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Article

Trace elements in soils, their uptake by crops and potential health risks: Insights from a legacy mining area in Oruro, Bolivian Altiplano

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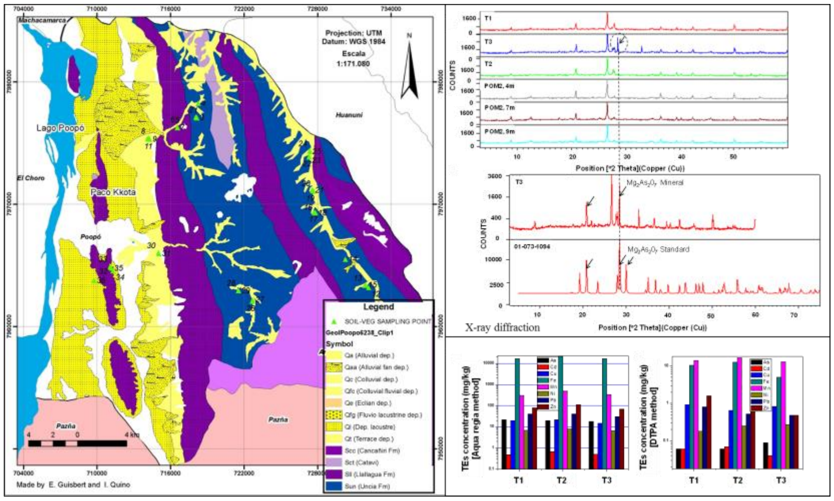

Highlights

- This study analyzed trace elements in soils and crops in a legacy mining area of the Bolivian Altiplano.
- Secondary iron oxides strongly adsorb As, Cu, and Zn, thereby decreasing their mobility.
- DTPA extracted only 2% of total As, but sequential extractions showed up to 12% as mobile.
- Pb in beans, alfalfa, and potatoes exceeded limits, while other metals remained within safe levels.

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Abstract

A geochemical study was conducted in the legacy mining area in Oruro, the Bolivian Altiplano to examine the distribution of trace elements (TEs) in agricultural soils and their uptake by crops. The pseudo-total, bioavailable fractions of TE and sequential extraction fraction of As contents were determined in soils. The pseudo-total concentration of TEs in soils suggests naturally elevated background levels. The strong correlation ($p < 0.01$) between Fe_{regia}/Mn_{regia}-As_{regia}, Cu_{regia}, and Zn_{regia} suggests that secondary iron oxides play a key role in adsorbing these TEs. Species linked to carbonates are also present, but negative ($r = -0.51$; $p < 0.01$) correlation between soil pH and As_{DTPA} suggests that the retention of TEs in carbonate is not dominant. The chelate diethylene-triamine-pentaacetic acid (DTPA) method extracted less than 2% of total As, whereas sequential fractionation reported up to 12% as potentially mobilized (F1–non-specifically-bound + F2–specifically-bound), posing a risk of transfer to crops or groundwater. As, Cd and Pb tend to accumulate in soils by binding to amorphous and crystalline Fe oxide surfaces. Arsenic levels in beans and alfalfa (0.19 mg/kg), barley (0.17 mg/kg), and peeled potatoes (0.11 mg/kg), Cd levels in beans (0.03 mg/kg), alfalfa (0.017 mg/kg), barley (0.012 mg/kg), and peeled potatoes (0.023 mg/kg), remained within Chilean, FAO, WHO, and European regulatory limits. However, Pb concentrations exceeded permissible limits in beans (0.32 mg/kg), and alfalfa (0.22 mg/kg); however peeled potatoes (0.16 mg/kg) and barley (0.16 mg/kg) remained below the threshold of European guidelines.

Keywords: Bolivian Altiplano; Crops; Bioavailable Trace Elements; Accumulation; Transfer Factor.

1. Introduction

Occurrence of trace elements (TEs) in soil, stream sediments and groundwater systems can raise risk concerns for environmental and human health (Shaw, 1990; Ormachea et al., 2015; Bundschuh et al., 2017; Sikakwe et al., 2023). The long-term accumulation of TEs in soils resulting from anthropogenic activities such as mining, industrial operations, can lead to contamination of drinking water sources and agricultural lands, thereby posing significant risks to ecosystem health and humans and live stocks (Shaw, 1990; Maity et al., 2012; Bundschuh et al., 2017; Taghavi et al., 2023; Mukherjee et al., 2024). The most common TEs released due to anthropogenic activities especially in the mining environments include arsenic (As), antimony (Sb), beryllium (Be) cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn) and distributed in different environmental compartments including the air, water, soil, and biota (Kabata-Pendias and Pendias, 2001). The complex behavior of TEs is triggered by environmental biogeochemical cycles, which may exert significant control on their fate in terms of mobility, transport and residence time (Bundschuh et al., 2017; Peirovi-Minaee et al., 2024). The bioavailability of TEs depends on their speciation and soil properties (Adamo et al., 2024). Plants often serve as intermediate reservoirs, facilitating the transfer of TEs from soils and water to humans and animals (Kabata-Pendias and Pendias, 2001; Adamo et al., 2024).

The total TE concentration in soils is considered to be an indicator of geoaccumulation from various sources and long-term enrichment, but these values do not give any information about the potential availability of the TEs, and the pathway by which they can affect the soil, crop and/or human being (Massas et al., 2013). However, available TEs in soils extracted by a single diethylene-triamine-pentaacetic acid (DTPA) step can probably be an indicator of recent soil enrichment (Massas et al., 2013; Tziouvalekas et al., 2024) and additionally provide a reasonable estimation of plant-available TEs reservoir in soils (Lindsay and Norvell, 1978).

Bundschuh et al. (2012) discussed the presence of As in the food chain across Latin America. Among the countries in Latin America, significant levels of TEs, including As, have been reported in food in Mexico (Prieto-García et al., 2005), Argentina (Perez-Carrera et al., 2009), and Chile (Muñoz et al., 2002; Díaz et al., 2004; Sancha and Marchetti, 2009; Díaz et al., 2011). Queirolo et al. (2000) in Andean villages of northern Chile reported high As, Cd and Pb contents in vegetables. In other areas of Chile, studies show that the levels of total As in vegetables were below the maximum limit of Chilean legislation (Muñoz et al., 2002; Calderon et al., 2023). Rötting et al. (2013) reported high content of As and heavy metals in soils and crops near the Vinto Metallurgical Company (VMC) in Oruro (Bolivian Altiplano).

