12 (Chacalleta), high As levels were identified at depth of 3 m below the ground surface, containing 62.9 and 84.8 mg/kg respectively. High As_{total} contents were found in several sites such as Isakacaspa (PK2) (depth 2.2 m: 24.5 mg/kg; depth 3 m: 26.4 mg/kg), Caleria (PK10) (depth 2.7 m: 25.8 mg/kg), Chacalleta (PK13) (depth 2 m: 24.6 mg/kg; depth 5 m: 28 mg/kg), Cajé (PK14) (depth 3 m: 29.6 mg/kg), Cajé (PK15) (depth: 3 m 27.9 mg/kg), Mucuña (PK16) (depth 2 m: 20.3 mg/kg) and Chacalleta (PK19) (depth 2.5 m, 23.1 mg/kg) (Fig. 3a). In general, there is a tendency to increase the As_{total} content with depth. With the exception of Fe ($R^2 = 0.46$), the mean content of As and some TEs (Fe, Al, Sb, B) by layer depth (0.5–5.0 m) show a low correlation; this might be explained by the fact that oxides and hydroxides especially of Fe and Al commonly adsorb As.

In SPB, Condo K sediment samples contain a mean of As_{tot} of 24.3 mg/kg. There are two layers with elevated levels of As at 3 and 6 m below the soil surface, with 40.6 and 50.6 mg/kg of As, respectively. The mean concentration of As in Quillacas is 10.4 mg/kg. In Quillacas, the highest concentration of As (36.6 mg/kg) was found at 1 m below land surface, whereas the As concentration was 9.3 mg/kg at a depth of 3 m. Thus, in Quillacas, the amount of As decreases with depth. In Condo K, the amount of As in the layers are randomly distributed. The As correlates with Fe, Al and Mn whose oxides and hydroxides normally adsorb As.

The contents of As in the sediments of different piezometric profiles varies according to depth. In case of LKB, the second (2–3.5 m) and third layer (3.5–4.5 m) have clays, silts and fine sands of lacustrine origin with a high content of As (63–84 mg/kg). This characteristic also occurs in the sediments of Condo K (SPB) that have more than twice of the mean As content than the thickest sediments in Quillacas. In both LKB and SPB, there is a great spatial variation in sediment characteristics in addition to the variation in As contents at different sampling points. In case of SPB, much of the material originated upstream of the basin comes from volcanic formations in the south of the basin, where the

Table 3
Total extraction of arsenic for core sediment samples from piezometers in LKB.

Katari River (LKB)					
Left side (flat area)			Right side (flat area)		
Code	Place	As (mean) mg/kg	Code	Place	As (mean) mg/kg
PK1	Iskacaspa	10.4	PK12	Chacalleta	37.6
PK2	Iskacaspa	23.2	PK19	Chacalleta	15.7
PK3	Iskacaspa	7.5	PK13	Chacalleta	26.3
PK4	Masaya	9.5	PK14	Cajé	19.8
PK5	Masaya	9.7	PK15	Cajé	20
PK6	Masaya	31.1	PK16	Mucuña	13.4
PK7	Caleria	11.7	PK17	Mucuña	11.1
PK8	Caleria	13.6	PK18	Coachijo	13.7
PK9	Caleria	11.2			
PK10	Caleria	20.3			
PK11	Catavi	15			

trace element (Li, B, and V) concentrations are observed higher (Ormachea Muñoz et al., 2013). The variety of concentrations of As in LKB and SPB is a consequence of the alluvial processes of the paleolakes and due to the redistribution of sediments throughout the Altiplano caused by the wind (Ormachea Muñoz et al., 2013). Another source is

evaporites (sedimentary rocks that are formed by the crystallization of dissolved salts in lakes) intermingle with sediments found in places with high As content, which makes their distribution irregular (Banks et al., 2004).

