REVISTA BIO CIENCIAS
http://revistabiociencias.uan.edu.mx
https://doi.org/10.15741/revbio.13.e1950
ISSN 2007-3380

*Artículo original/Original Article*

# Soil, water and forage quality in an agricultural area impacted by mining activities in Zacatecas, Mexico.

# Calidad del suelo, agua y forraje en zona agrícola impactada por actividades mineras en Zacatecas, México.

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**Please cite this article as/Como citar este artículo:** Solís-Rodríguez, X., Espinoza-Canales, A., Gutiérrez-Bañuelos, H., Escot-Espinoza, V.M., Flores-De la Torre, J.A. (2025). Soil, water and forage quality in an agricultural area impacted by mining activities in Zacatecas, Mexico. Revista Bio Ciencias, 13, e1950. https://doi.org/10.15741/revbio.13.e1950

**Article Info/Información del artículo**
Received/Recibido: May 21th 2025.
Accepted/Aceptado: September 19th 2025.
Available on line/Publicado: October 13th 2025.

## ABSTRACT

The presence and dispersion of potentially toxic elements from mining waste can affect the quality of soils used in agricultural systems. In the present work, the presence of heavy metals in soils, water, and forage from agricultural systems was evaluated, as well as the nutritional quality of the latter in the community of Valdecañas, Fresnillo, Zacatecas. Heavy metal concentrations in the samples were determined using flame atomic absorption spectrophotometry, and the nutritional quality of the forage was assessed through proximal analysis. Maximum concentrations (μg $L^{-1}$) of lead (34.6) and cadmium (4.25) were determined in the analyzed water samples, exceeding the limits established by national and international regulations, with water bodies in the community being the most affected. In the evaluated soils, maximum concentrations (mg $kg^{-1}$) of 43.57 for lead, 21.56 for chromium, and 1.62 for cadmium were determined, associated with biomagnification processes in areas used for grazing and as watering troughs near the community's pond. Proximal analysis indicated average values of 14 % crude protein, 37.5 % neutral detergent fiber, and 34 % acid detergent fiber, with chromium present in 100 % of the samples, with a maximum concentration of 41.7 mg $kg^{-1}$. The results reflect the importance of studying the presence and mobility of heavy metals in agricultural areas near mining activities, as well as evaluating the quality of food products produced in the area.

**KEY WORDS:** Agricultural activities, pollution, mining, metals.

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Revista Bio ciencias
ISSN 2007-3380

## RESUMEN

La presencia y dispersión de elementos potencialmente tóxicos provenientes de residuos mineros puede afectar la calidad de los suelos utilizados en sistemas agropecuarios. En el presente trabajo se evaluó la presencia de metales pesados en suelo, agua y forrajes de uso agropecuario, así como la calidad nutricional de estos últimos en la comunidad de Valdecañas, Fresnillo, Zacatecas. Las concentraciones de metales pesados en las muestras fueron determinadas mediante espectrofotometría de absorción atómica de flama, asimismo, la calidad nutricional del forraje se determinó mediante un análisis proximal. En las muestras de agua analizadas se determinaron concentraciones máximas (μg $L^{-1}$) de plomo de 34.6 y cadmio de 4.25, los cuales superan los límites permisibles establecidos en la normativa nacional e internacional, siendo los cuerpos de agua cercanos a la comunidad los más afectados. En los suelos evaluados se determinaron concentraciones máximas (mg $kg^{-1}$) de 43.57 para plomo, 21.56 para cromo y 1.62 para cadmio, asociadas a procesos de biomagnificación en áreas usadas para pastoreo y como abrevaderos cerca del estanque de la comunidad. El análisis proximal indicó valores promedio de 14 % de proteína cruda, 37.5 % de fibra detergente neutra y 34 % de fibra detergente acida, con presencia de cromo en el 100 % de las muestras y una concentración máxima de 41.7 mg $kg^{-1}$. Los resultados reflejan la importancia de estudiar la presencia y movilidad de metales pesados en zonas agropecuarias cercanas a actividades mineras, así como evaluar la calidad de los productos alimenticios generados en la zona.

**PALABRAS CLAVE:** Actividades agropecuarias, contaminación, minería, metales.

## Introduction

Mining is one of the most important economic activities in Mexico, and the state of Zacatecas is among the country’s main mining regions (SE, 2016c). The state is divided into 17 mining areas based on location and mineral types. One of the most important is the Fresnillo Mining District (FMD), located in the municipality of the same name, recognized as one of the largest producers of silver and gold both nationally and internationally (SGM, 2020). The FMD is near rural communities such as Valdecañas, which has 1,670 residents involved in farming and livestock activities, including growing maize and beans, as well as raising and selling livestock (INEGI, 2010; SGM, 2012).

Mining and metallurgical activities can cause negative environmental impacts, mainly

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due to waste generated after extraction processes. These impacts include soil, surface water, groundwater, and vegetation contamination caused by heavy metals and toxic elements like arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), lead (Pb), and zinc (Zn). These elements can accumulate in the soil and be absorbed by plants through various mechanisms, risking food safety through biomagnification in food chains (Gómez-Álvarez *et al*., 2007; Khan *et al*., 2016; Aznar-Sánchez *et al*., 2018; Zhu *et al*., 2019). Consequently, the quality of soil, water, and forage in agricultural areas near mining sites is an increasing concern, as the presence and mobility of toxic elements may impact agriculture, crops, livestock, and human health (Hu *et al*., 2017; Vetrimurugan *et al*., 2019; Archundia *et al*., 2024). Previous studies have found As, Pb, Zn, and Cu in agricultural soils, irrigation water, stream sediments, and forage in mining regions of Mexican states such as San Luis Potosí, Sonora, Hidalgo, Tlaxcala, Puebla, Guanajuato, and Baja California Sur (Razo *et al*., 2004; Ramos-Arroyo & Siebe-Grabach, 2006; García-Gutiérrez & Rodríguez-Meza, 2012; Duarte-Zaragoza *et al*., 2015; Castro-González *et al*., 2017; Alvarado-Zambrano & Green-Ruiz, 2019; Loredo-Portales *et al*., 2020; González-Méndez, 2022; Silva-Gigante *et al*., 2024). Specifically, in Zacatecas, studies have evaluated the impact of Pb, As, and Hg on the quality of soils affected by mining residues and their accumulation in vegetables grown in these soils (Dávila *et al*., 2012; Salas-Muñoz *et al*., 2021.

The quality of forage used as feed in ruminant production for meat and milk depends on its chemical composition, environmental factors, soil type, and exposure to contaminants (Almaraz-Buendía *et al*., 2019; Navarro-Ortiz & Roa-Vega, 2020; Abedi *et al*., 2022; Vasilachi *et al*., 2023). Therefore, analyzing forage from areas near mining sites is crucial to evaluate its nutritional value and identify any contaminants that could be harmful. This analysis includes measuring parameters such as crude protein (CP), acid detergent fiber (ADF), neutral detergent fiber (NDF), ash, minerals, and quantifying heavy metals and other pollutants (Rezaeian *et al*., 2020 Ge *et al*., 2022; Elik & Gül, 2025). In Valdecañas, livestock trade is one of the main economic activities, emphasizing the importance of assessing how mining and metallurgical activities affect the local agricultural system. This study conducted an environmental assessment by measuring heavy metal concentrations in soil, water, and forage samples from Valdecañas and evaluated the nutritional quality of the forage through proximal analysis.

