

Heavy metals and selenium in pastures of a high Andean mining area and its relationship with their content in water and soil

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ABSTRACT

The aim of this study was to determine whether high levels of heavy metals and selenium in water and soil affected pastures in Peru's high Andean mining zone beyond the maximum permitted levels. Data on heavy metals and selenium were collected from water ($n = 25$), soil ($n = 95$), and pastures ($n = 20$) in areas suspected of contamination and in control zones, using specific sampling protocols and laboratory analyses compared to environmental standards. Although elevated concentrations of manganese were detected in groundwater (0.47 mg/l) and surface waters of rivers (0.3 mg/l), no increase exceeding the maximum permissible limits of this metal was recorded in the soils or pastures of the affected areas. Similarly, despite the presence of high concentrations of arsenic, lead, and selenium in the soils of areas impacted by mining activity, the levels of these metals in the evaluated pastures did not exceed the maximum permissible limits. Correlation analysis revealed highly significant negative correlations ($P \leq 0.01$) for iron in soil with arsenic in pastures ($r = -0.701$) and copper in soil with cadmium in pastures ($r = -0.81$). The results indicate that despite the existence of metal and selenium values exceeding established limits in both soil and water, no toxicity levels for these minerals were observed in the pastures that could pose a risk to the health of grazing animals.

Keywords: Andes, contamination, mineral, pastures.

INTRODUCTION

Mining in Peru, one of the primary economic activities, currently accounts for approximately 10% of the country's gross domestic product (GDP) (global business reports [GBR], 2023). However, its development has led to waste generation that negatively impacts the environment, particularly in the high Andean regions such as Cerro de Pasco, Cajamarca, Puno, and Arequipa (Motta-Delgado et al., 2019). These mining activities not only affect the quality of water and soil but also have repercussions on grazing systems that are vital for food security and the local economy, serving as the main source of sustenance for cattle, sheep, and camelids (Escobar, 2016).

This type of environmental pollution is not unique to Peru. In Ecuador, recent studies have reported arsenic and mercury levels in fish from

the Napo and Pastaza rivers that exceed World Health Organization (WHO) limits, primarily due to artisanal mining (Echevarría et al., 2024). In Bolivia, mining has also been identified as a major source of heavy metal pollution, affecting aquatic ecosystems and the health of nearby communities (Reyes et al., 2016). Similarly, in Mongolia, high concentrations of arsenic and selenium have been documented in soils and livestock forage near mining zones, with potential risks for human health through the consumption of contaminated meat and organs (Bataa et al., 2022).

Among the most concerning elements are arsenic, cadmium, lead, mercury, and selenium, whose presence in soil and groundwater is linked to both anthropogenic and natural sources. For example, mine tailings leachate contribute significantly to local metal loads, while geologic sources such as volcanic rocks may release naturally occurring

arsenic (Alloway, 2013). These elements are characterized by their persistence, bioaccumulation, and toxicity, affecting livestock physiology (Bataa et al., 2022; Torbati et al., 2024), and posing health risks to humans through consumption of milk, meat, or internal organs (Bataa et al., 2022).

In forages and grasses, the extent of metal uptake varies widely depending on the metal involved. While Cd and Pb can accumulate in plant tissues and be transferred to grazing animals (Anderson et al., 2022), Cu, Fe, and Se although essential micronutrients may become harmful when present in excess (Cruz et al., 2022; Research group, 2023; Vallieres, 2017; Rajabpour et al., 2017). Moreover, the bioavailability of these metals depends on soil characteristics such as pH, organic matter, and texture, which influence their mobility and plant absorption (Kabata-Pendias et al., 2001).

Although environmental regulations – such as mandatory Environmental Impact Assessments (EIAs) for new mining projects – are in place, enforcement and oversight are often weak, especially in older mining operations (García and Dorronoro, 2005). As a result, there is a significant lack of data on contamination levels in pasture soils.

Heavy metal contamination in mining areas and its effects on livestock production warrant further investigation. The aim of this study was to determine whether high levels of heavy metals and selenium in water and soil affected pastures in Peru's high Andean mining zone beyond the maximum permitted levels.

MATERIALS AND METHODS

Study area

The study was conducted in the Simón Bolívar district, located in the province and region of Pasco, in the central highlands of Peru. The area lies at altitudes ranging from 4280 to 4420 meters above sea level, with approximate coordinates of 10°41'23"S latitude and 76°18'57"W longitude. It has an arid to semi-arid climate, with annual precipitation averaging 500 mm and prevailing trade winds from south to north (National Institute of Meteorology and Hydrology [INMET], 2020).

