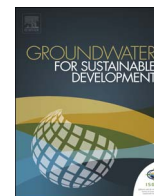




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Research paper

## Geochemistry of naturally occurring arsenic in groundwater and surface-water in the southern part of the Poopó Lake basin, Bolivian Altiplano



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### ABSTRACT

Groundwaters from shallow aquifers and surface water from rivers of the southern part of Poopó Lake basin within the Bolivian Altiplano have significant quality problems such as high salinity and high concentrations of arsenic (As). The extent of As contamination is observed in the studied groundwater over large parts of the study area. Surface-waters are generally alkaline (pH 8.2–8.7) and oxidizing with dissolved oxygen (DO) concentrations in a range of 2.5–6.6 mg/L. The water chemistry is predominantly of Na–Cl–HCO<sub>3</sub>-type, with concentrations of dissolved As in the range of 8.6–117 µg/L with As(V) as the main aqueous species. The concentration of Li varies in the range of 1.1–4.4 mg/L, while other trace elements occur in low concentrations.

Groundwaters have a very large range of chemical compositions and the spatial variability of As concentrations is considerable over distances of a few km; dissolved As in groundwater spans over 4 orders of magnitude (3–3497 µg/L), while concentrations of Li have a range of 0.05–31.6 mg/L. Among the investigated drinking-water wells, 90% exceed the WHO guideline value of 10 µg As/L. Electrical conductivity ranges between 295 and 20,900 µS/cm; high salinity is resulting from evaporation under ambient semi-arid climatic conditions. The pH values of the groundwaters are generally slightly alkaline (5.5–8.7) and universally oxidizing, under these conditions As(V) is the prevalent species. Groundwater As correlates positively with pH, electrical conductivity, Cl<sup>-</sup>, Na<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. Weathering/dissolution of carbonates, evaporites, halite and plagioclase minerals incorporate Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> in solution with consequent pH and alkalinity increase; these are favorable conditions for high mobility of As species. Stable isotopic signatures indicate recharge at the Altiplano with seasonal effects. All surface water and some groundwater samples are enriched due to evaporation, which probably increased concentration of dissolved As.

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## 1. Introduction

The presence of arsenic (As) in drinking-water is a major

concern to human health due to its neurotoxicity and potential to cause cardiovascular diseases and different types of cancer, of which skin and bladder cancers are the most common (Kapaj et al., 2006; Chen, 2010). Globally, an estimated 150 million people are directly affected by As contamination; a number which is constantly increasing as new contaminated areas are discovered (Ravenscroft et al., 2009). The presence of As in water, mainly in groundwater, is attributed to natural geochemical processes but also due to anthropogenic activities such as mining (Bhattacharya

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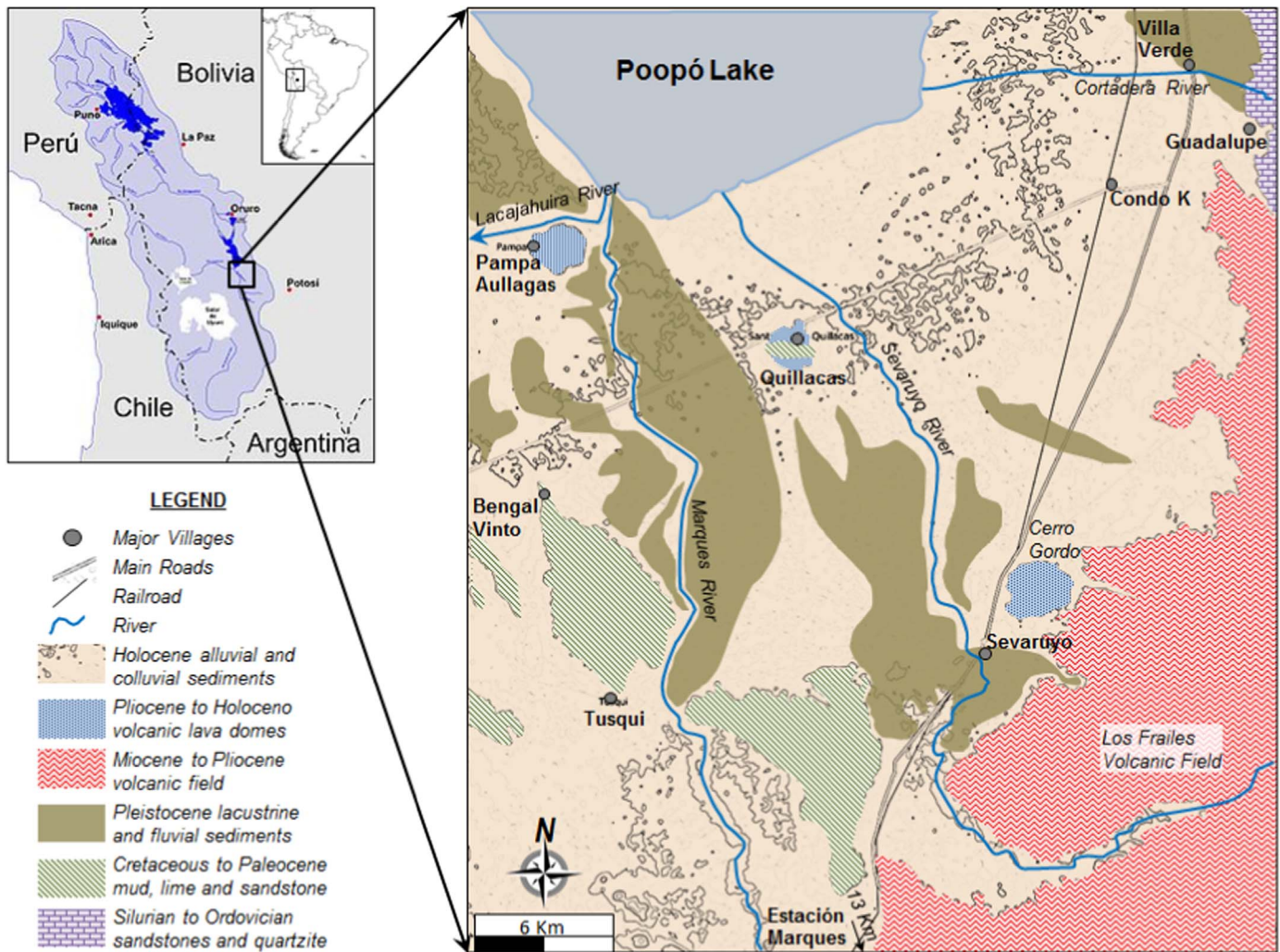