In LKB, the mean concentrations of Fe and Al in all piezometers were

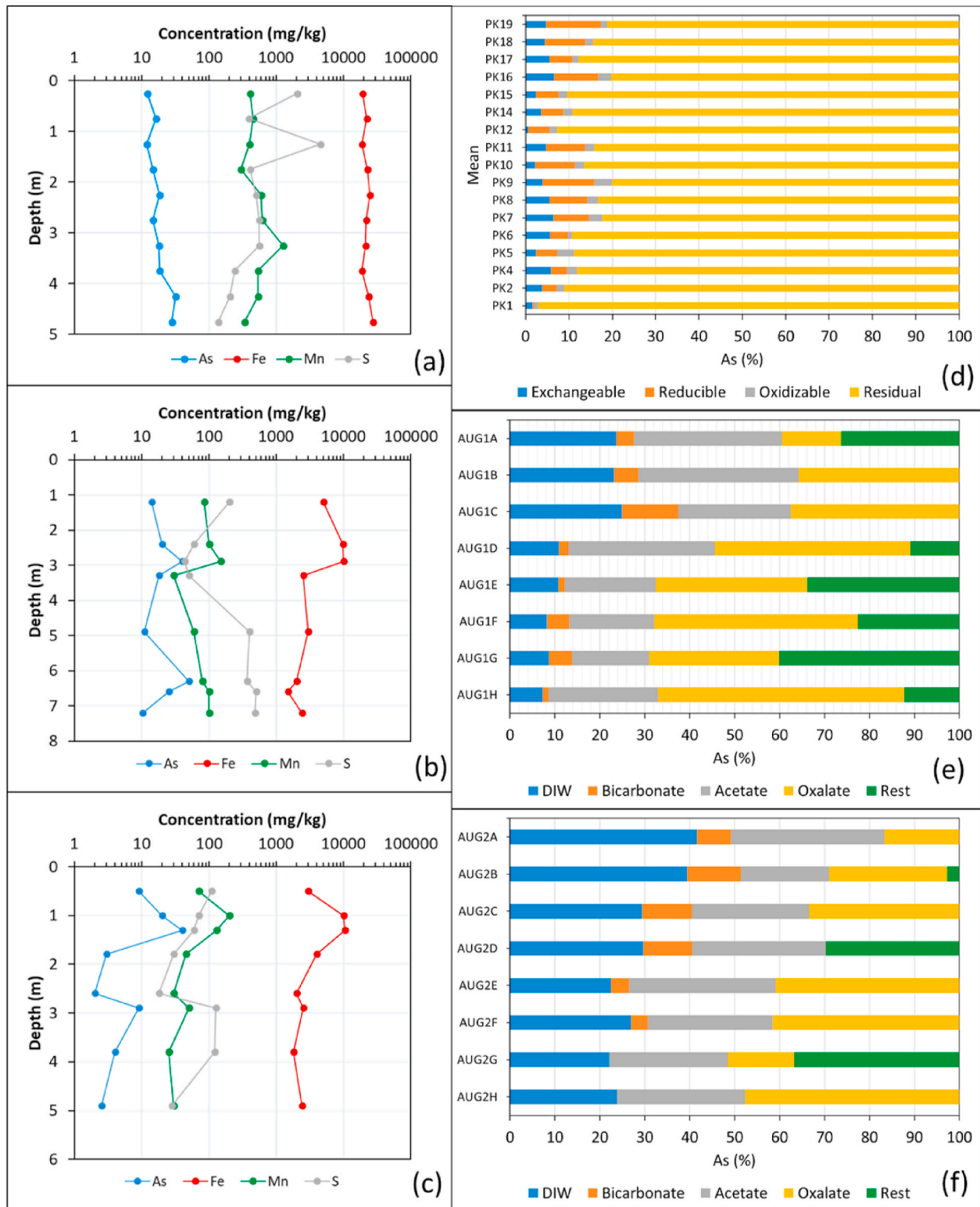


Fig. 8. Trace elements (TEs) content from total extraction of the core sediments from the piezometers (mean values) in LKB (a) and in Condo K (b) and Quillacas (c) from SPB. Mean values of sequential extraction of As from each sediment by piezometer (d) in LKB. Sequential extraction of As from each sediment layer in Condo K (e) and Quillacas (f) in SPB.

observed in the range of 18600–27100 mg/kg and 9600–24600 mg/kg respectively, where the mean Mn contents were 300–1200 mg/kg. There is a tendency to increase the concentration of these elements with depth (Fig. 8a). There is a significant difference in the content of sulfur (S) in Iskakaspá (PK1 mean: 118.9 mg/kg) and Caleria (PK8 mean: 7278.0 mg/kg). In Caleria (PK8), the high values of S observed in the sediments at depths of 0.5–3 m. The calcium (Ca) content was found to be higher in Catavi (PK11 mean: 11100 mg/kg), Iskakaspá (PK3 mean: 12800 mg/kg), Caleria (PK7 mean: 13200 mg/kg), Coachijo (PK18 mean: 15700 mg/kg) and Caleria (PK8 mean: 22700 mg/kg), at depths of 0.5–3 m. The Ca content was observed to decrease with depth in the sediments.