Methodology

The Environmental Assessment and Oversight Agency (OEFA) conducted a sampling of

natural water, soil, and pastures in both suspected affected areas and a control zone, utilizing specific protocols for each component and performing the corresponding analyses. These reports were used for the analysis presented in this article, which includes assessments of heavy metals such as arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), mercury (Hg), manganese (Mn), iron (Fe), lead (Pb), zinc (Zn), and selenium (Se) in the area, with the methodology detailed below.

Since the specific detection limits (LOD) of the laboratory analyses were not available, typical reference values reported for EPA methods 6020A/6020B were used. For relatively simple matrices, detection limits are generally below 0.1 µg/L, although elements such as As and Se may present LODs around 1.0 µg/L (U.S. EPA, 2017). Complementary data reported for EPA method 6020B indicate the following indicative LODs: Ag 0.005 µg/L; Cr 0.08 µg/L; Cu 0.03 µg/L; Pb 0.003 µg/L (isotopic sum); As 0.08 µg/L; Fe 0.4 µg/L; Hg 0.02 µg/L; Se 0.06 µg/L; Cd 0.01 µg/L; Mn 0.05 µg/L; Zn 0.04 µg/L (Shimadzu, 2020). These values are intended as literature-based references and may vary depending on specific analytical conditions.

Samples collection

1. Water

Sampling of natural water bodies – including rivers, lakes, and groundwater – was conducted following established national and international protocols. Surface water sampling adhered to the National Protocol for Monitoring the Quality of Surface Water Resources (National Water Authority [ANA], 2016), while groundwater sampling followed the Manual of Best Practices for Investigating Contaminated Sites: Groundwater Sampling from the Ministry of the Environment (Ministry of the Environment of Peru [MINAM], 2017), as well as the National Field Manual for the Collection of Water-Quality Data (Book 9) from the U.S. Geological Survey. Samples were collected from affected zones in lakes and groundwater sources, and from both affected and control zones (upstream) in rivers. In total, 11 surface water samples from rivers (9 affected, 2 control), 2 lake samples (affected), and 12 groundwater samples (affected) were collected.

Water was sampled using clean polyethylene bottles – 1 L for surface water and 500 mL for groundwater – rinsed three times with the

corresponding sample prior to collection. All sampling points were georeferenced with a GPS device accurate to ± 3 meters, with site distances ranging from 100 to 800 meters. Sampling was carried out during the dry season (June to August) over an 18-day period. Immediately after collection, samples were stored in ice boxes at 4 ± 2 °C and transported to the AGQ Perú laboratory within 48 hours. Quality control procedures included the use of field blanks and transport blanks to detect potential contamination during collection, handling, and transport.

2. Soil

The soil sampling protocol was based on the guidelines established in the Soil Sampling Guide (MINAM, 2014), Criteria for the Management of Contaminated Sites (MINAM, 2017), and the Manual of Guidelines and Procedures for the Preparation and Evaluation of Contaminated Site Identification Reports (MINAM, 2015). Before determining sampling points, a preliminary assessment was conducted, which involved gathering and analyzing information to understand the chronological evolution of land use and occupation, the location of major production processes and operations, characteristics and management of emissions, effluents, and waste generated; as well as geological, landscape, climatic, meteorological, hydrological, ecological, water, and pasture conditions. This information was analyzed collectively to preliminarily identify

homogeneous land units where areas of potential interest, test pits, and specific samples would be located. This approach enabled us to identify locations that had been sites of mining activities that could have affected soil development (samples from affected zones) and to determine areas suitable for studying natural soil development (to obtain control samples).

A total of 95 soil samples were evaluated, consisting of 63 from affected zones and 32 from control zones. The samples were collected from the upper 30 cm of soil after removing the surface layer. At each sampling point, the soil was mixed and homogenized to obtain a 1 kg composite sample. Each sample was then air-dried, sieved to remove particles larger than 2 mm, and homogenized again to ensure consistency. Finally, the samples were placed in labeled polyethylene bags for storage and transport. The distribution of sampling points in both affected and control areas is illustrated in Figures 1 and 2.