Trace elements ingestion through food is one of the main pathways for accumulation in the human body over time (Romero-Crespo et al., 2023). Metals such as Cr, Cd, Mn, and Ni can be very toxic and their accumulation inside the body can cause serious diseases (Khan et al., 2010; Sun et al., 2010; Khan et al., 2013). Food contaminated with Cd can cause bone fracture, kidney dysfunction, hypertension, and even cancer (Nordberg et al., 2002; Turkdogan et al., 2003; Charkiewicz et al., 2023). High content of Mn and Cu can cause mental diseases such as Alzheimer disease (Dieter et al., 2005; Liu et al., 2022). Nickel ingestion can cause dizziness, fatigue, headache, heart problems, fatal cardiac arrest, and respiratory illness (Muhammad et al., 2011). Excessive Zn can cause sideroblastic anemia; however, in contrast Zn deficiency can cause anorexia (poor appetite), diarrhea, dermatitis, depression immune dysfunction, and poor wound healing. Therefore, an adequate amount of Zn is very important for normal body functions (Muhammad et al., 2011; Khan et al., 2013; Stiles et al., 2024).

In the Oruro (Bolivian Altiplano), TE concentrations in soils exhibited high median concentrations in mining areas (PPO, 1993-1996; Tapia et al., 2012; Tapia et al., 2022). Elevated natural geochemical background and the presence of mining activities (PPO–03, 1996; PPO–04, 1996; PPO–13, 1996) are the most important sources of TEs in surface and groundwater (Banks et al., 2002; Banks et al., 2004; Ramos Ramos et al., 2010; Ramos Ramos et al., 2012; Ormachea et al., 2013; Ramos Ramos et al., 2014), lake sediments (Cáceres Choque et al., 2013; Tapia and Audry, 2013). Rötting et al. (2013) have studied the As and Pb contents in soils and crops near to smelter of the Vinto Metallurgical Company (VCM) in Oruro. Their results suggested that all crops cultivated around VCM by far exceeded As and Pb (FAO/WHO, UK and Chilean) guidelines for human and/or animal consumption.

Agricultural crops, especially potato, beans and barley, are the main crops grown for human consumption and they are sold in the markets of mining villages (Huanuni, Poopó, Pazña, Bolivar, and Challapata) and Oruro city. Potato, beans, and barley form an important part of the diet in the Bolivian Altiplano; additionally, alfalfa is also studied. However, distributions of TEs in the soil, their bioavailable fractions and their content in crops is a key issue that has to better understood in mining and rural areas of the Poopó Basin.

The present study aimed to i) determine the pseudo-total concentrations and sources of As and TEs, ii) evaluate the bio-available concentrations of As and TEs in plants, iii) analyze As speciation in soil and crops, and iv) assess the uptake the As and TEs by crops in three small sub-basins of Oruro, Bolivian Altiplano. Additionally, the study also evaluates the potential health risks for consumers in mining areas. The findings could be essential for developing effective soil management strategies to enhance food quality in the future.

2. Materials and methods

2.1 Study area

The study area is located in three small sub-basins in the Oruro province of the Bolivian Altiplano. The sampling sites were along the Coriviri, Ventaimedia and Poopó sub-basins (**Fig. 1**) within the small agricultural areas in the drainage sub-basins. It is located between 18°10′ and 18°30′ S latitude and 66°47′–67°01′ W longitude and between 3,795 and 4,160 m a.s.l. (above sea level). The land use is agriculture and livestock (61%; INE, 2005) and the farmers are dependent on surface water for irrigation as well as on seasonal rainfall. Farmers cultivate primarily during the rainy season (from November to March). The average annual rainfall is 372 mm (Pillco and Bengtsson, 2006).

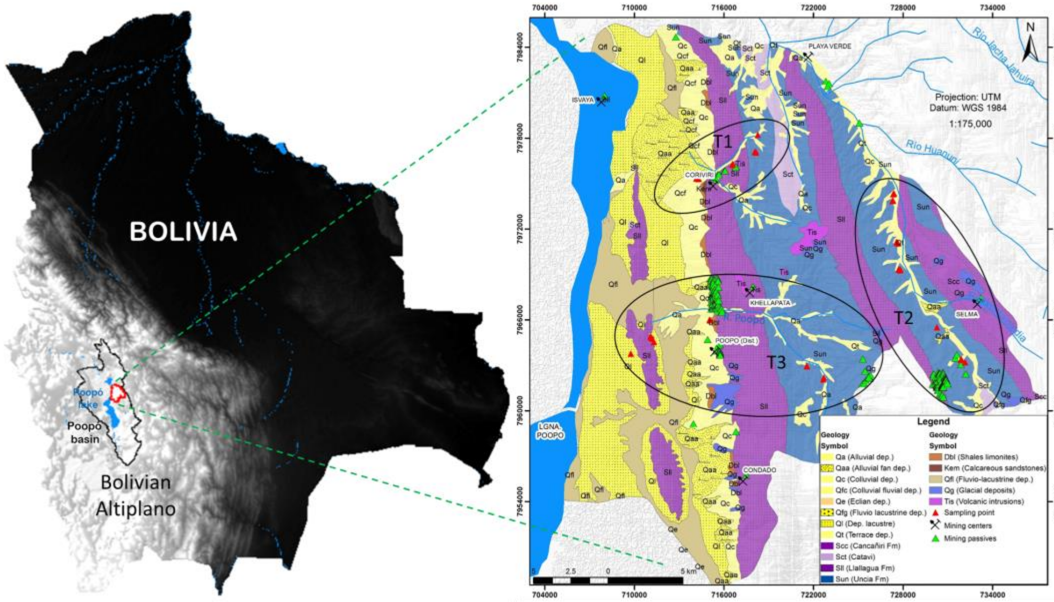

Figure 1. The study area and location of sampling points along the transects (Coriviri –T1, Ventaimedia –T2 and Poopó –T3).

The agricultural soils are generally prepared for cultivation during August to September by applying animal manure (sheep, bovine and camelid) and crop rotation is usually practiced, and the cycles begin with potato, quinoa or beans, alfalfa, and finally barley.

2.2 Sample collection and preparation

Soil samples were collected (n = 36) along three transects in Coriviri (T1), Ventaimedia (T2) and Poopó (T3) (**Fig. 1**). Samples (~2 kg) were collected from the arable layer (0 – 45 cm depth). The soil samples were air dried at ambient temperature, sieved through a 2 mm sieve, and all the analyses were made on the fine earth fraction (< 2 mm) (Cornejo-Ponce and Acarapi-Cartes, 2011) (**Table 1**). The crops were collected concurrently with the surface soil samples (0 – 20 cm depth) at the same sites during the period of harvesting. In the laboratory, the stems of alfalfa (*Medicago sativa*, n = 4), edible portion of barley *(Hordeum vulgare*, n = 13), bean (*Vicia faba*, n = 7) and potato (*Solanum tuberosum*, n = 12) were washed thrice with de-ionized water, air dried at ambient temperature for a day followed by oven drying at 70 – 80°C for 24 h to remove the moisture (Del Rio et al., 2002) and crushed with mortar and pestle.