## Material and Methods

### Study area

The community of Valdecañas belongs to the Fresnillo municipality, Zacatecas, Mexico (Figure 1). It is located at an elevation of 2,250 meters above sea level and lies in a valley with intermittent river flows, surface water bodies, agricultural fields, and grazing areas. It is located approximately 2 km from the mining facilities of the “Saucito del Poleo” project (Figure 1c).

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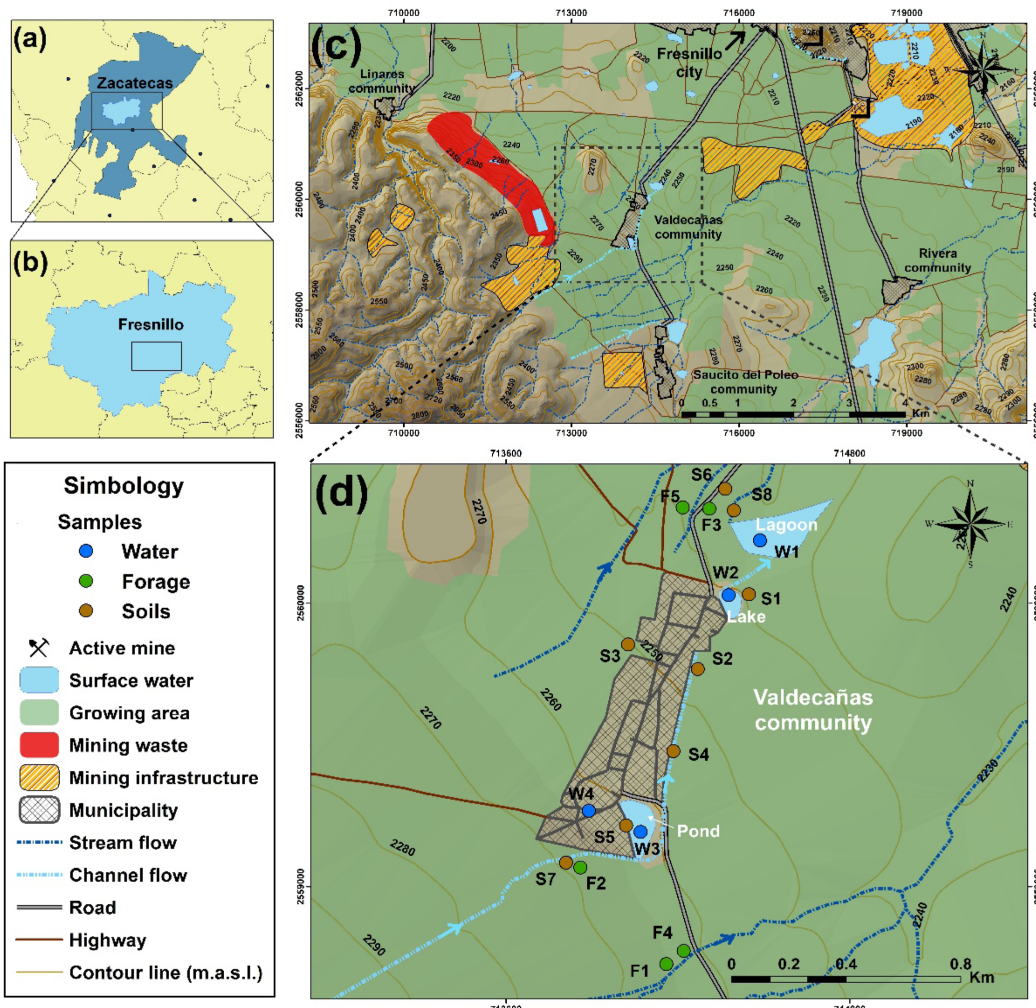


**Figure 1. Map of the study area showing the location of: (a) map of Zacatecas state, (b) map of Fresnillo municipality, (c) active mining area, and (d) sampling points of water (blue circle), soil (brown circle), and forage (green circle).** Source: Own elaboration.

## Water, soil, and forage sample collection

Table 1 displays the characteristics and locations of the water, soil, and forage samples collected in October 2024 for agricultural purposes. Water samples were taken from three surface water bodies called “lagoon”, “lake”, and “pond”. These bodies receive runoff from an artisanal channel that comes directly from the mining facilities and are occasionally used as drinking sources for livestock in the community (Figure 1c). For analysis, 500 mL of water was collected in

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polypropylene bottles, filtered through 45 µm syringe nylon filters, and acidified in the field with 70 % $HNO_3$. This sample was used for heavy metal analysis (SE, 2016b).

Soil samples were taken from croplands and areas used for grazing by community livestock. A targeted exploratory sampling was performed, collecting approximately 500 g of soil at a depth of 30 cm, following the Mexican Standard NMX-132-SCFI-2016. Samples were stored in plastic bags and transported to the laboratory (SE, 2016a). Forage samples were gathered using a random quadrat method. A 50 x 50 cm quadrat was randomly placed ten times in each sampling area. The plant material within each quadrat was harvested until reaching 500 g of forage, then placed in paper bags for laboratory analysis processing.

**Table 1. Characteristics and location of the samples collected in the community of Valdecañas, Fresnillo, Zacatecas.**

| Type of Sample | Label Sample | Characteristics | UTM Coordinates Longitude X (East) | Latitude Y (North) | Altitude (m.a.s.l.) |
|---|---|---|---|---|---|
| | W1 | Lagoon water | 714486.41 | 2560220.66 | 2,240 |
| Water | W2 | Lake water | 714407.91 | 2560010.09 | 2,246 |
| | W3 | Pond water | 714065.16 | 2559209.23 | 2,265 |
| | W4 | Tap water | 713910.17 | 2559198.01 | 2,268 |
| | S1 | | 714461.06 | 2560004.90 | 2,243 |
| | S2 | Grazing soil | 714265.43 | 2559755.92 | 2,252 |
| | S3 | | 714151.18 | 2559780. 60 | 2,255 |
| Soil | S4 | | 714184.04 | 2559477.82 | 2,258 |
| | S5 | Watering trough floor | 714045.75 | 2559198.89 | 2,266 |
| | S6 | Corn cultivation soil | 714369.96 | 2560403.62 | 2,239 |
| | S7 | Bean cultivation soil | 713848.34 | 2559072.98 | 2,271 |
| | S8 | Pasture soil | 714343.22 | 2560418.07 | 2,238 |
| | F1 | Bean forage | 714315.63 | 2558625.85 | 2,266 |
| Forage | F2 | | 713848.34 | 2559072.98 | 2,271 |
| | F3 | Corn forage | 714369.96 | 2560403.62 | 2,239 |
| | F4 | | 714367.27 | 2558679.85 | 2,264 |
| | F5 | Grass forage | 714351.06 | 2560430.23 | 2,238 |