3. Pastures

The pasture sampling protocol was derived from the Flora and Vegetation Inventory Guide (MINAM, 2015), the Manual of Basic Sampling and Analysis Methods in Plant Ecology (Mostacedo and Fredericksen, 2000), the Sampling Protocol for Determining Cadmium Levels in Soils, Leaves, Water, and Cocoa Beans (Ministry of Agrarian Development and Irrigation [MINAGRI], 2019), and the Sampling Protocols

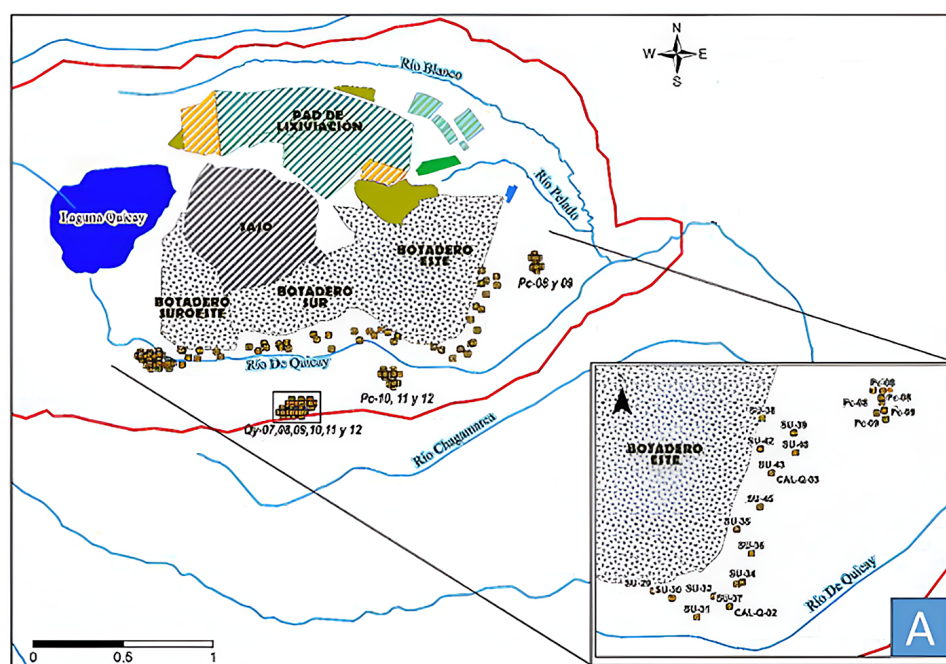


Figure 1. Strategic soil sampling points in affected (A) area

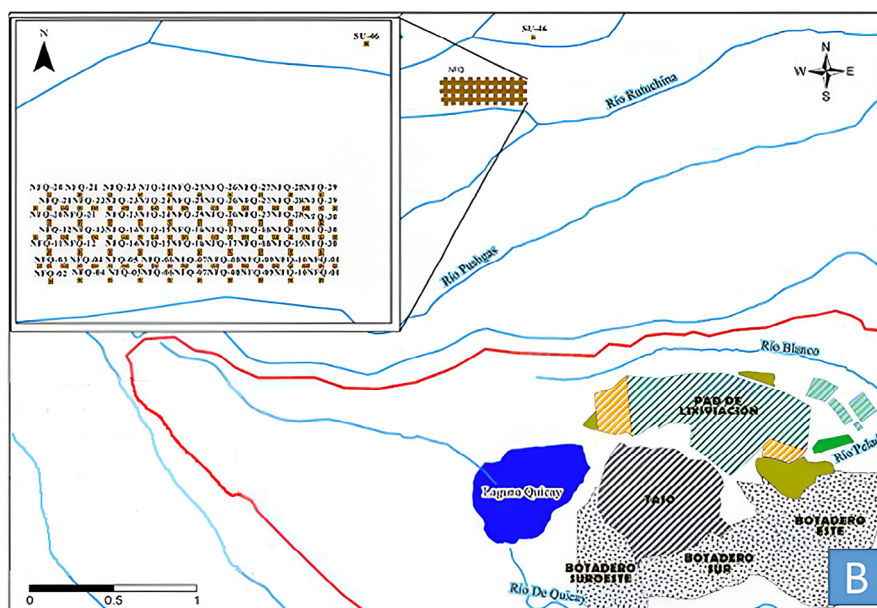


Figure 2. Strategic soil sampling points in control (B) area

in Crops for Micronutrient Analysis (Stangoulis and Sison, 2009).

The sampling points for pastures were the same as those for soils, covering both affected and control zones. For sampling herbaceous vegetation, a 1×1 m quadrat was placed randomly at each site, and dominant herbaceous species were collected. Samples were collected in manila envelopes and stored in containers for transport to the laboratory. A total of 20 samples were evaluated from pastures, consisting of 16 from affected zones and 4 from control zones.

Analysis carried out on metals and selenium

The analysis of heavy metals and selenium in water, soil, and pastures was conducted at AGQ Perú SAC laboratory using inductively coupled plasma mass spectrometry (ICP-MS). This was performed in accordance with the Environmental Protection Agency (EPA) method 6020A (2017) for water, EPA method 3050B Rev. 2 (1996) for soil, and EPA method 6020B Rev. 2 (2014) for soils.

