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Trace Element Transfer and Distribution in the Rock-Soil-Plant System: La Oriental Mine, Uruguay

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Abstract

The study of systems associated with mining activities is essential to understand the transfer of trace elements from the lithosphere to the biota. This research evaluated the origin and availability of metals in the Mina La Oriental area, in Uruguay. Rock and soil samples were collected from waste rock dumps and control sites, alongside specimens of *Plantago brasiliensis*, *Nierembergia ericoides*, and *Blepharocalyx salicifolius*. Results suggest that the high concentration of trace elements in soils derives from materials accumulated due to base metal mining (Cu, Pb, Zn), showing a heterogeneous distribution where Pb exhibits a lithogenic dominance associated with these waste structures. Extreme enrichment factors (EF > 40) were recorded throughout the area, exceeding the natural geochemical baseline even in locations distant from the dumps. Regarding vegetation, metal transfer was regulated by species identity: *P. brasiliensis* acted as an Al and Pb accumulator, whereas *B. salicifolius* exhibited an excluder behavior driven by effective root barriers. Meanwhile, *N. ericoides* showed intermediate transfer levels dependent on soil availability. Finally, cation exchange capacity, pH, and organic matter content were determined to be the primary geochemical controls of metal mobility. These findings allow for the characterization of retention mechanisms in a mining-impacted system, providing key data for the management of environmental liabilities.

Keywords: trace elements, base metals, soil-plant transfer, weathering

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Transferencia y distribución de elementos traza en el sistema roca-suelo-planta: El caso de Mina La Oriental, Uruguay

Resumen

El estudio de sistemas asociados a la actividad minera es fundamental para comprender la transferencia de elementos traza desde la litosfera hacia la biota. Esta investigación evaluó el origen y la disponibilidad de metales en el área de Mina La Oriental, Uruguay. Se recolectaron muestras de rocas, suelos en escombreras y sitios de control, junto a ejemplares de *Plantago brasiliensis*, *Nierembergia ericoides* y *Blepharocalyx salicifolius*. Los resultados sugieren que la elevada concentración de elementos traza en los suelos deriva de los materiales acumulados por la minería de metales de base (Cu, Pb, Zn), con una distribución heterogénea en la que el Pb muestra predominio litogénico asociado a dichas estructuras. Se registraron Factores de Enriquecimiento extremos (EF > 40) en toda el área, superando la línea de base natural incluso en puntos alejados de las escombreras. Respecto a la vegetación, la transferencia estuvo regulada por la identidad de la especie: *P. brasiliensis* se identificó como acumuladora de Al y Pb, mientras que *B. salicifolius* presentó un comportamiento excluidor mediante barreras radiculares eficaces. Por su parte, *N. ericoides* mostró niveles intermedios de transferencia supeditados a la disponibilidad del suelo. Finalmente, se determinó que la capacidad de intercambio catiónico, el pH y el contenido de materia orgánica son los controles geoquímicos principales de la movilidad metálica. Estos hallazgos permiten caracterizar los mecanismos de retención en un sistema impactado por la minería y aportan datos clave para la gestión de pasivos ambientales.

Palabras clave: elementos traza, metales de base, transferencia suelo-planta, meteorización

Transferência e distribuição de elementos-traço no sistema rocha-solo-planta: O caso de Mina La Oriental, Uruguai

Resumo

O estudo dos sistemas associados à atividade mineradora é fundamental para compreender a transferência de oligoelementos da litosfera para a biota. Esta pesquisa avaliou a origem e a disponibilidade de metais na área da Mina La Oriental, no Uruguai. Foram coletadas amostras de rochas, solos em escombreiras e sítios de controle, juntamente com espécimes de *Plantago brasiliensis*, *Nierembergia ericoides* e *Blepharocalyx salicifolius*. Os resultados sugerem que a elevada concentração de elementos-traço nos solos decorre dos materiais acumulados pela mineração de metais de base (Cu, Pb, Zn), com uma distribuição heterogênea na qual o Pb apresenta predominância litogênica associada a essas estruturas mineralizadas. Foram registrados fatores de enriquecimento extremos (EF > 40) em toda a área, superando a linha de base natural mesmo em pontos distantes das escombreiras. No que diz respeito à vegetação, a transferência foi regulada pela identidade da espécie: *P. brasiliensis* foi identificada como acumuladora de Al e Pb, enquanto B. salicifolius apresentou um comportamento de exclusão por meio de mecanismos de exclusão radicular eficazes. Por sua vez, *N. ericoides* apresentou níveis intermediários de transferência, dependentes da disponibilidade no solo. Por fim, determinou-se que a capacidade de troca catiônica, o pH e o teor de matéria orgânica são os principais controles geoquímicos da mobilidade dos metais. Essas descobertas permitem caracterizar os mecanismos de retenção em um sistema impactado pela mineração, fornecendo dados essenciais para a gestão de passivos ambientais.