2.3 Determination of physicochemical properties and trace element contents

2.3.1 Determination of soil properties

Soil pH was determined in 1M KCl solution (1:2 solid:solution ratio) with a pH meter. The soil texture was determined with a soil hydrometer (ASTM 152H), and the electrical conductivity (EC) was determined in deionized water extraction procedure (1:5 solid:solution ratio) with an electrical conductivity meter. Cation exchange capacity (CEC) was determined using the CH_3COONH_4 method and plant-available phosphorus (P_{as}) was determined by the Bray-Kurtz method (Bray and Kurtz, 1945). The organic matter (OM) was determined by the modified Walkley-Black method (Walkley, 1946; Jackson, 1958) and soil water content was determined gravimetrically.

2.3.2 Determination of soil mineralogical characteristics

The identification of minerals in selected soils samples was carried out by powder X-Ray Diffraction method (model Seifert XRD 3003 TT, with Cu Kα1, 1.5418Å, radiation) to identify the bulk mineral composition at the Instituto de Geología y Medio Ambiente (IGEMA) at Universidad Mayor de San Andrés (UMSA) in La Paz, Bolivia.

2.3.3 Pseudo-total extraction of trace elements

Pseudo-total extraction of TEs (As, Cd, Cu, Pb and Zn) was carried out by digestion of 0.5 g of soil in 12 mL of Aqua Regia (1:3 mixture of HNO_3 and HCl; sub-boiling acids). The extraction method is considered suitable for total-recoverable TEs in soils (ISO/DIS 11466, 1994; Chen and Ma, 2001; Burak et al., 2010). Analytical grade reagents were used for digestion. The analytical work involved determination of TEs in the < 2 mm grain size fraction of the soils. The soils were digested in microwave pressure vessels (3000 Anton Paar) at 280°C temperature and an operating pressure of 79 bar. The residual suspension was filtered through Whatman quantitative filter paper (grade 50, pH resistance) after cooling.

The TEs concentrations in soil extractions were determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Varian Instruments, model Varian Vista Pro Ax) at the Department of Geological Sciences, Stockholm University, Sweden. Following the run of every 10 samples, certified standards (NIST 1643e), and synthetic multi-element chemical standards were run. Relative percentage difference among the duplicate runs and deviations from the certified and synthetic standards was within ±10%.

2.3.4 Extraction of bioavailable fraction of trace elements

The bioavailable fractions of TEs (As, Cd, Cu, Pb and Zn) were determined through diethylene-triamine-pentaacetic acid (DTPA) extraction (analytical grade, 0.005 M DPTA, 0.01 M calcium chloride, $CaCl_2$), and 0.1 M triethanolamine (TEA), $(HOCH_2CH_2)_3N$) adjusted to pH 7.3 with hydrochloric acid (HCl) (Lindsay and Norvell, 1978). The soil samples (5.0 g) were taken in a polypropylene tube and then 10 mL of the DTPA extraction solution was added and shake for 2 hours shaking in a horizontal shaker. Then, the extract was separated from the solids by centrifugation at 3,000 rpm (revolutions per minute) and the supernatants were filtered through 0.45 µm paper filters (ASA, 1982). Analytical grades reagents were used throughout the analyses. The bioavailable TE in soil extractions were determined by ICP-OES at the Department of Geological Sciences, Stockholm University, Sweden.

Table 1. Physical and chemical properties of soil (n = 36) in Coriviri –T1, Ventaimedia –T2 and Poopó –T3.

Soil properties	Transect 1			Transect 2			Transect 3		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Soil (depth, cm)	11	40	33	12	45	30	10	30	21
Sand (%)	27	56	48	17	56	46	38	63	46
Silt (%)	23	44	31	20	54	35	16	36	30
Clay (%)	16	28	22	16	30	22	17	25	22
pH	6.1	7.1	6.8	5.4	7.7	6.1	5.8	7.8	6.5
EC (dS/cm)	0.06	0.20	0.12	0.07	1.50	0.14	0.05	2.40	0.13
CEC (cmol+/kg)	5.7	16.9	8.1	5.7	18.5	9.4	5.9	26.1	9.2
P_{as} (mg/L)	7.3	16.8	9.2	5.1	28.3	8.3	7.3	16.8	7.4
OM (%)	0.5	2.3	1.1	0.7	2.5	1.2	0.6	2.2	0.9

2.3.5 Sequential extraction of As in soil

The amount of 2.0 g dry soil was used to determine the As content in different fractions by a sequential extraction following the procedure of Wenzel et al. (2001). The sequential extraction is represented by: i) Fraction 1 (F1); (0.05 M $(NH_4)_2SO_4$, recovers the non-specifically-bound As_{F1}; ii) Fraction 2 (F2); releases specifically-bound As_{F2} using phosphate solution $(NH_4)H_2PO_4$, 0.05 M; iii) Fraction 3 (F3); recovers amorphous hydrous oxide-bound As_{F3} (0.2 M $(NH_4)_2C_2O_4/H_2C_2O_4$); iv) Fraction 4 (F4); extracts As_{F4} bound to crystalline hydrous oxide (0.2 M $(NH_4)_2C_2O_4/H_2C_2O_4$) + 0.1 M $C_6H_8O_6$) and v) Fraction 5 (F5); (HNO_3, 65% m/v) recovers the residual As_{F5} fraction. After each step, the extracted solution was filtered using Munktell quantitative filter paper (pure cellulose and alpha-cellulose, grade 00H; 1-2 µm). An internal check on the sequential extraction procedure was performed by comparing the sum of the five fractions with the total concentrations measured in the Aqua Regia extract.

The TEs concentrations in soil at sequential extractions were determined by ICP-OES at the Department of Geological Sciences, Stockholm University, Sweden. TEs concentration associated to a specific extractant was expressed as follows: $[i]_j$ where i is the TE and j relates to the extractant (i.e., $[i]_{regia}$ for HNO_3/HCl, $[i]_{DTPA}$ for DTPA and $[i]_{F1-F5}$ for the sequential extraction with fractions 1 – 5.

2.3.6 Estimation of trace elements (As, Cd and Pb) in crops

Total As, Cd and Pb concentrations in crops were determined by digesting the dry samples (0.30 g) in a mixture of 4 mL ultra-pure H_2O_2 (30% v/v), 0.5 mL HNO_3 and 4 mL HCl (chemical grade, bi-distilled, Merck, Germany) using microwave (3000 Anton Paar) digestion system at 280°C temperature (Cui et al., 2004). After cooling the digested samples were filtered through Whatman quantitative filter paper (grade 50, pH resistance).

The TEs concentrations in crops extractions were determined ICP-OES at Department of Geological Sciences, Stockholm University, Sweden. The quality control included the preparation of blanks (blanks, spiked blanks) and samples (duplicate and spiked samples) were digested randomly and analyzed. The duplicates showed a difference of ±10%, and the spiked addition gave between 90 and 105 recovery percentage.

2.4 Statistical analysis

The data were analyzed using SPSS to calculate mean values, standard deviations and nonparametric Spearman correlations for the measured physical and chemical parameters across transects. The significance of differences between mean values of different subgroups was determined by Student´s t-test.