W1: Lagoon water. W2: Lake water. W3: Pond water. W4: Tap water. S1: Grazing soil 1. S2: Grazing soil 2. S3: Grazing soil 3. S4: Grazing soil 4. S5: Watering trough floor. S6: Corn cultivation soil. S7: Bean cultivation soil. S8: Pasture soil. F1: Bean forage 1. F2: Bean forage 2. F3: Corn forage 1. F4: Corn forage 2. Source: Own elaboration

## Heavy metal quantification by flame atomic absorption spectrophotometry

To determine the concentrations of As, Pb, Cd, Cr, Cu, Fe, and Zn in soil and forage samples, 2.5 g of previously sieved samples were used, with a particle size of less than 250 µm for soil and 1 mm for forage. Samples were subjected to acid digestion by adding 50 mL of an HCl-$HNO_3$ mixture in a 3:1 ratio (aqua regia). The mixtures were left to stand for 24 hours and then heated to

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ISSN 2007-3380

95 °C for 3 hours. Finally, samples were filtered and diluted with $HNO_3$ (1 %) to a final volume of 50 mL. For the quantification of As, Pb, Cd, Cr, Cu, Fe, and Zn in water samples, 50 mL of each sample was filtered through a 45 µm filter and acidified with 1.5 mL of $HNO_3$ (70 %) (ISO, 1995; EPA, 1996).

Metal concentrations in water, soil, and forage samples were measured using the flame atomic absorption spectrophotometry technique, with a Thermo Scientific iCE 3300FL spectrophotometer (Cambridge, United Kingdom). For quality control of acid digestion and trace element analysis, reference material NIST-2586 containing 500 mg $kg^{-1}$ of Pb was used (96 % recovery), along with high-purity standards from Thermo Scientific to generate four-point calibration curves adjusted with the least squares method. The wavelengths (nm) used for element analysis were: 193.7 for As, 217 for Pb, 228.8 for Cd, 357.9 for Cr, 248.3 for Fe, 324.8 for Cu, and 213.9 for Zn. All analyses were conducted in duplicate.

### Physicochemical analysis of soil samples

To evaluate the physicochemical parameters of the soil samples, a 1:10 dilution was prepared by adding 2 g of soil to 20 mL of deionized water in a 50 mL Falcon tube. The sample was shaken for 20 minutes at 30 r.p.m. After sedimentation, the supernatant was analyzed for pH, oxidation-reduction potential (ORP), electrical conductivity (EC), and total dissolved solids (TDS). Measurements were taken using a digital benchtop multiparameter instrument (Multifunction, EZ-9909, China) (SEMARNAT, 2002).

### Proximal and nutritional characterization of forages: bean, corn, and grass

For the chemical composition analysis of forage samples, fresh material was weighed and dried at 60 °C for 65 hours. The dried material was then ground and sieved through a 1 mm mesh. Ash content was determined by incinerating the samples in a muffle furnace (Novatech MD-12, Lynchburg, VA, USA) at 550 °C for 6 hours. Organic matter (OM) was calculated by subtracting ash content from dry matter. Crude protein (CP) was obtained through total nitrogen determination using the Dumas combustion method (Leco FP-528, Leco Corporation, St. Joseph, MI, USA). Neutral detergent fiber (NDF) and acid detergent fiber (ADF) were sequentially determined using Van Soest's detergent fiber analysis, with an Ankom fiber analyzer (Ankom Technology, Ankom 200, Macedon, NY USA).

### Statistical analysis

A one-way analysis of variance (ANOVA) was conducted, followed by Tukey's mean comparison test ($p < 0.05$). Before applying ANOVA, normality was checked using the Shapiro-Wilk test at a significance level of $\alpha = 0.05$ (Figure C1). If the data did not meet the normality assumption, a power transformation (X^0.5) was used. Pearson correlation analysis and principal component analysis (PCA) were performed to identify relationships among the variables and sample types (Escot-Espinoza *et al*., 2021).

For metals with concentrations below the limit of detection (LOD), a censored data approach was employed. The percentage of samples with values below the LOD was calculated for each metal. When this percentage exceeded 15 %, specific methods for censored data, such as substitution with LOD/√2, were considered, as recommended in the literature (Helsel, 2012; Hewett & Ganser, 2007). Descriptive statistics—mean, minimum, maximum, and standard deviation—were used to summarize the results of the proximal analysis. All statistical analyses were performed using Minitab® 18.1 software.

## Results and Discussion

Table 2 displays the concentrations of As, Pb, Cd, Cr, Fe, Cu, and Zn in several water, soil, and forage samples. Lead (Pb) was detected in all soil samples, with the highest concentration (43.57 mg $kg^{-1}$) found in sample S3, collected from a grazing area near the Valdecañas community, influenced by a stream originating upstream from nearby mining facilities (Figure 1d). For cadmium (Cd), the highest concentration (1.62 mg $kg^{-1}$) was observed in sample S2, from an agricultural area on flat terrain affected by a water channel coming directly from mining operations (Figure 1d). All soil Pb and Cd levels (Table 2) remained below the permissible limits (PL) of 400 mg $kg^{-1}$ for Pb and 37 mg $kg^{-1}$ for Cd, according to the NOM-147-SEMARNAT/SSA1-2004 regulation (SEMARNAT, 2007). However, ongoing mining waste generation—from operations that began in 2011 (Minería en línea, 2022)—may promote biomagnification of heavy metals in various environmental receptors. In this context, Belmonte-Serrato *et al*. (2010) studied a 100 km² area in Spain’s Cartagena-La Unión Mining District, characterized by Fe, Pb, and Zn deposits. Their findings revealed average concentrations of 66.12 mg $kg^{-1}$ of Fe, 1 751 mg $kg^{-1}$ of Pb, and 1.21 mg $kg^{-1}$ of Zn in agricultural soils, illustrating how hydrological mobilization processes in semi-arid regions can enable the biomagnification of these contaminants in environmental compartments.

In water sample W3, the highest concentrations of Pb, Cu, Fe, and Zn were observed—34.6, 30.7, 915.45, and 853 µg $L^{-1}$, respectively. The highest Cd concentration (4.25 µg $L^{-1}$) was found in sample W1 (Table 2). These water sources are fed by the channel running from the mining facilities and are located near agricultural areas, accessible to community livestock (Figure 1d, Figure C2a). It was found that 75 % of the water samples exceeded the permissible limit for Pb in drinking water established by the NOM-127-SSA1-2017 (10 µg $L^{-1}$), while 100 % exceeded the WHO guideline value (1 µg $L^{-1}$). For Cd, 25 % of samples surpassed the national limit of 3 µg $L^{-1}$ (WHO, 2017; SSA,2022). The presence of these elements in agricultural fields near mining and metallurgical industries has been documented (Rodríguez-Eugenio *et al*., 2019). Therefore, water bodies in the Valdecañas community are potential sources of contamination, and the area’s topography promotes runoff from the mining site to local ponds and lagoons, facilitating biomagnification processes (Figure 1d, Figure C2b).