Environmental quality standards

1. Water

The results obtained from surface water sampling in rivers were compared with the environmental quality standards (EQS) for water, Category 3 (for irrigation of vegetables and livestock consumption). Similarly, the surface waters from lakes were compared with the EQS for water, Category

4 (lakes and lagoons), as established by Peruvian regulation D.S. 004-2017-MINAM (MINAM, 2017). Regarding groundwater, there is currently no national regulatory standard for comparison. However, the results were compared with the EQS for water, Category 3 (D.S. 004-2017-MINAM), considering that groundwater may flow into surface waters that could subsequently be used for pasture irrigation or animal consumption.

2. Soils

The results obtained from the sampling were compared with the Peruvian environmental quality standards (EQS) for agricultural soils (MINAM 2013 and MINAM 2017), as well as the reference guidelines for agricultural soils from the Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health provided by the Canadian Council of Ministers of the Environment (2007).

3. Pastures

The results obtained from the sampling of metals such as Cd, Cu, Cr, Fe, Mn, Pb, Se, and Zn were compared with the maximum tolerable levels for cattle feed set by the National Academies of Sciences, Engineering, and Medicine (NASEM, 2021). Additionally, the values obtained for As were compared with the maximum tolerable limits established by Spain's Royal Decree 465 (2003) concerning undesirable substances in animal feed.

Quality assurance

To ensure the representativeness of the results, quality assurance measures were implemented, including duplicate samples, a transportation blank (to account for contamination during transport), a field blank (to assess contamination that may occur during monitoring), as well as equipment and material blanks.

Identification of toxic levels

The information on the concentration of heavy metals and selenium was systematically organized for both the affected area and the control zone, which showed no signs of contamination from mining activities. Concentrations of heavy metals and selenium were determined in water, soil, and pastures.

For each case, samples that, on average, exceeded the reference values for heavy metals and selenium were identified. In instances where water samples contained heavy metals or selenium that exceeded official standards, these values were compared with the concentrations of heavy metals or selenium found in pastures from both the affected and control zones. Similarly, soil samples with heavy metals or selenium that exceeded official standards were also compared with the corresponding values in pastures from both areas.

Statistical analysis

Box plots (Tukey, 1977) were used to visualize the data distribution and identify any potential outliers. After confirming the normal distribution of the data, descriptive statistics and a Student's t-test for two samples with unequal variances were conducted. The Student's t-test was employed to compare the concentrations of heavy metals and selenium between the affected area and the control zone, particularly when the concentrations in the affected area exceeded toxicity thresholds.

For surface water and lake samples, only descriptive statistics were considered due to the lack of control zone data. Pearson correlation coefficients between heavy metals and selenium in soil and pastures were calculated using the PROC CORR procedure in SAS v. 9.4.

RESULTS AND DISCUSSIONS

Water

The average concentrations of As, Cd, Cu, Hg, Pb, Zn, and Se analyzed in lakes within the affected area fell within the parameters established by the EQS (Table 1). This suggests, at the surface level, the water still meets the expected safety levels for natural water bodies. On the other hand, the absence of maximum permissible limits for chromium, iron, and manganese in lakes makes it more difficult to fully evaluate the potential risks these elements may pose. This is particularly important because iron and manganese are commonly present in mining areas (Park et al., 2018) and can negatively impact water quality and aquatic life.

In the case of groundwater, all heavy metals and selenium, except for manganese, were within the values indicated by the EQS (Table 1). High levels of manganese in groundwater from mining areas can result from both natural and human related processes. Naturally, Mn is found in underground rocks such as pyrolusite and rhodochrosite, which can dissolve and release manganese into the water under certain chemical conditions (Stumm and Morgan, 1996). In mining zones, activities like blasting and digging expose these rocks to air and water, increasing the chance of manganese entering the groundwater. When the underground environment has little oxygen Mn stays dissolved more easily and moves through the water, leading to higher concentrations (Hem, 1985).

In addition, Schwartz and Kgomanyane (2008) elucidated that highly acidic leachate waters (pH 1.7–2.8) enriched with sulfate (SO_4^{2-}) at concentrations of 5680 g/L and heavy metals (6230 mg/L Ni, 1860 mg/L Cu, and 410 mg/L Co) infiltrate through fractured aquifers, which is considered the primary source of groundwater contamination. This was determined by comparing these values with reported heavy metal concentrations in lakes located in the same region as this study, which also indicated potential contaminant presence.