Palavras-chave: elementos traço, metais de base, transferência solo-planta, meteorização

1. Introduction

Trace elements are those that occur in nature and are found in low concentrations (<100 mg/kg) in both plants and rocks. Soils contain the largest inventory of these elements, although their capacity to retain them is finite (Adriano, 1986). Consequently, the soil acts as a sink, performing regulatory and buffering functions (Davies, 1980).

Soil properties –including pH, organic matter, Fe/Al oxides, and redox potential– strongly influence trace element speciation and uptake, with cationic species (e.g., Cu, Pb, Zn, Cd) generally becoming more bioavailable under acidic conditions (Lambrechts et al., 2011; Zhou et al., 2018).

Vega et al. (2006) have determined that many of the soils that develop on waste rock dumps are physically, chemically, biologically, and mechanically deficient, as they are shallow, possess a no-equilibrated texture, and –due to the scarcity of soil organic matter– remain unstructured, while exhibit high acidity due to rapid and intense oxidation. This results in the leaching of large quantities of cations (Al^{3+}, Fe^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}), thereby creating an unfavorable environment for biological development. Furthermore, these materials are highly susceptible to wind and water erosion due to their low internal cohesion, making them potential sources of trace elements to the surrounding environment.

This study focuses on the historical La Oriental copper mine (Maldonado, Uruguay), which was active at various times between the 18th and 20th centuries. Historically, copper extraction at this site was carried out through underground mining, with the main tunnel measuring 360 m in length (1.80 m × 1.80 m, strike 75° NE; Bossi, 1978). The accumulated waste consists strictly of waste rock and gangue dumps, with no evidence of on-site industrial chemical processing. The mineralogical paragenesis consists of an assemblage dominated by pyrrhotite –with local alteration to pyrite and marcasite– accompanied by chalcopyrite, sphalerite, and fine-grained galena, hosted in a gangue of carbonates and quartzose to quartz-feldspathic fragments (Midot, 1984).

Geologically, the area is associated with the Mesoproterozoic Parque UTE Group, according to Chiglino et al. (2010) and Gaucher et al. (2014), as a low-grade metamorphosed volcanic-sedimentary sequence composed of metabasites, metarhyolites, and acidic metatuffs, dolomites, limestones, metamarls, and metapelites. This geological unit is significant for its associated mineral resources, including deposits of base metals containing Cu, Pb, Zn, and Ag (Bossi, 1978).

In Uruguay, studies of baseline trace element levels have been related to mining exploration and prospecting campaigns; the most notable being the Mining Inventory (Zeegers et al., 1982). As part of Uruguay's Geominero inventory, the cartographic data for the Fuente del Puma map sheet documents the presence of regional metal anomalies; however, no specific geochemical analyses or detailed characterizations have been published for La Oriental Mine in those official reports. Subsequent research (Oyhantçabal, 2004) in anomalous areas has reported discrepancies in element concentrations –such as Ba, P, Pb, and Cr– compared to those in the inventory, which were attributed to variations in sampling and digestion methods, as well as analytical error.

According to Castaño et al. (2011), the region's climate is classified as Cfa (humid temperate without a dry season) according to the Köppen-Geiger classification, with an average annual precipitation of 1,202 mm distributed evenly throughout the year and an average annual temperature of 17 °C (average maximum of 22 °C, average minimum of 12 °C).

The land cover in the immediate surroundings consists of natural grassland with spontaneous vegetation.

The hypotheses of this study suggest that soils developed on the Parque UTE Group contain trace element levels that exceed natural background values, due to secondary accumulation processes related to the weathering of mineralized zones and the dispersion of mine waste within the mining concession area. Specifically, soils within the surrounding area and waste rock dumps exhibit elevated levels of trace elements (Pb, Cd, Zn, Cu) compared to those from control sites, which represent undisturbed conditions developed on the same parent lithology and supporting the same target plant species as the waste rock dump area.