**Table 2. Metal concentrations of the different types of samples collected in the community of Valdecañas, Fresnillo, Zacatecas.**

| Label Sample | As | Pb | Cd | Cr | Cu | Fe | Zn |
|---|---|---|---|---|---|---|---|
| | | | | $\mu g\ L^{-1}$ | | | |
| **W1** | UD | 30.35 ± 2.76$^{A}$ | 4.25 ± 0.35$^{A}$ | UD | 24.4 ± 0$^{B}$ | 464.9 ± 24.5$^{B}$ | 724.5 ± 12.3$^{AB}$ |
| **W2** | UD | 12.3 ± 2.12$^{B}$ | 3.0 ± 0.85$^{A}$ | UD | 26.5 ± 2.97$^{AB}$ | 218.95 ± 2.05$^{C}$ | 10.4 ± 0.57$^{C}$ |
| **W3** | UD | 34.6 ± 1.13$^{A}$ | 3.75 ± 0.07$^{A}$ | UD | 30.7 ± 0.42$^{A}$ | 915.45 ± 8.7$^{A}$ | 853 ± 17.4$^{A}$ |
| **W4** | UD | 2.95 ± 2.62$^{C}$ | UD | UD | UD | UD | 426.3 ± 87.1$^{B}$ |
| | | | | $mg\ kg^{-1}$ | | | |
| **S1** | UD | 8.2 ± 0.9$^{E}$ | 0.70 ± 0.03$^{C}$ | 3.63 ± 1.57$^{B}$ | 5.50 ± 0.25$^{B}$ | 1508.5 ± 8.61$^{C}$ | 7.6 ± 0.0$^{D}$ |
| **S2** | UD | 9.8 ± 1.2$^{DE}$ | 1.62 ± 0.09$^{A}$ | 3.83 ± 0.08$^{B}$ | 13.65 ± 0.38$^{A}$ | 1526.4 ± 3.96$^{C}$ | 18.4 ± 1.9$^{BC}$ |
| **S3** | UD | 43.57 ± 1.6$^{A}$ | 1.23 ± 0.01$^{B}$ | 11.84 ± 1.15$^{AB}$ | 13.46 ± 1.92$^{A}$ | 1892.5 ± 20.9$^{B}$ | 65.5 ± 4.7$^{A}$ |
| **S4** | UD | 28.2 ± 0.1$^{B}$ | 1.15 ± 0.18$^{B}$ | 17.62 ± 6.35$^{A}$ | 7.44 ± 0.61$^{B}$ | 1944.1 ± 20.1$^{A}$ | 60.8 ± 1.4$^{A}$ |
| **S5** | UD | 16.3 ± 0.1$^{C}$ | 0.74 ± 0.02$^{C}$ | 13.98 ± 2.18$^{AB}$ | 6.78 ± 0.25$^{B}$ | 279.4 ± 0.01$^{D}$ | 25.8 ± 0.9$^{B}$ |
| **S6** | UD | 12.6 ± 0.9$^{CD}$ | UD | 21.56 ± 9.15$^{A}$ | 6.58 ± 0.65$^{B}$ | 262.4 ± 4.44$^{D}$ | 19.5 ± 1.2$^{B}$ |
| **S7** | UD | 5.8 ± 0.05$^{E}$ | UD | 20.87 ± 3.09$^{A}$ | 4.33 ± 0.72$^{B}$ | 277.2 ± 0.93$^{D}$ | 11.0 ± 0.4$^{CD}$ |
| **S8** | UD | 15.7 ± 1.3$^{C}$ | 0.62± 0.017$^{C}$ | 13.33 ± 0.24$^{AB}$ | 4.38 ± 0.03$^{B}$ | 272.2 ± 2.3$^{D}$ | 20.0 ± 0.6$^{B}$ |
| **F1** | UD | UD | 0.48 ± 0.62$^{A}$ | 41.7 ± 24.7$^{A}$ | 6.97 ± 5.57$^{A}$ | 137.1 ± 26.6$^{A}$ | 16.0 ± 4.1$^{AB}$ |
| **F2** | UD | UD | UD | 22.29 ± 4.19$^{A}$ | 2.43 ± 2.81$^{A}$ | 153.9 ± 16.1$^{A}$ | 18.7 ± 0.8$^{AB}$ |
| **F3** | UD | UD | UD | 30.78 ± 1.81$^{A}$ | 6.26 ± 0.12$^{A}$ | 141.1 ± 12.01$^{A}$ | 9.7 ± 0.3$^{B}$ |
| **F4** | UD | UD | UD | 13.88 ± 7.05$^{A}$ | 1.05 ± 0.04$^{A}$ | 104.4 ± 0.19$^{A}$ | 23.9 ± 2.2$^{AB}$ |

As: Arsenic. Cd: Cadmium. Cr: Chrome. Cu: Copper. Fe: Iron. Pb: Lead. Zn: Zinc. W1: Lagoon water. W2: Lake water. W3: Pond water. W4: Tap water. S1: Grazing soil 1. S2: Grazing soil 2. S3: Grazing soil 3. S4: Grazing soil 4. S5: Watering trough floor. S6: Corn cultivation soil. S7: Bean cultivation soil. S8: Pasture soil. F1: Bean forage 1. F2: Bean forage 2. F3: Corn forage 1. F4: Corn forage 2. UD: Undetectable. One-way analysis of variance with Tukey mean test is shown ($p < 0.05$), different letters (A, B, C, or D) indicate statistically significant differences between samples. Source: Own elaboration

In forage samples, the highest Cr concentration (41.7 mg kg$^{-1}$) was found in sample F1 (bean forage), collected near soil sample S7, which contained 20.87 mg kg$^{-1}$ of Cr. Similarly, sample F3 (corn forage) had 30.78 mg kg$^{-1}$ of Cr, while the corresponding soil sample S6 contained 21.56 mg kg$^{-1}$ (Figure 1c, Table 2). This indicates a potential mechanism of bioaccumulation and biomagnification of Cr in plants consumed by local livestock (Guzmán-Morales *et al.*, 2021). In a related study, Castro-González *et al.* (2018) reported increased Cr levels in alfalfa grown in soils irrigated with wastewater for eight months. They observed a rise in Cr content from 1.36 to 2.78 mg kg$^{-1}$ in edible parts (leaves and stems) and from 1.34 to 2.14 mg kg$^{-1}$ in roots.

Although Pb was not detected in the forage samples, its presence in grazing and cropland soils remains concerning, as it can transfer through trophic chains and potentially impact animal and human health. Khan *et al.* (2023) evaluated Pb concentrations in animal blood, forage corn, and agricultural soils, reporting levels of up to 2.39 mg L$^{-1}$, 10.34 mg kg$^{-1}$, and 10.73 mg kg$^{-1}$, respectively, confirming that Pb can move from soil to forage and then to livestock.

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ISSN 2007-3380

Elements like Fe, Zn, and Cu are essential minerals for livestock's physiological functions; therefore, their presence in forage may not be harmful. However, the safe amount depends on factors such as species, age, breed, and production level. Accurate information on dietary mineral requirements is essential (Rosero-Noguera & Posada-Ochoa, 2016; Bernardis *et al*., 2017).