2.5 Availability ratio and transfer factor

The available TEs ratio (Massas et al., 2009; Massas et al., 2010) in soil was calculated as follows:

$$AR = \frac{(Available\ trace\ element\ concentration, mg/kg)}{(Total\ trace\ element\ concentration\ in\ soil, mg/kg)} \qquad (1)$$

The availability ratio (AR) (*Eq. 1*) is used to estimate the soil TE enrichment, or even a slow transformation to more stable forms that has been discussed in previous studies (Massas et al., 2009; Massas et al., 2010; Massas et al., 2013).

The transfer factor (TF) soil-to-plant (edible part) is a measure of the uptake of TEs by plants from soil (Cui et al., 2004; Rötting et al., 2013) and is calculated using the element content data in crop and soil samples (Eq. 2):

$$TF = \frac{(Total\ trace\ element\ concentration\ in\ plant, mg/kg_{fw})}{(Total\ trace\ element\ concentration\ in\ soil, mg/kg_{dw})} \qquad (2)$$

where mg/kg_{fw} and mg/kg_{dw} represent TE content on fresh weight (fw) and dry weight (dw) basis, respectively.

3. Results and discussion

3.1. Soil characteristics

3.1.1 Chemical characteristics

The soil geochemical characteristics are listed in **Table 1**. The soil pH values (pH 5.4 – 7.8) were weakly acid to weakly basic (**Fig. 2a**). The minor variability of pH shows a homogeneous trend in the cultivated area. The soil texture was broadly homogeneous among all sites with the grain size distribution dominated by sand (mean 45%) and silt (mean 33%) fractions. The clay contents in the soils along the transects do not show a major difference, with a maximum value of 30% (**Fig. 2b**).

The mean values of EC in the soil extracts at three transects indicate salt accumulation in the soils. The highest EC values of 2.40 dS/cm was observed in the T3 transect, likely due to the fact that many samples are located near the Lake Poopó (**Fig. 1**). The data show a large variability in EC values in soil of T3 transect. The high EC values in soils could be explained by the occurrence of underground paleoevaporites dissolution (Coudrain-Ribstein et al., 1995; Argollo and Mourguiart, 2000; Zapata, 2011; Liu et al., 2021).

The CEC values were relatively low (5.7 – 26.1 cmol[+]/kg). The CEC classification show that the soils are moderate and low, a few samples show a high value. Even though there were high CEC values in some samples with high clay and OM contents, the lower CEC values were due to clay types (kaolinite 3 – 15 cmol[+]/kg) and OM contents. The mean OM contents were 1.1%, 1.2% and 0.9% for T1, T2, and T3, respectively (**Table 1**).

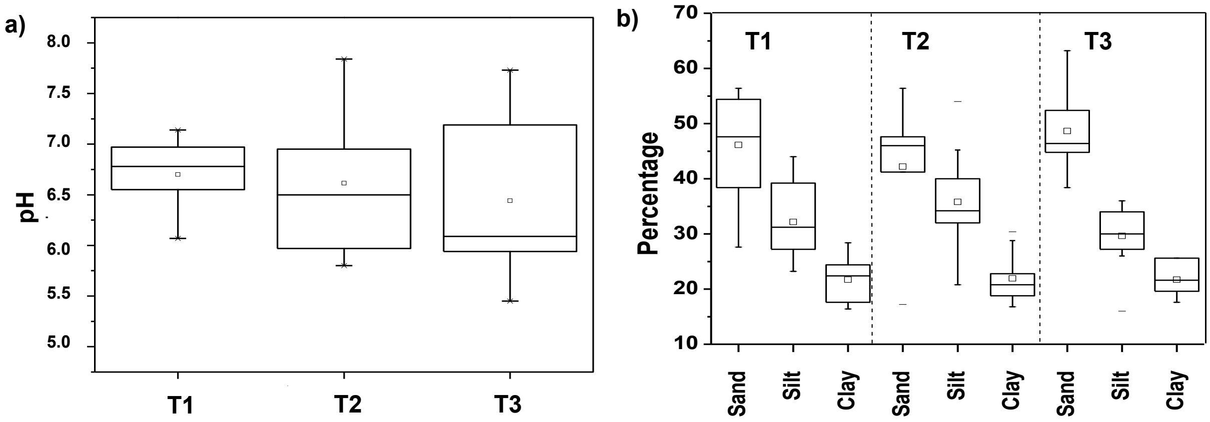

Figure 2. Box and Whisker plots of a) pH and b) % clay, sand and silt content in the study area transects (Coriviri –T1, Ventaimedia –T2 and Poopó –T3).

3.1.2 Soil mineralogy

The colluvial/fluvial soils were developed on parent materials derived from surrounding geological formations in the three studied areas (**Fig. 1**). The mineralogical analyses of samples from the three sites revealed that in transect T1 the predominant minerals were silicate (quartz) and alumino-silicates (muscovite, merlinoite and chlorite). Transect T2 also contains silicate (quartz) and alumino-silicates (muscovite, albite and kaolinite), while T3 contain silicate (quartz), alumino-silicates (anorthite, muscovite, kaolinite) and magnesium arsenate (**Fig. 3**). It is highlighted that magnesium arsenate mineral only occurs in T3, this area near to the waste mineral deposit from the San Francisco mine and other old mine activities in the area. The occurrence of kaolinite in inundated alluvial plains indicates the ultimate chemical alteration of the predominant silicate rocks present at the three sites.

3.2 Pseudo-total TEs and identification of their origin

The As_{regia} content was not significantly different among the three transects ($p < 0.05$, one-way ANOVA, significance level of 0.23). The As_{regia} contents in soil were ranging from 9.3 to 40 mg/kg (mean 23.3, 22.1, 18.4 mg/kg at sites T1, T2, and T3, respectively) (**Table 2, Fig 4**). There was a moderately high total As content in transect T1 (13 – 38 mg/kg), which may be related to the high OM content (0.5 – 2.3 %) in the study area. The values for Cd, Cu, Pb and Zn and ANOVA analysis show that there are no significant differences among the three sub-basins ($p < 0.05$) for each analyzed TEs, possibly indicating that they have common sources.

The concentrations of As, Cd, Cu, and Pb in aqua regia extracts are lower than the median values reported by Oruro Pilot Plan (PPO, 1993-1996; **Table 2**); only the Zn concentrations are slightly higher than the reported concentrations in the PPO report. In comparison with the world soils database (Han, 2007), As, Cd, Pb and Zn concentrations are higher, while Cu concentrations are lower than the world soils average values (Han, 2007), suggesting that the three areas could have high background values. These high contents are probably related to the geological conditions in the Eastern Cordillera with the abundant presence of the polymetallic elements (Ag-Pb-Zn-Sn-Sb) in this mining district (Arce-Burgoa and Goldfarb, 2009; Tapia et al., 2012). The TEs extracted with aqua regia are used to estimate the maximum TE availability to plants (Chen and Ma, 2001; D'Souza et al., 2023).