In SPB, the amounts of Fe and Al in Condo K vary between 1700 and 12300 mg/kg and 900–3400 mg/kg, respectively, where as in Quillacas, the ranges are 2600–11300 mg/kg and 1100–3600 mg/kg respectively. Mn concentrations are observed as low as 32–158 mg/kg in Condo K (Figs. 8b) and 27–208 mg/kg in Quillacas (Fig. 8c). The mean S content in Condo K is 297.9 mg/kg (5–7 m higher values) and in Quillacas 67.6 mg/kg (Fig. 8b). The mean of Ca concentration in Condo K is 7189 mg/kg and in Quillacas it is 2697 mg/kg (Fig. 8c), probably due to a greater presence of shells.

4.6.2.2. Elemental characteristics of river sediments. In LKB, the As content in the Pallina River (Laja; PAS1) was 17.5 mg/kg and in the confluence between the Pallina and Katari rivers (Pujri; KAS2) was 25.9 mg/kg. The content of As along the Katari River was 9.0 mg/kg in Quellani (KAS1) and 22 mg/kg in Caleria (KAS6). The highest As content (42.3 mg/kg) was found in the Lacaya region (COS3) to the northwest of the study area (Table 1 and Fig. 1b). Another important elements were Fe (range: 18200–26900 mg/kg), Al (range: 5900–15400 mg/kg), Mn (range: 270.1–474.4 mg/kg), zinc (Zn) (range: 74.7–491.1 mg/kg), Si (range: 98–170.7 mg/kg), B (range: 50.2–88.9 mg/kg), Sb (range: 3.4–60.3 mg/kg) and Li (range: 34.3–92.4 mg/kg). The spatial distribution of TE contents in sediments does not follow a trend.

In SPB, the river beds were dry during the field work in November 2009, only one sample of river sediment (MAR3) was collected, which presented medium to coarse sand of greyish color, containing low amounts of As (1.42 mg/kg).

4.6.2.3. Sequential extraction of As in core sediments of piezometers. In all the cases (Table 4), the concentrations of As in LKB were found higher in fraction 4 (F4 - residual fraction), followed by fraction 2 (F2 - reducible fraction), fraction 1 (F1 - exchangeable fraction) and fraction 3 (F3 - oxidizable) (Fig. 8d). The concentrations of extracted As are much higher in profiles 2 and 3. In general, being the main proportion within

Table 4
Sequential extraction of As in core sediments of Lower Katari Basin by layer, depth and fraction.

Lower Katari Basin (LKB)					
Layer	Depth (m)	Fraction	Min (mg/kg)	Max (mg/kg)	Mean (mg/kg)
First	0.1–1.5	F4	6.4	33.4	15.2
		F2	0.3	2.6	1.5
		F1	0.2	1.7	0.8
		F3	0.1	0.9	0.5
Second	1.5–2.5	F4	11.7	94	29.8
		F2	0.03	5.7	1.7
		F1	0.1	5.1	1.2
		F3	0.2	1.2	0.6
Third	2.4–3.2	F4	10.2	38.7	21.7
		F2	0.5	3.6	1.7
		F1	0.2	1.9	1.0
		F3	0.3	1.0	0.5
Fourth	2.5–3.3	F4	12.1	16.4	14.1
		F2	1.3	1.6	1.5
		F1	0.5	1.0	0.8
		F3	0.3	0.4	0.3

the residual fraction (approximately 84%), it is considered that As is associated with primary and secondary minerals, and it probably does not dissolve under natural conditions (Mäkelä et al., 2011), which indicates that As has low mobility in the central plain. The reducible fraction of As is approximately 9%, which indicates that the largest percentage of mobile As is associated with oxides of Mn and Fe, that are the forms normally known as sinks of trace elements in the surficial environment (Silveti et al., 2013). In 5% of the extractions, As is found in the exchangeable form, and it could be released by ion exchange processes or co-precipitated with carbonates, this fraction would be the most readily available (Gleyzes et al., 2002). Finally, only 2% of the extractions are in oxidizable form (sulfides), which are considered as immobile or bioavailable form of As (Filgueiras et al., 2002).