### Evaluation of physicochemical parameters in soil samples

Table 3 displays the values of physicochemical parameters obtained from soil samples. On average, the samples had a pH of 7.03 and an oxidation-reduction potential (ORP) of 78.0 mV-SHE. However, samples S6 and S7 showed reducing potentials of -41.5 and -4.5 mV-SHE, respectively. Both also had low salt content, as indicated by their TDS and EC values, which is typical of croplands experiencing erosion processes (Gutiérrez & Llerena, 2019).

Electrical conductivity (EC) and total dissolved solids (TDS) varied across sampling sites. Sample S5 showed the highest EC (977.5 µS $cm^{-1}$) and TDS (488.5 mg $L^{-1}$) levels; this sample was collected near the pond and at the entrance of the channel originating from the mining facilities (Figure 1d). These findings suggest particle movement caused by water erosion from higher elevation areas, such as the mining zone, toward the Valdecañas valley. This interpretation is supported by the area's topography and the EC values observed in transitional soil samples near water bodies (S2, S3, and S4), which were lower than those in valley bottom soils (S1 and S8), where fine particle sedimentation is more prominent (Figure 1c, d; Figure C2a) (Escot-Espinoza *et al*., 2021).

**Table 3. Analysis of physicochemical parameters determined in the different soils collected in the community of Valdecañas, Fresnillo, Zacatecas.**

| Label sample | pH | ORP (mV-SHE) | EC (µS $cm^{-1}$) | TDS (mg $L^{-1}$) |
|---|---|---|---|---|
| **S1** | 7.4 ± 0.07$^{AB}$ | 77 ± 9.9$^{B}$ | 282.5 ± 47.4$^{B}$ | 141.5 ± 23.3$^{B}$ |
| **S2** | 6.7 ± 0.49$^{B}$ | 158.5 ± 16.3$^{A}$ | 219 ± 21.2$^{BC}$ | 109.5 ± 10.61$^{BC}$ |
| **S3** | 6.9 ± 0.21$^{AB}$ | 86.5 ± 3.54$^{B}$ | 72 ± 2.83$^{C}$ | 35.5 ± 2.12$^{C}$ |
| **S4** | 7.0 ± 0$^{AB}$ | 59.5 ± 13.44$^{B}$ | 43 ± 4.24$^{C}$ | 43 ± 4.24$^{BC}$ |
| **S5** | 6.7 ± 0$^{B}$ | 158 ± 0$^{A}$ | 977.5 ± 132.2$^{A}$ | 488.5 ± 65.8$^{A}$ |
| **S6** | 8.2 ± 0$^{A}$ | -41.5 ± 2.12$^{D}$ | 50.5 ± 20.5$^{C}$ | 35 ± 4.24$^{C}$ |
| **S7** | 6.4 ± 0$^{B}$ | -4.5 ± 0.71$^{C}$ | 33.5 ± 3.54$^{C}$ | 16.5 ± 2.12$^{C}$ |
| **S8** | 7.0 ± 0.84$^{AB}$ | 138 ± 4.24$^{A}$ | 213.5 ± 6.36$^{BC}$ | 106.5 ± 3.54$^{BC}$ |

**S1: Grazing soil 1. S2: Grazing soil 2. S3: Grazing soil 3. S4: Grazing soil 4. S5: Watering trough floor. S6: Corn cultivation soil. S7: Bean cultivation soil. S8: Pasture soil. ORP: Oxidation-reduction potential. EC: Electrical conductivity. TDS: Total dissolved solids. One-way analysis of variance with Tukey mean test is shown ($p < 0.05$), different letters (A, B, C, or D) indicate statistically significant differences between samples.** Source: Own elaboration

### Proximal and nutritional analysis of forages

The results of the proximal analysis for forage samples are shown in Table 4. The observed crude protein (CP) values were 20.5 % for bean forage, 10 % for corn forage, and 11.4 % for grass forage. These percentages correspond to forage harvested at phenological stages before full maturity and are comparable to values reported for other forage types such as alfalfa (Palmonari *et al*., 2014; Guo *et al*., 2019; Vuković *et al*., 2025). The use of these forages has been linked to moderate weight gain and milk production in livestock (Mobashar *et al*., 2018; Hansen *et al*., 2022). However, they are considered adequate for supporting the maintenance and function of ruminal microorganisms in ruminants, which require a minimum CP content of 7–10 % (Posada-Ochoa *et al*., 2016).

**Table 4. Proximal and nutritional characterization of the different forages collected in the community of Valdecañas, Fresnillo, Zacatecas.**

| Parameters | Mean (%) | Standard deviation | Minimum (%) | Maximum (%) |
|---|---|---|---|---|
| | | **Grass forage** | | |
| Ash | 10.77 | 0.57 | 10.37 | 11.17 |
| OM | 88.58 | 0.2 | NA | NA |
| NDF | 41.96 | 3.02 | 39.82 | 44.1 |
| ADF | 41.85 | 3.01 | 39.72 | 43.98 |
| CP | 11.44 | 6.27 | NA | NA |
| | | **Bean forage (*Phaseolus vulgaris*)** | | |
| Ash | 10.65 | 0.51 | 10.30 | 11.01 |
| OM | 89.35 | 3.35 | NA | NA |
| NDF | 41.96 | 3.02 | 39.82 | 44.1 |
| ADF | 41.85 | 3.01 | 39.72 | 43.98 |
| CP | 20.51 | 0.62 | NA | NA |
| | | **Corn forage (*Zea mays*)** | | |
| Ash | 11.07 | 1.04 | 10.3 | 11.80 |
| OM | 89.43 | 0.23 | NA | NA |
| NDF | 28.61 | 7.64 | 23.2 | 34.01 |
| ADF | 18.43 | 2.84 | 16.43 | 20.44 |
| CP | 10.06 | 0.23 | NA | NA |

Ash: Ashes. OM: Organic matter. NDF: Neutral detergent fiber. ADF: Acid detergent fiber. CP: Crude protein. NA: Not applicable.
Source: Own elaboration

The average NDF content in the evaluated forages was approximately 37.5 %, while ADF was 34 %. Ash content, which indicates the mineral level in forages, was 10.6 % for bean forage, 11 % for corn forage, and 10.7 % for grass forage. These values fall within acceptable ranges for forages used in bovine diets (Bernardis *et al*., 2017). Forages are a key source of minerals for grazing livestock, supporting their growth, reproduction, ruminal microbial functions, and disease resistance. However, any deficiency or excess of these minerals can negatively affect animal productivity and health. Using wastewater for irrigation can increase mineral levels in soil and forage, potentially affecting both development and nutritional quality (Bernardis *et al*., 2017; Khan *et al*., 2023).

The proximal and nutritional results for the grass forages fall within the normal ranges (Table 4), considering that high-quality forages should have CP content > 7 %, NDF < 60 %, and ADF <40 % to meet livestock nutritional needs. However, grasses exposed to contaminants may experience changes in nutritional composition—such as the accumulation of metals in plant tissues reducing CP content and increasing ash levels (Miranda *et al*., 2005; Calderón *et al*., 2023). Similarly, the presence of toxic elements may interfere with the absorption and utilization of essential nutrients by livestock through the soil–plant–animal continuum, potentially impacting animal health and productivity (Pérez-Vázquez *et al*., 2016; Archundia *et al*., 2024).