The strong positive correlations ($r > 0.5$; Spearman´s correlation) among the TE pairs (As_{regia}-Cd_{regia}, Cu_{regia}, Pb_{regia}), (Cd_{regia}-Cu_{regia}, Pb_{regia}, Zn_{regia}), (Cu_{regia}-Pb_{regia}, Zn_{regia}), (Pb_{regia}-Zn_{regia}) pairs could indicate a relationship between them (**Table 3**). The correlation ($p < 0.01$) observed between Fe_{regia}/Mn_{regia}-As_{regia}, Cu_{regia}, and Zn_{regia} possibly indicates the potential role of secondary iron oxides for the adsorption of As and other TEs, as already described in the literature (Burak et al., 2010). Also, Cd_{regia}-Cu_{DTPA}, Cd_{DTPA}-Pb_{DTPA} and Cd_{DTPA}-Zn_{DTPA} are significantly correlated at the $p < 0.01$ level (**Table 3**).

A geogenic origin for the TEs in the soils at the three sites is more likely than an anthropogenic origin, given the high background levels observed in these locations (Tapia and Audry, 2013).

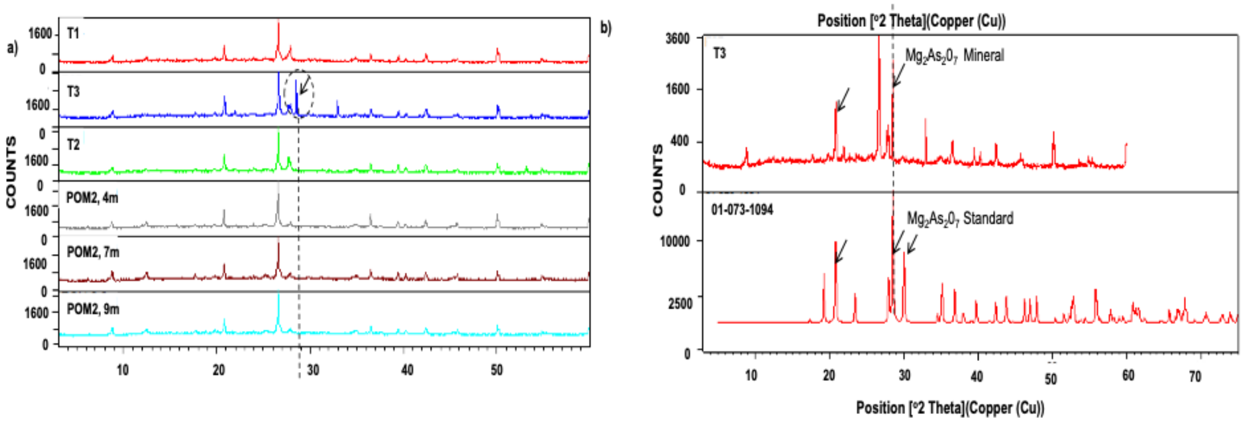

Figure 3. X-ray diffraction of selected soils samples: a) three transects (T1, T2, and T3) and profile POM2 (4, 7, and 9 m), and b) standard magnesium arsenate ($Mg_2As_2O_7$) mineral.

Table 2. Trace element concentration, aqua regia extracts, DTPA extracts and arsenic fractionation (concentration expressed as mg/kg, dry weight basis, dw) and availability ratio (AR) in the Coriviri –T1, Ventaimedia –T2 and Poopó –T3.

Location	Transect 1, n = 11				Transect 2, n = 14				Transect 3, n = 11				§ Oruro	¤ World soil
	Min	Max	Median	Mean	Min	Max	Median	Mean	Min	Max	Median	Mean	Median	Average
Aqua regia extracts														
As	13.8	38.5	21.52	23.3	9.3	40.2	19.48	22.1	14.3	27.0	17.49	18.4	25	5-10
Cd	0.2	0.9	0.8	0.52	0.3	1.2	0.66	0.65	0.2	2.1	0.51	0.73	3	0.35
Cu	8.7	48.6	20.11	20.52	9.4	41.1	21.47	21.04	9.3	21.0	15.11	15.74	26	30
Pb	20.4	104.4	40.3	49.35	15.8	85.9	40.51	45.83	16.6	138.7	30.9	45.54	49	15-25
Zn	54.5	232.5	81.38	92.99	58.0	203.0	112.88	120.18	45.5	246.6	69.09	96.78	77	90
DTPA extracts	Transect 1, n = 8				Transect 2, n = 13				Transect 3, n = 6					
As	0.04	0.12	0.06	0.07	0.03	0.35	0.06	0.09	0.06	0.11	0.09	0.08	na	na
Cd	0.03	0.11	0.06	0.06	0.03	0.39	0.07	0.13	0.02	0.41	0.04	0.11	na	na
Cu	0.58	1.21	0.93	0.91	0.36	1.24	0.65	0.78	0.64	1.77	0.84	1.07	na	na
Pb	0.48	1.66	0.81	0.98	0.42	1.64	0.52	0.75	0.20	1.04	0.48	0.55	na	na
Zn	1.16	2.45	1.59	1.67	0.70	16.09	2.75	4.96	0.13	36.81	0.48	7.00	na	na
Availability Ratio (AR)	Transect 1, n = 8				Transect 2, n = 13				Transect 3, n = 6					
As	0.001	0.007	na	0.003	0.001	0.020	na	0.005	0.003	0.005	na	0.004	na	na
Cd	0.035	0.280	na	0.157	0.050	0.328	na	0.174	0.010	0.802	na	0.202	na	na
Cu	0.017	0.067	na	0.052	0.025	0.069	na	0.041	0.031	0.089	na	0.058	na	na
Pb	0.005	0.047	na	0.027	0.011	0.033	na	0.018	0.002	0.034	na	0.014	na	na
Zn	0.006	0.031	na	0.020	0.009	0.101	na	0.035	0.001	0.484	na	0.092	na	na
Arsenic fractionation	All transects combined (n = 12)													
As-F1	0.14	0.29	0.14	0.17	na	na	na	na	na	na	na	na	na	na
As-F2	0.60	2.84	1.00	1.13	na	na	na	na	na	na	na	na	na	na
As-F3	4.29	12.06	6.48	7.14	na	na	na	na	na	na	na	na	na	na
As-F4	2.30	9.96	5.59	6.05	na	na	na	na	na	na	na	na	na	na
As-F5	1.68	28.35	6.28	7.62	na	na	na	na	na	na	na	na	na	na

§ PPO 93-96. Trace elements content in soils of Oruro, aqua regia digestion method; ¤ Han, 2007. World soil content (average). na – not available.