The average concentrations of heavy metals (As, Cd, Cu, Fe, Hg, Pb, and Zn) and selenium (Se) analyzed in the affected area and control zone of surface water from rivers were within the permissible limits established by the EQS for irrigation of crops and livestock consumption (Table 2), it suggests the use of these waters does not, for the moment, represent a direct

Table 1. Average content and maximum values allowed by EQS (mg/l) of heavy metals and selenium of lagoon and groundwater in the affected area

Lagoon water	As	Cd	Cu	Fe	Mn	Hg	Pb	Se	Zn
Average	0.0030	0.0000	0.0017	0.1650	0.0146	0.0001	0.0017	0.0000	0.0060
N	2	2	2	2	2	2	2	2	2
Standard Deviation	0.0001	0.0000	0.0010	0.0210	0.0100	0.0000	0.0010	0.0000	0.0040
Minimum	0.0029	0.0000	0.0011	0.1500	0.0100	0.0001	0.0008	0.0000	0.0030
Maximum	0.0031	0.0000	0.0023	0.1800	0.0200	0.0001	0.0025	0.0000	0.0100
ECA–lagoon and lakes ¹	0.15	0.00025	0.10	NA	NA	0.0001	0.0025	0.0050	0.1200
Groundwater	As	Cd	Cu	Fe	Mn	Hg	Pb	Se	Zn
Average	0.0016	0.0001	0.0040	1.2100	0.4700	0.0001	0.0019	0.0007	0.0180
N	10	10	10	10	11	12	9	12	12
Standard Deviation	0.0015	0.0001	0.0038	1.6900	0.5100	0.0001	0.0016	0.0009	0.0230
Minimum	0.0004	0.0000	0.0003	0.0300	0.0007	0.0001	0.0001	0.0000	0.0020
Maximum	0.0046	0.0003	0.0115	4.4000	1.3916	0.0004	0.0039	0.0026	0.0740
EQS – irrigation vegetables ²	0.100	0.010	0.200	5	0.200	0.001	0.050	0.020	2

Note: NA – not available, ¹MINAM (2017). Category 4: Conservation of the aquatic environment. E1 Lagoons and lakes, ²MINAM (2017). Category 3: Irrigation of vegetables (D1).

Table 2. Average content and maximum permissible values (mg/l) of heavy metals and selenium in natural surface water from affected and control areas

Control area	As	Cd	Cu	Fe	Mn	Hg	Pb	Se	Zn
Average	0.0017	0.0000	0.0051	0.0900	0.0087*	0.0001	0.0006	0.0003	0.0030
N	2	2	2	2	2	2	2	2	2
Standard Deviation	0.0014	0.0000	0.0053	0.0424	0.0041	0.0000	0.0007	0.0004	0.0014
Minimum	0.0007	0.0000	0.0013	0.0600	0.0058	0.0001	0.0001	0.0000	0.0020
Maximum	0.0027	0.0001	0.0088	0.1200	0.0116	0.0001	0.0011	0.0006	0.0040
Affected area	As	Cd	Cu	Fe	Mn	Hg	Pb	Se	Zn
Average	0.0013	0.0009	0.0111	0.5800	0.3000*	0.0001	0.0004	0.0006	0.0180
N	9	9	9	9	9	9	9	9	9
Standard Deviation	0.0015	0.0010	0.0150	0.5093	0.3179	0.0001	0.0006	0.0005	0.0203
Minimum	0.0002	0.0000	0.0014	0.0300	0.0092	0.0000	0.0001	0.0000	0.0020
Maximum	0.0041	0.0024	0.0489	1.4000	0.8207	0.0004	0.0021	0.0014	0.0540
GI	9	9	9	9	9	9	9	9	9
<i>t</i> – value	0.37	-1.16	-0.54	-1.3	-1.23	-0.38	0.42	-0.56	-1.01
<i>p</i> – value	1	0.0541	0.5345	0.1287	0.0198	0.4725	1	1	0.1077
EQS – irrigation vegetables ¹	0.1	0.01	0.2	5	0.2	0.001	0.05	0.02	2
EQS – animal drink ²	0.2	0.05	0.5	NA	0.2	0.01	0.05	0.05	24

Note: * significant values 5% ($p < 0.05$), NA= Not available, ¹ MINAM (2017). Category 3: Irrigation vegetables (D1), ² MINAM (2017). Category 3: Animal drink (D2).

risk for local agriculture or livestock. However, Mn was found in much higher amounts in the affected area compared to the control area. This may be related to the higher levels of Mn also found in groundwater (Table 1). Regarding Cr, the recorded values were low (<0.001 mg/L) in

both the affected and control zones, indicating low mobility or low industrial presence of the element in the study area. This result is consistent with what is expected in areas where chromium is not a main byproduct of mining activities, unlike lead, cadmium, or arsenic.