In SPB, layer with high As content were found in total extraction and also were identified with sequential extraction (SE) (Fig. 8e and f), with the exception of AUG1C (lower concentration). In the upper layer, the extracted As concentrations by de-ionized water (DIW) (mean AUG1: 15%; mean AUG2: 29%) were much higher in Quillacas (AUG2) (1.0–8.6 mg/kg) (Fig. 8e), than in Condo K (AUG1) (1.1–4.1 mg/kg) (Fig. 8f). In the deeper strata, the fractions are more similar. In Condo K, the values are low in relation to the other extraction steps, while in Quillacas they are high; this indicates a large fraction of As can be easily mobilized. The As extracted by sodium bicarbonate (NaHCO_3) (mean AUG1: 5%; mean AUG2: 6%) was low in both profiles compared to the other extraction steps (<LD - 2.8 mg/kg). The extraction by sodium acetate ($\text{C}_2\text{H}_3\text{NaO}_2$) (mean AUG1: 26%; mean AUG2: 28%) produced a high extraction of As in both profiles (2.6–11.0 mg/kg in Condo K and 1.3–6.6 mg/kg in Quillacas). This correlates well with the high carbonate content, especially in Condo K. The ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$) (mean AUG1: 37%; mean AUG2: 28%) extracts significant amounts of As from most sediment samples, especially those with a high As content (Condo K: 1.4–23.1 mg/kg and Quillacas: < DL - 6.5 mg/kg).

4.7. Rock - sediment - water interactions

The direct effect of volcanic rocks on the GW in both basins (LKB and SPB) is limited, since As concentrations are lower compared to those in the region, where lacustrine sediments predominate. In the case of the SPB, SW shows significant concentrations of As due to the weathering of volcanic rocks (Smedley and Kinniburgh, 2002; Banks et al., 2004; Schnoor, 1996; Ormachea Muñoz et al., 2013; 2016) from Los Frailes formation that is located upstream of this basin. This geological formation has a great influence on the general water chemistry of the entire study area (Ormachea Muñoz et al., 2013). Higher level of pH and Na^+ indicate that the volcanic rocks (Smedley and Kinniburgh, 2002) affect the GW quality.

The salinity (quoted as EC) of the GW is correlated with As (in the north region of LKB: $R^2 = 0.26$ and SPB: $R^2 = 0.39$), B (in LKB: $R^2 = 0.59$ and SPB: $R^2 = 0.36$) and Li (in LKB: $R^2 = 0.79$ and SPB: $R^2 = 0.37$). The As and B are elements present in volcanic rocks of the northwest region of LKB and the As, B in addition to Li are elements typically present in ignimbrites (Ormachea Muñoz et al., 2013) in SPB. Due to this correlation, these elements are expected to persist in SW and contaminate GW. The salinity in the northern plain (in LKB) and in the lowlands (in SPB), the semi-arid climate and evaporation could be favoring the mobilization of some types of exchangeable As present from the sediments to the GW.

The oxidant conditions (Eh), in addition to high pH values (>7.5) are common in areas rich in As (Smedley and Kinniburgh, 2002; Bhattacharya et al., 2006), due to the decrease in the adsorption of As in the oxides and hydroxides of Fe and Al that vary according to pH (Appelo and Postma, 2005). A small increase in pH could cause an increasing concentration of As in the GW due to the high content of As in sediments. These characteristics are present in some regions of both basins, for example, in the northern plain of LKB (range pH = 7.3–7.9) and in the plain of SPB (mean pH = 7.7). With the current pH levels (6.4–9.6), the

adsorption of Fe and Al oxides and hydroxides decreases in a slightly oxidizing medium and a higher increase in pH could cause a major impact.

The result of the extraction of acetate in the sediments of the SPB indicates the importance of carbonates in As levels in GW. Although this characteristic in the GW is not entirely clear, SIs indicate that GW is not saturated or is in equilibrium with respect to calcite in some wells of both basins, but carbonate in sediments could interact with As. The adsorption of As in calcite or clay minerals could be one of the most important As immobilization processes in areas with a pH range of 7–9 (Stollenwerk, 2002; Romero et al., 2004; Ormachea Muñoz et al., 2013). Another study indicates that carbonates have a negative effect on the adsorption of As to Fe-oxides (Claesson and Fagerberg, 2003; Stollenwerk, 2002; Ormachea Muñoz et al., 2013).