The overall objective is to characterize, from a geochemical perspective, the origin and behavior of trace elements (Pb, Zn, Cd, Cu, Cr, As) in soil and vegetation and their relationship with exposed geological units in the Mina La Oriental area, in the Department of Maldonado, Uruguay.

2. Materials and Methods

2.1 Experimental Design and Sampling

2.1.1 Sampling Strategy and Study Sites

Sampling was conducted across five established points (E1, E2, E3 on waste rock dumps, and C1, C2 as control sites; Figure 1). Control sites were selected on the same lithologic unit (Parque UTE Group) and natural grassland vegetation community, outside the influence of mine waste dispersion. At each point, paired samples of surface soil (0-20 cm depth), parent rock/waste rock, and dominant vegetation were collected.

2.1.2 Soil Samples

Composite soil samples were obtained at each of the five sampling points by combining five simple subsamples collected randomly. Sampling depth was restricted to the upper 0-20 cm. At the control sites, soils correspond to shallow profiles with lithic contact at this depth. At the waste rock dumps, the sampled "soil" corresponds to the upper layer of weathered fine-grained matrix formed directly over the coarse, fragmented waste rock material.

Samples were collected using shovels, which were cleaned between samples to prevent cross-contamination. They were then placed in sealed plastic bags, along with their respective UTM coordinates (Table 1).

The samples were dried in an oven at 70 °C for 24 hours, homogenized using a 2-mm sieve, and finely ground with an agate mortar to prevent contamination by metals.

2.1.3 Physical-Chemical Soil Analyses

All physical-chemical soil analyses were conducted at the Soil Laboratory of the Department of Soils and Water in the Faculty of Agronomy.

The pH of each sample was measured in water (Thomas, 1996; van Lierop, 1990) using a PHSJ-3F pH meter equipped with a COLE PALMER double-junction electrode (DJSE 3 Ft). For total carbon and nitrogen, the Dumas dry combustion method (Nelson & Sommers, 1996) was used on a VELP Scientifica CN 802 instrument. Extraction of Ca, Mg, K, and Na was performed using 1M ammonium acetate buffered to pH 7, and concentrations were determined by atomic absorption (Ca, Mg) and emission (K and Na) (Isaac & Kerber, 1971). For texture, the clay content (particles <2 µm) was measured using the hydrometer method (Forsythe, 1975) after removal of organic matter by oxidation with H_2O_2. The sand content was determined by sieving, and the silt content by difference.

To determine the concentrations of major, minor, and trace elements in soils, geochemical analyses were conducted at the international laboratory ActLabs (Canada). These analytical determinations included X-ray Fluorescence (XRF), used to quantify the weight percentage of major element oxides, and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), used primarily to determine the concentration in ppm (mg/kg) of minor and trace elements.

2.1.4 Rock and Waste Material Sampling

To characterize the geochemical baseline and waste rock matrix, representative rock samples were collected at points E1 and E3 (unprocessed coarse waste rock from the dumps) and at the two control sites (unaltered bedrock at the base of the soil profile). These samples were prepared in the Geology laboratories of the Department of Geosciences at CURE (Treinta y Tres campus), where coarse grinding was performed in a jaw crusher and fine grinding in a Retsch RS 200 mill, with particle size controlled using a Retsch AS 200 sieve shaker until a particle size of less than 125 µm was achieved, as required for the geochemical analyses performed at the ActLabs laboratory (Canada). Analytical determinations included XRF, used to quantify the weight percentage of major element oxides, and ICP-OES, used primarily to determine the concentration of minor and trace elements.

2.1.5 Plant Material Sampling

Specimens of the most abundant native plant species common to both control and waste dumpsites were collected: *Blepharocalyx salicifolius* (species 1), *Nierembergia ericoides* (species 2), and *Plantago brasiliensis* (species 3) (Figure 2). These samples were dried at 70 °C in an oven for 24 hours and were ground in an agate mortar before being sent for analysis.



Figure 1. Sampling area

Note. Prepared by María Magdalena Benítez Cardellino. *Source.* Google Satellite basemap, accessed through QuickMapServices. Map prepared using QGIS (version 3.40) and Inkscape (version 1.4).