Soil

The concentrations of heavy metals and selenium in the soil of the affected area, for which reference parameters are available, indicate that As, Pb and Se exceed the maximum levels established by MINAM (2017) and Canadian Council of Minister of the Environment (CCME) (2007) (Table 3). These findings suggest clear evidence of contamination likely related to historical or ongoing mining activities in the region.

When comparing the average values of these metals with those from the control zone, all were found to be statistically higher ($p < 0.01$) in the affected area. The elevated concentration of arsenic aligns with findings by Kaninga et al. (2020), who reported high levels in soils near a mining waste storage facility. However, when comparing arsenic and lead values with data reported by Fernández et al. (2022), which evaluated heavy metals in agricultural soils influenced by mining waste in Puno, the arsenic concentration was lower (5.35 mg/kg) while the lead concentration was higher (276.74 mg/kg).

On the other hand, it is noteworthy that the cadmium Cd concentration in the control zone (1.5 mg/kg) is higher than that in the affected area and exceeds the maximum levels established by

MINAM (2017) and CCME (2007). This phenomenon can be attributed to various factors. For instance, the composition of high Andean soils naturally contains cadmium, contributing to its presence even in non-mining areas (García and Dorronsoro, 2005). Additionally, agricultural practices in the region, such as the use of fertilizers that contain cadmium, may further increase the concentration of this metal in the soil.

Regarding Mn, which showed concentrations in groundwater exceeding the EQS, the average value of this mineral in the soil was lower in the affected area (103 mg/kg) compared to the control zone (437 mg/kg). Therefore, it is not possible to establish any impact of mining activity on manganese levels in the soil.

The higher concentrations observed in the control zone may have various origins, such as geological formations that naturally contain manganese, contributing to its presence in the soil regardless of mining activities (García and Dorronsoro, 2005). Additionally, manganese can be released into the environment through natural processes such as erosion and weathering of manganese-containing rocks. This indicates that even in areas without mining activities, manganese can accumulate in the soil due to its natural origins (Islam and Mostafa, 2024).

Table 3. Average content and maximum permissible values (mg/kg) of heavy metals and selenium in soils from affected and control areas

Control area	As	Cd	Cu	Cr	Fe	Mn	Hg	Pb	Se	Zn
Average	44.9*	1.5	30.6	12.0	16493	437	0.29	112*	1.1*	105
n	32	32	32	32	32	32	32	32	32	32
Standard deviation	15.0	0.4	5.7	3.7	4435	196.7	0.1	29.3	0.3	21.4
Minimum	7.3	0.39	20.00	1.74	6956	14.80	0.03	17.30	0.66	26.00
Maximum	87.9	2.5	44	19.9	23550	1190	0.416	181	2.16	142
Affected area	As	Cd	Cu	Cr	Fe	Mn	Hg	Pb	Se	Zn
Average	74.0*	0.92	51.1	7.7	36719	103	0.16	150*	2.1*	71
n	55	58	52	63	58	57	57	59	56	60
Standard Deviation	31.3	0.6	21.1	4.1	20034	102.2	0.1	70.7	0.8	44.3
Minimum	13.9	0.017	20	1.569	5507	4.97	0.01	10.6	0.886	8.2
Maximum	143	2.262	105	16.1	82637	319	0.38	326	3.807	192
gl	54	88	82	93	88	87	87	89	86	90
<i>t</i> – value	-4.93	4.99	-5.35	5.04	-5.62	10.57	6.92	-2.88	-7.39	4.07
<i>p</i> – value	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	0.005	<.0001	0.0001
Reference ¹	50	1.4	NA	NA	NA	NA	6.6	NA	NA	NA
Reference ²	12	1.4	63	64	NA	NA	6.6	50	1	200

Note: * significant values 1% ($p < 0.01$), NA= Not available, ¹MINAM (2017),

²Canadian Council of Ministers of the Environment (2007).

These findings highlight the complexity of soil contamination, where both anthropogenic (mining, agriculture) and natural factors must be considered. While some elements clearly point to mining impacts (As, Pb, Se), others (Cd, Mn) may reflect regional soil characteristics or land-use practices unrelated to mining.

Pastures

The dominant grass species in the study area were *Plantago tubulosa*, *Plantago rigida*, *Calamagrostis cf. brevifolia*, *Calamagrostis cf. tar-mensis*, and *Dactylis glomerata*. The average concentrations of heavy metals and selenium in the grasses were within the maximum permissible levels according to the references used (Table 4). It suggests that the pasture currently poses no risk to livestock in terms of toxic metal exposure.