Table 3. Spearman´s rank correlations between soil properties and metal and bio-available concentrations, values shaded in grey are correlated with $r > 0.50$ and statistically significant at the $p < 0.05$ and 0.01 level.

	pH	Clay	OM	P_{as}	As_{regia}	Cd_{regia}	Cu_{regia}	Fe_{regia}	Mn_{regia}	Pb_{Tregia}	Zn_{regia}	As_{DTPA}	Cd_{DTPA}	Cu_{DTPA}	Fe_{DTPA}	Mn_{DTPA}	Pb_{DTPA}	Zn_{DTPA}
pH	1																	
Clay	-0.06	1																
OM	-0.16	0.18	1															
P_{as}	0.18	0.29	0.42*	1														
As_{regia}	0.05	0.07	0.25	0.21	1													
Cd_{regia}	0.20	0.37*	0.09	0.31	0.56**	1												
Cu_{regia}	-0.12	0.39*	0.01	0.31	0.52**	0.62**	1											
Fe_{regia}	-0.35*	0.30	-0.06	0.15	0.31	0.39*	0.82**	1.00										
Mn_{regia}	-0.12	0.19	-0.04	-0.07	0.37*	0.31	0.57**	0.78**	1.00									
Pb_{Tregia}	0.08	0.36*	0.09	0.41*	0.72**	0.77**	0.77**	0.52**	0.39*	1								
Zn_{regia}	0.12	0.43**	0.03	0.36*	0.39*	0.79**	0.65**	0.52**	0.43**	0.68**	1							
As_{DTPA}	-0.51**	0.21	0.48*	0.16	0.07	-0.18	-0.22	-0.21	-0.38*	-0.26	-0.34	1						
Cd_{DTPA}	0.15	0.07	0.07	0.13	0.33	0.05	0.09	-0.08	0.23	0.05	-0.05	0.12	1					
Cu_{DTPA}	0.21	0.25	-0.30	0.31	0.32	0.52**	0.34	0.06	-0.04	0.47*	0.45*	0.09	0.38	1				
Fe_{DTPA}	-0.44*	0.07	0.24	-0.03	0.00	-0.42*	0.14	0.20	0.07	-0.32	-0.37	0.44*	0.49*	-0.06	1.00			
Mn_{DTPA}	-0.42*	0.34	-0.09	-0.07	-0.27	-0.39*	-0.07	0.09	-0.02	-0.24	-0.31	0.27	0.20	-0.16	0.47*	1.00		
Pb_{DTPA}	0.11	0.10	-0.25	0.18	0.14	-0.08	0.27	0.04	0.00	0.15	-0.14	0.05	0.63**	0.54**	0.47*	0.23	1	
Zn_{DTPA}	0.19	0.09	0.07	0.13	0.43*	0.07	0.22	0.08	0.41*	0.13	0.03	0.03	0.94**	0.24	0.47*	0.23	0.54**	1

** Correlation is significant at the 0.05 level (2-tailed); ** Correlation is significant at the 0.01 level (2-tailed).*

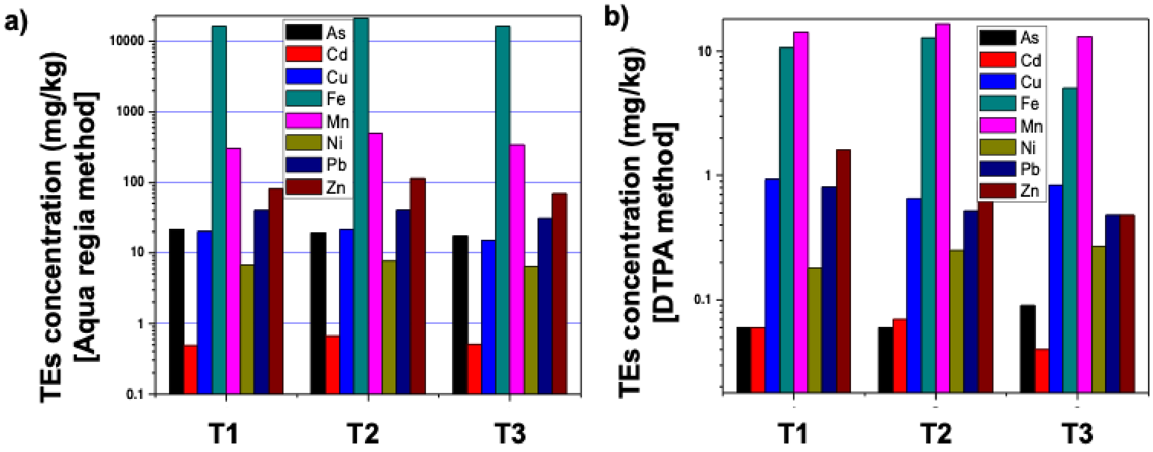

Figure 4. Mean trace elements concentrations in soils in the transects Coriviri –T1, Ventaimedia –T2 and Poopó –T3. determined by: a) Aqua regia extraction (pseudo total concentration), and b) DTPA extraction (bioavailable concentration). The values are on a dry weight basis.

3.3 Bio-available TEs for plants and their origin

Similar to the aqua regia extracts, the DPTA extractions, considered as the fraction of TEs available for crops (**Table 2, Fig. 4**), did not display a significant difference between mean concentrations of TEs at the three studied sites. Significant positive Spearman's rank correlations are found among the available TEs (**Table 3**), indicating that these TEs are potentially available for plants. Hong et al. (2008) concluded that the amount of Cu, Pb, Zn extracted by a single step chelating agent (i.e., DTPA) can be considered as the bioavailable fraction. Meanwhile, comparing with physical-chemical characteristics, only the bioavailable As_{DTPA}-OM shows a significant correlation at $p < 0.05$ level (**Table 3**), suggesting that this As could be a linked to OM. Furthermore, carbonate species are also established as potentially bioavailable, but the slightly negative ($r = -0.51$; $p < 0.01$). Spearman's rank correlation between soil pH-As_{DTPA} suggests that the retention of TEs in carbonates is not dominant, agreeing with the results of the step I As sequential extraction. The bioavailable content of TEs could be over-estimated since DTPA extraction can release the soluble, exchangeable, adsorbed and organically bound TEs and possibly also some of the metal and metalloids fixed on oxides (Levei et al., 2009).

The availability ratio (AR) of TEs contents in soil were as follows: less than 2% for As_{DTPA}; < 33% (except in one sample, 80%) for Cd_{DTPA}; < 9% for Cu_{DTPA}; < 5% for Pb_{DTPA} and < 10% (except in one sample, 48%) for Zn_{DTPA} (**Table 2**). The soils show a low AR for Cu, Pb and Zn; however, for Cd, more than 50% of the samples exhibit a relatively high ratio, ranging from 11 to 33. This range suggests both recent events and long-term soil enrichment are simultaneously influencing the three studied areas. This finding agrees well with the results of Tapia et al. (2012), who reported that Cd concentrations are higher in the superficial soils of the Eastern Cordillera. Fuge et al. (1993) states that Cd is a more chalcophile element than Zn and tends to persist as a sulfide, whereas ZnS weathers more rapidly. As a result, Cd becomes enriched relative to Zn in the soil, which explains its relative immobility in surface soils.