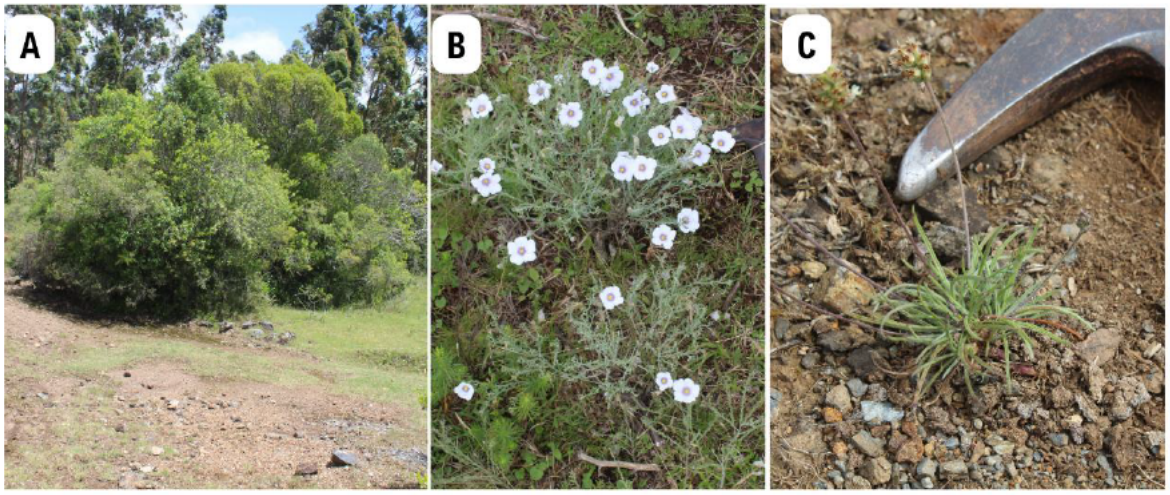

Figure 2. Plant species sampled at the study site: (A) *Blepharocalyx salicifolius*, (B) *Nierembergia ericoides*, and (C) *Plantago brasiliensis*

Table 1. Sampling locations for plants, soil, and rock

Point	CPx (m)	CPy (m)
Control 1 (C1)	660605	6175075
Control 2 (C2)	660561	6175075
Waste dump 1 (E1)	660553	6175113
Waste dump 2 (E2)	660555	6175114
Waste dump 3 (E3)	660588	6175128

2.2 Statistical Analysis

2.2.1 Calculation of the Normalized Transfer Factor (NTF)

The bioavailability and transfer of trace elements between the soil and the plant were evaluated using the Normalized Transfer Factor (NTF). This index applies the criterion of geochemical normalization using conservative elements as proposed by Reimann & de Caritat (2005), where variations in element concentrations due to differences in the sample matrix are corrected by normalizing the data to an immobile element. Zr was selected as the immobile reference element due to its resistance to weathering and geochemical alteration, in addition to having the lowest coefficient of variation (CV) compared to other normalizing elements (Al, Mn, Hf). Thus, the NTF was calculated as:

$$NTF = \left(\frac{CTE_plant}{CTE_soil}\right) / \left(\frac{CZr_plant}{CZr_soil}\right)$$

Where:

CTE _plant and CTE_soil correspond to the concentration of the trace element analyzed in plant tissue and soil (mg/kg dry weight), respectively; and CZr_plant and CZr_soil represent the concentrations of Zr in plant tissue and soil (mg/kg dry weight), respectively. Due to high data asymmetry spanning several orders of magnitude, values were logarithmically transformed (log 10) for variance stabilization and statistical comparison:

$$NTF(log) = log\ 10\ (NTF)$$

Interpretation of NTF (log) values is straightforward:

NTF(log) > 0 (corresponding to NTF > 1) indicates relative enrichment or preferential bioaccumulation of the trace element in plant tissue with respect to the geochemical soil baseline.

NTF(log) = 0 (corresponding to NTF = 1) indicates non-preferential transfer, equivalent to the geochemical background behavior of immobile Zr.

NTF(log) < 0 (corresponding to NTF < 1) reflects restriction of trace element transfer or exclusion mechanisms by the plant.

NTF(log) was used as the dependent variable in the correlation analyses.

2.2.2 Descriptive Statistics

The distribution of the NTF(log) variables and the soil's physicochemical properties was evaluated using descriptive statistics, including the calculation of the minimum, maximum, median, mean, and standard deviation to characterize the range and dispersion of the variables. Due to the geochemical nature of the samples and the presence of outliers, priority was given to using the median and the interquartile range (Q1 and Q3) to represent the central tendency and dispersion of the data.