In particular, mercury levels were notably low in both the affected and control zones (< 0.01 mg/kg), far below the 2 mg/kg limit set by NASEM (2021). This is consistent with the water quality results, where Hg and other elements such as As, Pb, and Se also stayed within safe levels. Notably, even though As, Pb, and Se concentrations were elevated in the soils of the affected area, these levels were not reflected in the grasses, suggesting limited transfer of these elements from soil to plant tissues under current conditions.

This could be due to several factors. First, metal accumulation in plants is typically a gradual process that depends on the duration of exposure (Sumalan et al., 2023) and in this study, such temporal information was not available. Therefore, it is reasonable that the exposure time was insufficient for significant bioaccumulation to occur in the grasses evaluated.

Second, the bioavailability of metals in soil depends not only on their total concentration but also on key soil properties such as pH, organic matter, texture, and cation exchange capacity (García and Dorronsoro, 2003; Abedini et al., 2019; Bautista, 1999). In the absence of detailed data on these soil characteristics, it is difficult to fully explain why elevated levels of As, Pb, and Se in soil did not result in higher uptake by the plants.

Statistically significant differences ($p < 0.01$) were observed for lead and zinc concentrations in grasses between the affected and control zones. However, in both cases, values remained within the safety limits for cattle feed according to NASEM (2021). Interestingly, zinc levels were higher in the control zone, which mirrors its higher concentration in the soil of that area (105 mg/kg), suggesting a likely link between soil content and plant uptake for this metal.

As for Mn, which exceeded environmental quality standards in surface water, the average

Table 4. Average content and maximum permissible values (mg/kg) of heavy metals and selenium in pastures from affected and control areas

Control area	As	Cd	Cu	Cr	Fe	Mn	Pb	Se	Zn
Average	1.15	0.27	8.58	1.78	357	277	4.2*	0.06	56*
n	4	4	4	4	4	4	4	4	4
Standard Deviation	1.27	0.13	7.23	0.31	246	237	4.61	0.02	13.00
Minimum	0.25	0.11	2.7	1.50	119	73	0.98	0.05	24
Maximum	3.00	0.44	19	2.20	592	583	10.90	0.09	100
Affected area	As	Cd	Cu	Cr	Fe	Mn	Pb	Se	Zn
Average	1.5	0.3	9.0	2.0	789	335	1.1*	0.08	29.5*
n	14	16	15	16	16	15	8	15	13
Standard Deviation	1.48	0.24	5.64	0.91	705.90	138.20	0.51	0.03	11.16
Minimum	0.40	0.06	2.90	0.81	130.00	129.00	0.75	0.05	14.00
Maximum	5.20	0.81	23.00	3.80	2601.00	570.00	2.29	0.14	49.00
gl	16.00	18.00	17.00	18.00	16.00	17.00	10.00	17.00	15.00
t – value	-0.43	-0.25	-0.13	-0.55	-1.18	-0.65	1.93	-1.19	2.67
p – value	0.90	0.36	0.45	0.10	0.11	0.14	<.0001	0.50	0.006
Reference ¹	2 ²	0.5	30	100	500	2000	30	5	500

Note: * significant values 1% ($p < 0.01$), ¹NASEM (2021), ²Royal decree 465/2003 Spain's Ministry of the Presidency (2003).

concentration in grass was 335 mg/kg in the affected zone and 277 mg/kg in the control zone. Although reference values for Mn in soil were not available, the values found in grasses did not exceed the permissible limits for animal feed, again indicating no immediate toxicological concern. This behavior is consistent with previous research indicating that Mn, despite its mobility in water, tends to have limited translocation to above-ground plant tissues under neutral or slightly acidic soil conditions (Broomandi et al., 2020).

Finally, it is important to acknowledge a key limitation of this study: all pasture sampling was conducted at a single point in time, during the dry season. This study approach may not capture seasonal variations in metal uptake or availability. Future studies should include longitudinal sampling across different seasons and incorporate soil property analyses to better understand metal mobility and bioavailability.

Correlation of heavy metals and selenium in soil and grass

The correlation analysis revealed complex relationships between heavy metal concentrations in soils and their presence in pasture grasses (Table 5). Among the six metals evaluated in the soil (As, Cd, Cu, Cr, Fe, and Hg), significant correlations were observed with six metals measured in the grasses (As, Cd, Cu, Fe, Pb, and Zn).