3.4 Arsenic fractionation in soil

The maximum concentration of exchangeable As_{F1} (readily available) is 0.29 mg/kg (mean 0.17; range 0.14 – 0.29 mg/kg) (**Table 2**). It constituted a negligible portion of total As, but it may represent the most important fraction related to environmental risk (Wenzel et al., 2001). The T2 samples have slightly higher As_{F1} contents than the T1 and T3 samples. The sample at T3 have the source of As likely from dissolution of magnesium arsenate ($Mg_2As_2O_7$) mineral (**Fig. 3**).

The fraction of specifically sorbed As_{F2} was in the range 0.60 – 2.84 mg/kg (mean 1.13 mg/kg). As released in this fraction can be potentially mobilized as a result of competition between phosphate (PO_4^{3-}) and arsenate (AsO_4^{3-}) for adsorption sites, due to changes of pH or phosphate application to these soils (Wenzel et al., 2001; Niazi et al., 2011; Khan et al., 2022) and this fraction reflects the pool that is directly bioavailable to plant roots

(Wenzel et al., 2001). Amorphous Fe oxides associated with As_{F3} represent the largest pool with a range from 4.29 to 12.06 mg/kg (mean 7.14 mg/kg).

Arsenic (As_{F4}) extracted from crystalline Fe oxides varies from 2.30 – 9.96 mg/kg (mean 6.05). The As_{F5} residual phase varies from 1.68 – 28.35 mg/kg (mean 7.62 mg/kg). The relatively high amount of As in the residual phase (18.6 – 65.2%) can be due to a low rate of formation of soils resulting in a large sand fraction containing minerals such as As-rich pyrite or arsenopyrite in accordance with the geology characteristics (USGS and GEOBOL, 1992) and the high As concentrations in surficial soils in the Altiplano and the Eastern Cordillera (Tapia et al., 2012). The last three fractions represent the largest pool of As (~ 90%). The order of the fractions, F3 = F5> F4, suggests that As is mainly associated with amorphous Fe oxides.

Fractions 2 – 4 can provide information into the lability of As in these soils, influenced by changes in pH, redox state, OM content (Wenzel et al., 2001), and environmental conditions such as mineral composition and drainage. The cropping period occurs during the rainy season (from November to March, with 372 mm/year of precipitation), when many agricultural areas are submerged, experiencing alternating anoxic and oxic conditions. These changes in Eh – pH conditions are partly due to the proximity of the cultivated areas to rivers (**Fig. 1**).

There is a six-fold difference between the amount of As extracted by DTPA (Lindsay and Norvell, 1978) and sequential extraction (Wenzel et al., 2001). The first method extracted less than 2% of the total As, while the second method extracted up to 12% (< 2%, fraction 1, F1; and < 10%, fraction 2, F2) of the total As content as a potentially mobilized fraction, which could be transferred to crops or dissolved in groundwater (Ramos Ramos et al., 2014). These differences can be explained by the specificity and selectivity of the reagents used by the sequential extraction procedure of Wenzel et al. (2001) and the DTPA reagent, which is specific for bound metal-complexes (Lindsay and Norvell, 1978). This suggests that the DPTA extraction is not a good predictor for available As.

3.5 Trace elements in edible parts of crops

The TEs concentrations are given on a fresh weight basis (fw), which was converted from dry weight basis assuming a mean water content of 90% (Rötting et al., 2013). The discussion in this section is limited to three TEs (i.e. As, Cd, and Pb) due to their phytotoxicity (McBride, 1994; Kabata-Pendias and Mukherjee, 2007; Zhao et al., 2022). The results are compared with study of crops by Rötting et al. (2013), in smelter areas near the study area Oruro (Bolivian Altiplano).

Among the crops, mean As contents are found in the decreasing order of beans and alfalfa (0.19 mg/kg) > barley (0.17 mg/kg) > potato (0.11 mg/kg); no samples exceeded the tolerable limits for crops. The Chilean regulation for food (Muñoz et al., 2002) establishes 0.5 mg/kg, fresh weight, for cereals and legumes, and 1.0 mg/kg for other products. The contents measured here are three-fold below the regulatory limit. Also, As contents are found lower than those in a review database (mean: 6.22 mg/kg; range: 0.005 – 56.9 mg/kg) reported by Rötting et al. (2013). Additionally, the one-way ANOVA depicts that there is no significant difference between As content in crops ($p < 0.05$, one-way, significance level of 0.09). The t-test (0.05 level of significance) of As indicates a significant difference between beans and potato.

The mean concentrations of Cd are in the decreasing order as follows: beans (0.03 mg/kg) > potato peeled (0.023 mg/kg) > alfalfa (0.017 mg/kg) > barley (0.012 mg/kg). The mean Cd content is 0.021 mg/kg, not exceeding the international (FAO, WHO, European) regulation guidelines which establish limits for potatoes (peeled) and stem/root vegetables (0.10 mg/kg, fresh weight) and other vegetables (0.05 mg/kg, fresh weight) (JECFA, 2005; European Commission Regulation (EC-1881), 2006).

The Pb contents are high in the decreasing order: beans (0.32 mg/kg) > alfalfa (0.22 mg/kg) > barley and potato peeled (0.16 mg/kg). The European regulation guidelines allow a maximum level of 0.20 mg/kg (fresh weight) for cereals and legumes (barley, alfalfa and beans), and 0.10 mg/kg for peeled potatoes (European Commission Regulation (EC-1881), 2006). The beans, alfalfa and potatoes exceeded the limits for cereals, legumes and potato. The mean value (0.19 mg/kg) found in our study is higher than the value of international regulations by ~ 2 fold. These Pb contents are much lower than the data in the review database (mean: 3.28 mg/kg; range: 0.03 – 43.5 mg/kg) reported by Rötting et al. (2013) (by 1.5 fold).

The one-way ANOVA for As (significance level of 0.09), Cd (significance level of 0.0004) and Pb (significance level of 0.07) indicates that there are no significant differences in mean values between crops for As and Pb, but there is a significant difference for Cd contents between crops. The Student's t-test for Cd found that there are significant differences between beans versus barley (0.0167) and barley versus potato (0.0167) crops.

3.6 Accumulation in crops

In principle, there are three pathways for human exposure linked to soil contamination: soil – plant – human (food chain pathway), soil – human (incidental soil ingestion), additionally in mining and arid zones especially the inhalation of dust pathway, the latter reported by Goix et al., (2011). They studied Oruro city where inhalation is an important factor for TEs intake.

The transfer factors (TF) calculated by equation (2) show different ranges for As (0.002 – 0.020), Cd (0.09 – 0.143), and Pb (0.0003 – 0.02) (**Table 4**). The mean values of TF_{As} are 2% for beans and barley, 0.8% for alfalfa, and 0.6% for potato, indicating that only a small fraction of As is transported from the soils to the plant, compared with the 12% available As. Arsenic can be accumulated in the soils due to its link to the amorphous and crystalline Fe oxide present in the soils, which was confirmed by the fixed As fraction (fractions 3, 4, and 5), and also given the aerobic conditions favorable to barley cultivation, where less mobile As(V) prevails with resulting stronger retention of As (Williams et al., 2007). No significant correlations between As concentration in crops and the exchangeable As fraction (step 2, extracted by ammonium phosphate, not shown here) was observed, taking into account the edible part of the crops as reported in other works (Niazi et al., 2011).