The presence of mining and metallurgical activities near agricultural and grazing areas can significantly impact the quality and safety of crops and pastures used in livestock diets. The corn and bean forages evaluated in this study fall within ranges considered normal, indicating that their cultivation near mining facilities does not compromise their nutritional quality. However, metals can affect food safety for consumers, as negative effects on human health have been reported, including neurological disorders and carcinogenic risks (Nuss & Tanumihardjo, 2010; Suárez-Martínez *et al*., 2016; Rai *et al*., 2019; Soto-Benavente *et al*., 2020). Likewise, grasses growing near mining zones may be exposed to various contaminants, such as heavy metals and other toxic elements, which can accumulate in plant tissues and subsequently in livestock products like milk and meat, posing a risk to human health (Miranda *et al*., 2005; Bermúdez *et al*., 2011; Liu *et al*., 2013; Pérez-Vázquez *et al*., 2016).

### Statistical analysis of soil and forage samples

Table 5 shows the Pearson correlation analysis for soil samples. The results indicate a significant positive correlation ($p < 0.05$) among the metals Pb, Cd, Cr, Fe, and Zn. The strongest correlation was observed between Pb and Cd ($p < 0.01$), suggesting a possible common anthropogenic source. A positive correlation was also noted between EC and TDS ($p < 0.05$), indicating that soil samples contain an ionic load related to dissolved salts. These salts may include secondary mineral phases that carry heavy metals (Escot-Espinoza *et al*., 2021).

The clustering and similar orientation of the Pb, Cd, Cr, and Cu vectors in the PCA (Figure 2a) further support the hypothesis of a common origin (Table C1). Additionally, the positive correlations observed between Fe and Cu, and between Zn and Pb ($p < 0.05$), could be linked to agricultural soils containing mineral particles typical of the Fresnillo Mining District (FMD), such as pyrite ($FeS_2$), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), and galena (PbS) (Rubalcaba-Ruiz & Thompson, 1988). These particles result from mineral processing and may be transported from the mine to water bodies in the Valdecañas community via the artisanal channel (Figure 1c). Their presence is also associated with the positive correlation between EC and TDS (Table 5, *p* <

0.05), potentially indicating ionic enrichment caused by the dissolution and release of elements in sediment accumulation zones (López-Díaz & Estrada-Medina, 2015; Escot-Espinoza *et al*., 2021).

**Table 5. Pearson correlation analysis for soil samples collected in the community of Valdecañas, Fresnillo, Zacatecas.**

| Variable | Pb | Cd | Cr | Cu | Fe | Zn | pH | ORP | EC | TDS |
|---|---|---|---|---|---|---|---|---|---|---|
| Pb | 1 | | | | | | | | | |
| Cd | 0.852** | 1 | | | | | | | | |
| Cr | 0.915** | 0.779* | 1 | | | | | | | |
| Cu | 0.729 | 0.864** | 0.52 | 1 | | | | | | |
| Fe | 0.631 | 0.73* | 0.385 | 0.731* | 1 | | | | | |
| Zn | 0.765* | 0.476 | 0.645 | 0.562 | 0.503 | 1 | | | | |
| pH | -0.261 | -0.298 | -0.283 | -0.122 | -0.046 | -0.087 | 1 | | | |
| ORP | 0.727 | 0.881** | 0.783* | 0.668 | 0.344 | 0.211 | -0.334 | 1 | | |
| EC | 0.164 | 0.288 | 0.142 | 0.142 | -0.268 | -0.239 | -0.159 | 0.628 | 1 | |
| TDS | 0.225 | 0.344 | 0.162 | 0.162 | -0.211 | -0.175 | -0.189 | 0.659 | 0.993* | 1 |

Cd: Cadmium. Cr: Chrome. Cu: Copper. Fe: Iron. Pb: Lead. Zn: Zinc. ORP: Oxidation-reduction potential. EC: Electrical conductivity. TDS: Total dissolved solids. $*p < 0.05$. $**p < 0.01$. Source: Own elaboration

Table 6 presents the Pearson correlation analysis for forage samples, showing a positive correlation between NDF and ADF ($p < 0.05$). Additionally, significant positive correlations were found between Cr and Cu, and between Fe and Zn ($p < 0.05$), similar to the correlations observed in soil samples. The presence of metals like Cr and Cu in forage may be associated with bioaccumulation processes from soil to plant. Moreover, bio-stabilization processes could occur due to the presence of organic matter, which promotes the formation of organometallic complexes in the rhizosphere (Salas-Ávila *et al*., 2021; Santos-Ubaldo *et al*., 2023).

**Table 6. Pearson correlation analysis for forage samples collected in the community of Valdecañas, Fresnillo, Zacatecas.**

| Variable | Cd | Cr | Cu | **Fe** | **Zn** | **Ash** | **OM** | **NDF** | **ADF** | **CP** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Cd** | 1 | | | | | | | | | |
| **Cr** | 0.627 | 1 | | | | | | | | |
| **Cu** | 0.59 | 0.999* | 1 | | | | | | | |
| Fe | 0.562 | 0.997 | 0.999* | 1 | | | | | | |
| **Zn** | 0.513 | 0.99 | 0.996 | 0.998* | 1 | | | | | |
| **Ash** | -0.725 | 0.082 | 0.128 | 0.162 | 0.219 | 1 | | | | |
| **OM** | 0.426 | 0.972 | 0.982 | 0.988 | 0.995 | 0.314 | 1 | | | |
| **NDF** | 0.5 | -0.361 | -0.404 | -0.435 | -0.487 | -0.959 | -0.57 | 1 | | |
| ADF | 0.5 | -0.361 | -0.404 | -0.435 | -0.487 | -0.959 | -0.57 | 1* | 1 | |
| **CP** | 0.99 | 0.508 | 0.468 | 0.437 | 0.384 | -0.817 | 0.291 | 0.62 | 0.62 | 1 |

Cd: Cadmium. Cr: Chrome. Cu: Copper. Fe: Iron. Pb: Lead. Zn: Zinc. Ash: Ashes. OM: Organic matter. NDF: Neutral detergent fiber. ADF: Acid detergent fiber. CP: Crude protein. $*p < 0.05$.

Source: Own elaboration

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ISSN 2007-3380

Figure 2a shows the principal component analysis (PCA) for the soil samples, where components 1 and 2 account for 77.6 % of the total data variance. Additionally, it can be observed that the vectors for Pb, Fe, Cu, Cd, Zn, and ORP are oriented toward the grazing soil samples (S2, S3, and S4), which exhibited the highest concentrations of these elements.