Fig. 1. Upper left: Geographical location of the Bolivian Altiplano. Right: Main geological characteristics of the study area.

et al., 2002a; Smedley and Kinniburgh, 2002; Herath et al., 2016). Concentrations of As in drinking-water above the World Health Organization (WHO) guideline ( $10 \mu\text{g/L}$ ) (WHO, 2011) have been documented across the world, including countries such as India, Bangladesh, China, Vietnam, Taiwan, Spain, Portugal and Hungary (Bhattacharya et al., 1997, 2002a, 2002b, 2007, 2011; Smedley and Kinniburgh, 2002), as well as numerous countries in Latin America such as Mexico, Nicaragua, Ecuador, Chile, Argentina, Peru, Brazil and Uruguay (Bundschuh et al., 2008, 2009, 2010, Mukherjee et al., 2014).

Relatively few studies have been conducted on the occurrence and distribution of As in the environment in the Bolivian Altiplano (BA), a high plateau enclosed between the Eastern and Western Cordilleras, with a topographic elevation between 3600 and 3900 m above mean sea level, (Fig. 1). The BA and both Cordilleras are rich in mineral resources, mining in this area commenced well before 16th century's Spanish conquest, but was greatly intensified thereafter, severely impacting quality of water and soils around mines with large discharges of acid mine drainage (AMD) and high concentrations of metals and metalloids such as Cd, Cu, Fe, Mn, Pb, Sb, Zn and As (PPO, 1992, 1996a, 1996b, 1996c; Garcia et al., 2005; Tapia et al., 2012). Regarding As occurrence, a very first investigation reported geogenic As concentrations of up to  $800 \mu\text{g/L}$  in the Desaguadero River located in the central BA (Quintanilla et al., 1995). Other study made by Banks et al. (2004) reported As concentrations of up to  $4600 \mu\text{g/L}$  (median  $34 \mu\text{g/L}$ ) in surface

water drainage in the catchment areas of the salt flats of Coipasa and Uyuni located to the southwestern part of the BA (Fig. 1). In the Poopó Lake basin within the BA (Fig. 1), As in surface and groundwater showed elevated concentrations associated with both natural and anthropogenic sources; groundwater contained As concentrations up to  $245 \mu\text{g/L}$  while in a stream affected by both AMD and thermal waters, As concentration as high as  $11,140 \mu\text{g/L}$  has been reported (Quintanilla et al., 2009).

Naturally occurring As in drinking-water was described only in recent years; high concentrations of As were measured in drinking-water samples collected from wells in areas not affected by mining located in the southern and western part of the Poopó Lake basin, As concentrations were reported to have up to  $299 \mu\text{g/L}$ , average  $181 \mu\text{g/L}$  ( $n=5$ ) (PPO, 1996a). Villagers settled around Poopó Lake drink water from excavated shallow wells containing As in a range from  $1.5 \mu\text{g/L}$  to  $245 \mu\text{g/L}$  (average  $47 \mu\text{g/L}$ ;  $n=23$ ) (Hermansson and Karlsson, 2004) while in villages located north and northeast of Poopó Lake, drinking-water wells contained As up to  $964 \mu\text{g/L}$  (average  $63.6 \mu\text{g/L}$ ) (Van Den Bergh et al., 2010). The area most affected by natural As is located in the southern part of the Poopó Lake basin, As in rivers reached concentrations up to  $87.8 \mu\text{g/L}$  (average= $39.2 \mu\text{g/L}$ ) while in drinking-water wells As concentrations reached up to  $242.4 \mu\text{g/L}$  (average= $72 \mu\text{g/L}$ ) (Ormachea Muñoz et al., 2011, 2013; Ramos Ramos et al., 2012), moreover, poor water quality, e.g. high salinity and high concentrations of lithium (Li) and boron (B), are characteristics of

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