Most of the significant correlations found were negative, suggesting potential interactions or competition between metals that may

influence their uptake by plants. For example, As in the soil showed a negative correlation with Cd and Cu in grass ($p < 0.05$), which may indicate that higher soil As levels limit the absorption of Cd and Cu by plants. Similarly, soil Cd correlated negatively with Fe in grass, and soil Fe showed negative correlations with As and Cu in grass. This is supported by studies showing that essential metals like Cu and Zn can antagonize Cd uptake, reducing its extractability and toxicity in plants (Patra et al., 2025). Moreover, research on quinoa demonstrated that elevated Cd and Pb levels decreased the uptake of other nutrients – including Zn, Fe, Mn – due to cation competition at root transporters (Bamagoos et al., 2022). Additionally, heavy metals often compete for binding sites on cell membranes and in the rhizosphere, which can immobilize certain elements and further limit their plant availability (Yan et al., 2020).

These findings could reflect competitive uptake at the root level or soil chemical interactions that reduce metal bioavailability.

Notably, the only positive correlation was observed between Cr in the soil and both Cd and Pb in grass ($p < 0.05$). This suggests that, under certain soil conditions, these metals may become simultaneously more available to plants—possibly due to shared solubility behavior in response to pH or organic matter, as reported by Zeng et al. (2011). Similar findings have been observed in contaminated agricultural soils, where Cr and Cd show parallel mobility patterns, especially in acidic environments.

Furthermore, the interaction between Pb and Cr may also explain this correlation, as previous

Table 5. Pearson correlation coefficients (r) between soil and grass minerals

Parameter	AsPas	CdPas	CuPas	CrPas	FePas	MnPas	PbPas	SePas	ZnPas
AsSo	-0.518	-0.639*	-0.633*	0.249	-0.238	0.124	-0.213	-0.253	-0.282
CdSo	-0.335	-0.223	-0.127	-0.349	-0.641*	0.434	-0.192	-0.429	0.012
CuSo	-0.725*	-0.810**	-0.785	0.058	-0.796	0.345	-0.655	-0.585	-0.717*
CrSo	0.352	0.542*	0.364	-0.395	0.264	-0.036	0.761*	0.091	0.210
FeSo	-0.701**	-0.452	-0.595*	0.309	-0.462	0.094	-0.142	0.180	-0.384
MnSo	0.546	0.461	0.305	-0.214	-0.146	-0.351	-0.077	0.309	-0.004
HgSo	-0.535	-0.588*	-0.519	-0.092	-0.506	0.393	-0.306	-0.519	-0.319
PbSo	-0.303	-0.371	-0.189	-0.170	-0.384	0.384	0.099	-0.429	-0.109
SeSo	-0.268	-0.209	-0.449	0.008	0.112	0.231	0.133	-0.140	-0.500
ZnSo	-0.131	0.189	-0.001	-0.430	-0.392	0.402	0.257	-0.253	0.190

Note: *, ** Significant correlation coefficient values 5% ($P \leq 0.05$) and 1% ($P \leq 0.01$), respectively, So – soil, Pas – pasture.

studies (Zhao, 2009) indicate that Pb can alter the mobility of Cr and vice versa, potentially enhancing their joint uptake in plant tissues.

Importantly, even though these correlations indicate interaction dynamics in metal uptake, all concentrations of heavy metals and Se in the grasses remained within the safe limits for cattle consumption (NASEM, 2021). This suggests that the observed correlations are not currently translating into toxic accumulation in pasture biomass, but they highlight a need for continued monitoring, particularly under changing environmental or soil conditions.

Overall, these results support the idea that metal uptake by plants is not only dependent on total soil concentrations, but also on chemical interactions, root competition, and soil properties. As Salazar-Matarrita et al. (2020) pointed out, negative correlations may reflect processes like metal competition for absorption sites or formation of non-bioavailable complexes in the soil matrix.

CONCLUSIONS

This study provides a comprehensive assessment of heavy metals and selenium in water, soil, and pastures within a high Andean mining area, revealing distinct patterns of contamination and transfer across environmental compartments. While concentrations of arsenic, lead, and selenium in soils of the affected area exceeded both national and international limits, and manganese levels in groundwater surpassed environmental quality standards, these elevated values were not reflected in pasture biomass. All pasture samples remained within safe thresholds for livestock consumption, indicating limited contaminant transfer from soil and water to plants under current conditions.

Correlation analysis between soils and grasses revealed mostly negative relationships, suggesting competitive uptake or chemical interactions that reduce bioavailability, with only isolated positive correlations indicating potential co-mobilization under specific conditions.

These findings suggest that, although there is no immediate toxicological risk to grazing livestock, the presence of certain metals above regulatory thresholds in soils and groundwater warrants continued environmental monitoring.

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