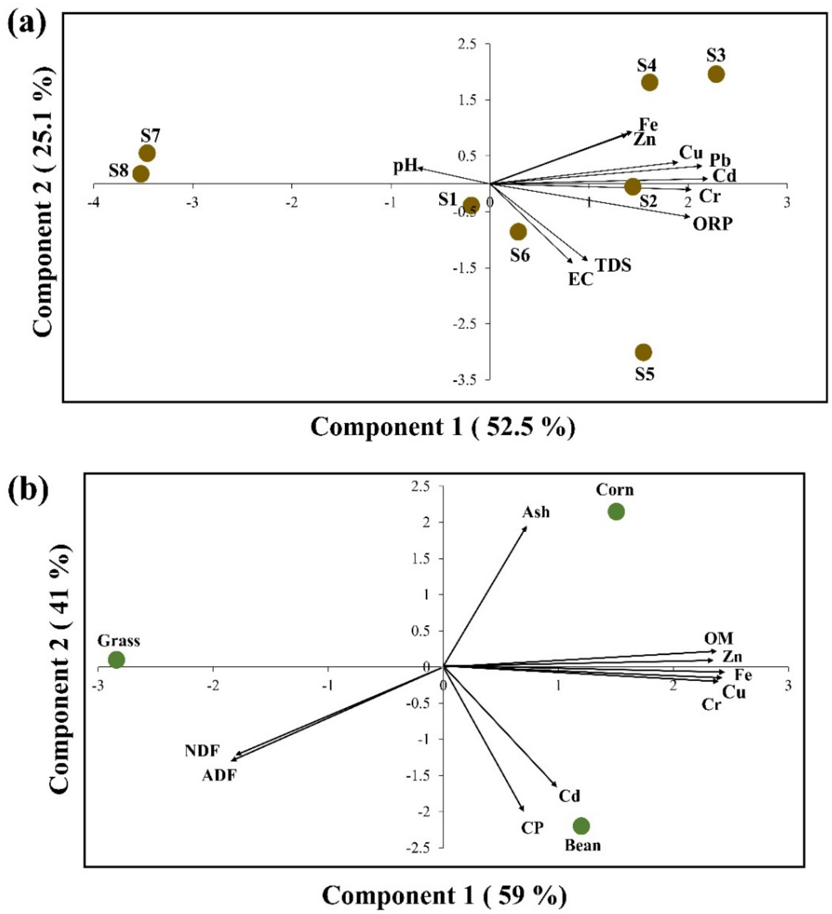


**Figure 2. Principal component analysis for (a) soil samples and (b) forage samples evaluated in the community of Valdecañas, Fresnillo, Zacatecas.** Source: Own elaboration.

Samples S7 and S8, corresponding to corn and bean cultivation soils, respectively, did not show a significant impact from the presence of heavy metals (Figure 2a). The associations identified in the PCA for soil samples indicate that the presence of metals is related to changes in physicochemical conditions promoted by the presence of organic matter, which contributes to metal accumulation through chelation and/or adsorption processes in grazing areas. When

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ISSN 2007-3380

metal-carrying particles come into contact with organic matter present in cultivation zones, they may dissolve into free ions, increasing their bioavailability and participating in cation exchange reactions with minerals, living organisms, or forage plants (Navarro-Aviñó *et al*., 2007; Aguirre *et al*., 2021.

In the PCA for forage samples (Figure 2b, Table C2), components 1 and 2 together account for 100 % of the total variance. Component 1 correlates the presence of heavy metals (Zn, Fe, Cu, and Cr) with organic matter, supporting the theory of organometallic complex formation processes in the evaluated agricultural areas. Component 2 correlates crude protein content with the presence of Cd. Although no mineral phases containing Cd have been reported in the Fresnillo Mining District, Cd may be associated with Zn or phosphorus minerals (as an impurity), suggesting a possible anthropogenic contribution from the use of fertilizers, pesticides, and/or agrochemicals in cultivated areas of the study site (Bonomelli *et al*., 2003; Lora-Silva & Bonilla-Gutiérrez, 2010).

## Conclusions

The results obtained in this study demonstrate an environmental impact caused by mining and metallurgical activities on the soil, water, and vegetation components of the Valdecañas community, located in Fresnillo, Zacatecas. These activities have negatively affected the quality of surface water bodies used by the community for agricultural and livestock purposes, as heavy metal concentrations exceeding the limits established by national and international regulations were detected. Additionally, the presence of heavy metals in agricultural and grazing soils—especially in areas near water bodies—suggests a process of transport and sedimentation of metal-bearing particles, magnified by the physiographic characteristics of the area, runoff, and water channels.

Although metal concentrations in soil do not exceed permissible limits, the correlation among concentrations in soil, water, and forage indicates a biomagnification process within the local agroecosystem, with medium- and long-term environmental and health consequences. Despite the proximal analysis showing that corn, bean, and grass forages have adequate nutritional value for ruminant diets, the presence of metals such as Cr, Cu, and Zn presents a latent risk to food safety, requiring continuous monitoring to prevent adverse impacts on various environmental receptors.

This study highlights the importance of evaluating the effect of heavy metals in agricultural areas near mining and metallurgical activities, as well as the potential biomagnification processes within trophic chains. Further studies are recommended to substantiate these findings.

### Author contributions

Conceptualization of the study: X.S.R., A.E.C., H.G.B., V.M.E.E., J.A.F.D.T.; methodology development: X.S.R.; software management: X.S.R., V.M.E.E.; experimental validation: J.A.F.D.T., A.E.C., H.G.B.; data analysis: X.S.R., V.M.E.E., H.G.B., A.E.C.; data curation: X.S.R., V.M.E.E.;

manuscript writing and preparation: X.S.R.; writing, review, and editing: X.S.R., V.M.E.E., H.G.B., A.E.C., J.A.F.D.T.; project administration: J.A.F.D.T., H.G.B. All authors have read and approved the final published version of this manuscript.

## Conflict of Interest

The authors declare no conflict of interest.

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ISSN 2007-3380

## Supplementary material

**Table C1. Principal component analysis for soil samples using metal concentration and physicochemical parameters.**

| | Eigenvectors | | | | |
|---|---|---|---|---|---|
| **Variable** | **PC1** | **PC2** | **PC3** | **PC4** | **PC5** |
| **Pb** | 0.409 | 0.128 | -0.068 | 0.243 | -0.144 |
| **Cd** | 0.419 | 0.037 | 0.076 | -0.258 | -0.163 |
| **Cr** | 0.387 | -0.041 | -0.127 | 0.425 | -0.404 |
| **Cu** | 0.362 | 0.154 | 0.245 | -0.298 | 0.601 |
| **Fe** | 0.274 | 0.373 | 0.191 | -0.408 | -0.189 |
| **Zn** | 0.265 | 0.354 | -0.125 | 0.547 | 0.469 |
| **pH** | -0.144 | 0.115 | 0.905 | 0.33 | -0.16 |
| **ORP** | 0.385 | -0.236 | 0.05 | -0.147 | -0.256 |
| **EC** | 0.163 | -0.567 | 0.154 | 0.05 | 0.232 |
| **TDS** | 0.188 | -0.55 | 0.125 | 0.08 | 0.165 |
| **Eigenvectors (Eg)** | 5.252 | 2.512 | 0.932 | 0.778 | 0.298 |
| **Variance (%)** | 52.5 | 25.1 | 9.3 | 7.8 | 3 |
| **Accumulated (%)** | 52.5 | 77.7 | 87 | 94.8 | 97.7 |