Table 4. Trace elements concentration (mg/kg) in edible part of crops (bean, barley, potato and alfalfa), the concentrations are expressed on a fresh weight basis (fw) and transfer factor (TF).

Parameters	Concentrations			I.R.	Transfer Factor		
	Min	Max	Mean	Max	Min	Max	Mean
Beans, n = 7							
As	0.186	0.242	0.194	0.5 §	0.006	0.020	0.011
Cd	0.015	0.049	0.034	0.1 #	0.018	0.143	0.068
Pb	0.077	0.499	0.319	0.2 #	0.002	0.024	0.009
Barley, n = 13							
As	0.09	0.40	0.17	0.5 §	0.002	0.020	0.009
Cd	0.01	0.03	0.01	0.1 #	0.009	0.054	0.022
Pb	0.04	0.40	0.16	0.2 #	0.000	0.012	0.005
Potato, n = 12							
As	0.093	0.208	0.122	0.1 §	0.004	0.013	0.006
Cd	0.008	0.044	0.023	0.1 #	0.015	0.095	0.047
Pb	0.038	0.493	0.156	0.1 #	0.000	0.016	0.005
Alfalfa, n = 4							
As	0.093	0.316	0.189	0.5 §	0.004	0.015	0.008
Cd	0.008	0.025	0.017	0.1 #	0.016	0.080	0.038
Pb	0.038	0.446	0.225	0.2 #	0.001	0.012	0.005
Global							
As	na	na	0.160	na	na	na	na
Cd	na	na	0.020	na	na	na	na
Pb	na	na	0.190	na	na	na	na

§ Chilean standard, Muñoz et al., 2002; I.R. International regulations; # JECFA, 2005; European Commission Regulation (EC-1881), 2006. Crop concentration (fresh weight basis, fw), soil concentrations (dry weight basis, dw). Crop concentrations on dry weight basis was converted to fresh weight basis assuming a mean water content of 90% (Rötting et al., 2013). Global, crop concentrations taken into account all crops in this study. na – Not available.

The mean observed TF_{Cd} value are 6.8% for beans, 4.7% for potato, 3.8% for alfalfa, and 2.2% for barley. Oporto et al. (2009) reported that the DGT flux experiments concluded that the enhancement in Cd uptake by chloride complexes is most pronounced at low Cd supply. However, Zheng et al. (2011) deduced that root hairs contribute to Cd uptake by barley, particularly in soils with elevated available Cd. The uptake of Cd increases in the presence of high Cd available concentrations, in agreement with the findings of Oporto et al. (2009). This is due to the relatively high amount available Cd_{DTPA} in the soils (i.e. availability ratio < 33%), with high EC values in the three transects (**Table 1**) and low concentrations in barley crops.

The mean values of TF_{Pb} are much lower than those for Cd, varying from 0.9% for beans to 0.5% for barley, potato and alfalfa, indicating that much of the Pb available could be fixed and retained on the roots. Previous studies reported excessive amounts of Pb in the crops in smelter areas (Rötting et al., 2013), near this study area.

Miller et al. (2004) examined four communities along the Pilcomayo River (southern Bolivia) which is influenced by mining activities in its upstream area and found that the most significant contamination of soils is by Cd, Pb, and Zn. The respective contents exceeded recommended guideline values for agricultural use, but the results also suggested that most vegetables do not accumulate significant quantities of TEs in their edible parts. Hence, the most significant exposure pathway appears to be the ingestion of contaminated soils attached to dust particles and consumed with vegetables, which are the usual meal in the Bolivian Altiplano. Therefore, peeling potatoes before consuming could be an effective way of reducing dietary intake of TEs, since there are higher concentrations of Cd, Pb and Zn in potato peel than in peeled potato (Yang et al., 2011).

4. Conclusions

In general, the pseudo-total TEs concentrations found in this study are higher than the world soils average values, but lower than the mean values of the Proyecto Piloto Oruro (PPO) report. These high contents are related to the geological conditions and the presence of polymetallic belts in the Eastern Cordillera of the Andes, suggesting that the geogenic signal is stronger than the anthropogenic signal.

In terms of bioavailable contents (DPTA extracts), TEs in soils follow the order Cd > Zn > Cu > Pb. The DTPA method extracted less than 2% of the total As, while the sequential extraction reported up to 12% (< 2%, step 1 and < 10.0%, step 2), which represents less than 3.1 mg/kg of the total As content, as a potentially mobilized fraction, which could be transferred to crops or dissolved in groundwater. The large pool of As can be accumulated in the soils due to amorphous and crystalline Fe oxides present in the soils, confirmed by the fixed As fractions (fractions 3, 4, and 5).

Evaluation of the edible parts of the crops (beans, barley and potato) found that As and Cd concentrations are lower than the values in international regulations. In contrast, Pb shows higher concentrations for beans and potato by a factor of about two, but the opposite is found for barley. Transfer factor (TF) values show that the amount transported from soil to the edible parts of the crops for As is 2% in beans and barley, 0.8% in alfalfa and 0.6% in potato; while, for Cd the value is 6.8% in beans, 4.7% in potato, 3.8% in alfalfa and 2.2% in barley. However, the TF for Pb varied from 0.9% for beans to 0.5% for barley, potato and alfalfa.

In future research, it is important to consider the speciation of TEs (e.g. organic-As and inorganic) and their bio-accessibility for human body, linked to the WHO/FAO provisional tolerable weekly intakes (PTWI). The studied TEs should be further explored in mining areas of the Bolivian Altiplano for minimizing the potential health risks for local population.

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6. Data availability statement

The data is presented in the manuscript as figures and tables. The data can be made available upon request from the corresponding author.

7. Author contributions

O.E. Ramos Ramos: conceptualization, data curation, investigation, methodology, writing – original draft, and writing – review & editing. M.I.C. Tapia and I.Q. Lima: formal analysis, investigation, software, validation and visualization. T.S. Rotting: validation, visualization, writing – original draft. V. Orsag and L. Chambi: conceptualization and data curation. J.Q. Aguirre: funding acquisition, resources and project administration. O. Sracek: conceptualization, data curation and writing – review & editing. J.P. Maity, A. Ahmad, and J. Bundschuh: writing – original draft. P. Bhattacharya: funding acquisition, resources, supervision, project administration, and writing – review & editing. All authors approved the final version of the manuscript.

8. Conflict of interest

The authors declare no conflict of interest related to this study.

9. Ethical statement

This study does not involve human or animal subjects. Ethical approval is not required for this research.

10. Copyright statement

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