The adsorption of As onto the surface of oxides and hydroxides of Fe, Al and Mn, which is one of the most studied processes regarding the mobility of As in natural waters (Bhattacharya et al., 2006; Gustafsson and Bhattacharya, 2007), is present in the second most important fraction of the sequential extraction of sediments in LKB (reducible fraction with hydroxylamine hydrochloride). Likewise the extraction with oxalate $[(\text{NH}_4)_2\text{C}_2\text{O}_4]$ in SPB confirms the important association between As and the surface of oxides and hydroxides of Fe, Al and Mn. The Fe and As are released and dissolved in aqueous phases under reducing conditions (Gustafsson et al., 2006), and leads to the elevated concentration of As in GW (Bhattacharya et al., 2006). This process explains the good correlation between As and Fe in the northern plain of LKB. Although at high pH levels, as in some sectors of both basins, As is desorbed even under oxidizing conditions.

SI indicates the probable precipitation of Fe and Al oxides and hydroxides in both basins, with the exception of the north and northeast region in LKB and the northern region of SPB. The results confirm the important function of Fe and Al oxides and hydroxides surfaces as As adsorbents. Although there is no trend indicating the specific presence of some mineral related to the low As content. There are several minerals (according to SI) that would be responsible for the low As values in some sectors of both basins, such as hematite $[\text{Fe}_2\text{O}_3]$, goetite $[\alpha\text{-FeOOH}]$, gibbsite $[\text{Al}(\text{OH})_3]$, K-mica $[\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2]$ and kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$.

The evaporation in shallow GW could be an important factor in As-enrichment of water in some sectors of both basins (Bhattacharya et al., 2006). The high concentrations of Si suggest that it could be competing with As for the adsorption sites on Fe-oxyhydroxides is especially in the sectors where As concentrations are higher in both basins. High Si values (10 mg/L or above) and high pH could decrease As adsorption (Stollenwerk, 2002; Davis et al., 2001; Ormachea Muñoz et al., 2013).

5. Conclusions

The southeast of Lake Titicaca (LKB) and the south of Lake Poopó (SPB) are the regions with a lack of good quality water. The northern and eastern parts of the LKB and the entire SBP, have a severe water shortage, due to low rainfall (semi-arid areas), high evaporation rates (salinity) and solid waste carried by SW (LKB). The water resources (GW and SW) are affected by the presence of high levels of As – B – salinity (both basins), Mn – NO_3 (LKB) and Li (SPB), which causes the water to be unsuitable for human consumption. The GW mineralization of both the basins is controlled by dissolution processes (of evaporitic/carbonate minerals surface and by base-exchange phenomenon).

Groundwater As concentrations are found to be highest in regions, where alluvial sediments are enriched with As in the northern region of LKB as well as the the PACK belt (region around of Lake Poopó) in SPB. The slow movement of GW facilitates the As release, probably due to the low surface slope and the large area of fine-grained sediments. Sequential extraction of sediments and geochemical modeling (SI) indicate that the As is associated with Fe and Al oxides and hydroxides,

which are the most important As adsorbents in sediments in the central and southern regions of both basins. The low As mobility in the central and southern regions of both basins is due to CaCO_3 (e.g. calcite), which would be another important As adsorbent mineral.

The geological characteristics of the terrain in both basins control spatial variability of As concentrations, due to the presence of As rich S minerals in SPB and by evaporites that are unevenly distributed in the sediments. The regions with volcanic formations in both basins, despite having lower concentrations of As in GW (LKB mean: 22 $\mu\text{g/L}$; SPB mean: 39 $\mu\text{g/L}$), remain detrimental to health. Another similarity between the two basins lies in the presence of As, B and Li in SW and GW. The As in the lowlands could be mobilized to GW due to increased salinity, arid climate and other evaporation processes.

Giving continuity to monitoring in both regions and increasing the number of sampling wells (piezometers) at farther depth are essential for a detailed understanding and evaluation of the As spatial distribution, because the characteristics and extension of the deeper aquifers are still unknown. Therefore, future research should focus on exploring the potential for deep aquifers to provide safe drinking water for both regions.

CRediT authorship contribution statement

Israel Quino Lima: Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing, Visualization, Resources, Investigation. **Mauricio Ormachea Muñoz:** Investigation, Visualization, Writing - review & editing, Supervision. **Oswaldo Eduardo Ramos Ramos:** Investigation, Visualization, Writing - review & editing, Supervision. **Jorge Quintanilla Aguirre:** Investigation, Visualization, Supervision, Funding acquisition. **Jyoti Prakash Maity:** Writing - review & editing, Formal analysis, Visualization, Supervision. **Arslan Ahmad:** Writing - review & editing, Formal analysis, Visualization. **Prosun Bhattacharya:** Conceptualization, Writing - original draft, Writing - review & editing, Visualization, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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