Source: Own elaboration

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**Table C2. Principal component analysis for forage samples using metal concentration and proximal analysis in forage.**

| | Eigenvectors | | | | |
|---|---|---|---|---|---|
| **Variable** | **PC1** | **PC2** | **PC3** | **PC4** | **PC5** |
| **Cd** | 0.195 | -0.435 | -0.162 | 0.191 | -0.221 |
| **Cr** | 0.405 | -0.09 | 0.158 | -0.027 | 0.571 |
| **Cu** | 0.408 | -0.068 | 0.002 | -0.252 | -0.521 |
| **Fe** | 0.41 | -0.051 | 0.246 | -0.078 | -0.316 |
| **Zn** | 0.411 | -0.022 | 0.182 | -0.031 | -0.064 |
| **Ash** | 0.108 | 0.476 | 0.173 | 0.795 | -0.19 |
| **OM** | 0.411 | 0.026 | 0.108 | 0.071 | 0.458 |
| **NDF** | -0.216 | -0.42 | 0.218 | 0.044 | 0.016 |
| **ADF** | -0.216 | -0.42 | 0.684 | 0.223 | -0.035 |
| **CP** | 0.141 | -0.464 | -0.547 | 0.452 | 0.057 |
| **Eigenvectors (Eg)** | 5.895 | 4.104 | 0 | 0 | 0 |
| **Variance (%)** | 59 | 41 | 0 | 0 | 0 |
| **Accumulated (%)** | 59 | 100 | 100 | 100 | 100 |

Source: Own elaboration.

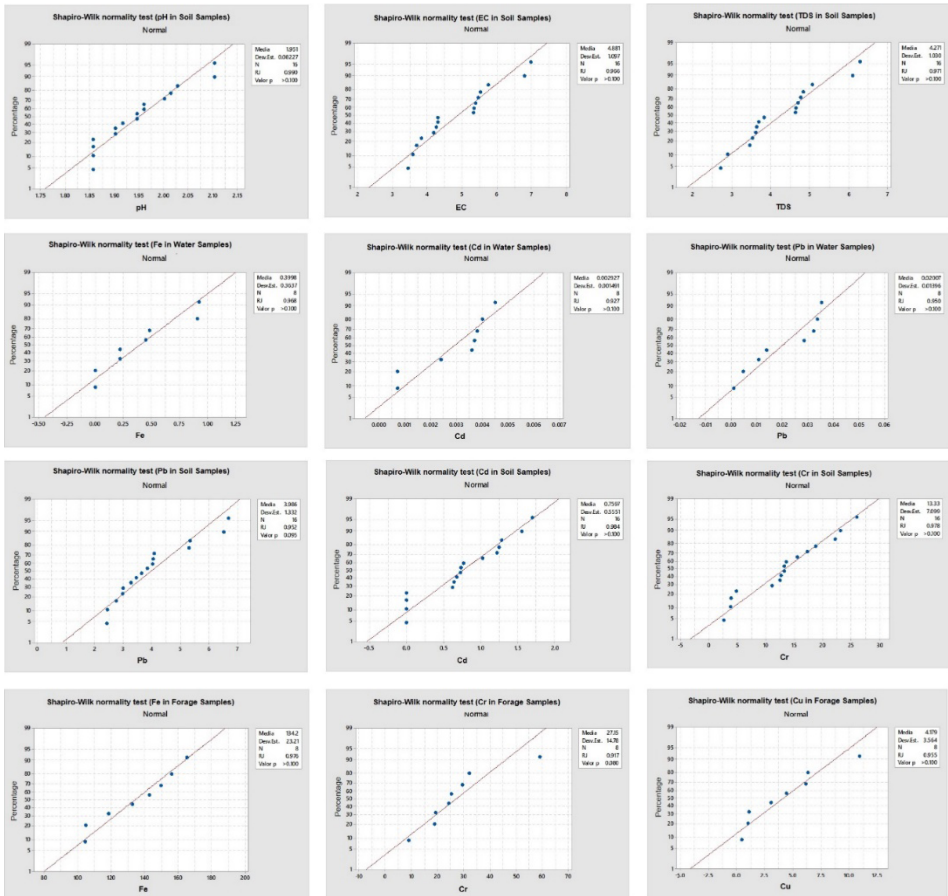


**Figure C1. Shapiro-Wilk normality test plots (α = 0.05). *p* > 0.05, the data are normal. *p* < 0.05, the data are not normal (normality is rejected).** Source: Own elaboration.

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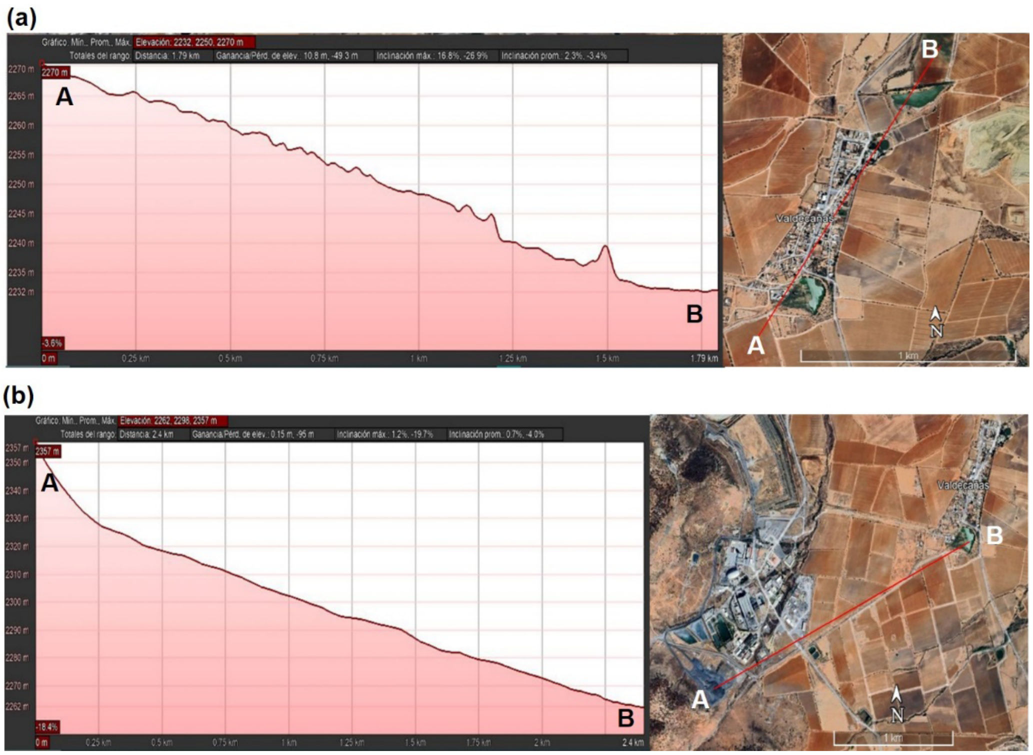


**Figure C2. Elevation profile of (a) the Valdecañas community and (b) the area between the mining facilities and the Valdecañas community.** Source: Own elaboration.