2.2.3 Robust Statistical Correlation

Due to the heterogeneous nature of the soil samples and the presence of outliers that cause non-normal distributions in the geochemical data, Kendall's tau correlation coefficient (τ) was used as the primary nonparametric test. The τ coefficient was selected over Spearman's (ρ) and Pearson's coefficients due to its robustness, as τ is less sensitive to extreme values, and for methodological validation, as it allowed for the identification of genuine relationships. The τ test was applied to the full correlation matrix between the NTF(log) variables of each trace element and the soil's physicochemical properties. Only robust correlations validated by τ were considered in the discussion of results.

3. Results

3.1 Soil Properties and Origin of Trace Elements

The particle size distribution across the evaluated soils showed median values of 49% sand, 35% silt, and 15% clay in waste rock dump areas, compared with 46% sand, 33% silt, and 21% clay in control sites, with loamy to sandy loam textures prevailing across all locations. Organic matter content had a median of 4.5% (2.9-4.6%) in waste rock dumps and 7.8% (7.3-8.3%) in control sites. Soil pH was consistently acidic across all sampled areas, with median values of 5.10 (4.75-5.77) in waste rock dumps and 4.85 (4.62-5.07) in control sites. Cation exchange capacity (CEC) had a median of 10.52 cmol(+)/kg (8.83-10.72 cmol(+)/kg) in waste rock dump soils, which was lower than the value recorded in control areas (median: 13.03 cmol(+)/kg; 10.03-16.03 cmol(+)/kg) (Table 2).

Table 2. Descriptive statistics for the physicochemical properties of the soil and concentrations of trace elements in soil and rock

Parameter	Unit	Sample	Dump_n	Dump_Min	Dump_Max	Dump_Median	Control_n	Control_Min	Control_Max	Control_Median
pH	--	Soil	3	4.75	5.77	5.1	2	4.62	5.07	4.845
CEC	cmol(+)/kg	Soil	3	8.83	10.72	10.52	2	10.03	16.03	13.03
SB	cmol(+)/kg	Soil	3	2.59	5.71	5.24	2	3.53	10.82	7.175
OM	%	Soil	3	2.9	4.6	4.5	2	7.3	8.3	7.8
Sand	%	Soil	3	47	62	49	2	46	47	46.5
Silt	%	Soil	3	28	38	35	2	32	34	33
Clay	%	Soil	3	10	16	15	2	19	23	21
S	%	Soil	3	< 0.25	< 0.25	< 0.25	2	< 0.25	< 0.25	< 0.25
P	mg/kg	Soil	3	440	650	620	2	470	630	550
V	mg/kg	Soil	3	46	52	48	2	38	64	51
Cr	mg/kg	Soil	3	41	43	41	2	36	63	49.5
Co	mg/kg	Soil	3	22.7	74.8	24.4	2	18.3	26.3	22.3
Ni	mg/kg	Soil	3	20.1	22.5	21.6	2	21.5	28.8	25.15
Cu	mg/kg	Soil	3	2360	9130	2530	2	423	529	476
Zn	mg/kg	Soil	3	2140	5000	2610	2	436	1460	948
As	mg/kg	Soil	3	6.6	13.8	8	2	3.6	7	5.3
Rb	mg/kg	Soil	3	28.1	40.5	37.1	2	14.6	29.4	22
Sr	mg/kg	Soil	3	10.6	14.8	13	2	10.2	16.7	13.45
Ba	mg/kg	Soil	3	67.8	94.4	91.1	2	45.4	109	77.2
Pb	mg/kg	Soil	3	373	1140	434	2	33.1	128	80.55
Th	mg/kg	Soil	3	2.6	4.2	3.5	2	3.8	5.2	4.5
U	mg/kg	Soil	3	0.7	0.9	0.8	2	0.5	0.7	0.6
S	%	Rock	2	ND	ND	ND	2	ND	ND	ND
V	mg/kg	Rock	2	67	79	73	2	89	97	93
Cr	mg/kg	Rock	2	70	80	75	2	100	140	120
Co	mg/kg	Rock	2	36	45	40.5	2	18	22	20
Ni	mg/kg	Rock	2	20	20	20	2	30	40	35
Cu	mg/kg	Rock	2	3190	10000	6595	2	60	180	120
Zn	mg/kg	Rock	2	3130	10000	6565	2	620	1040	830
As	mg/kg	Rock	2	5	18	11.5	2	5	5	5
Rb	mg/kg	Rock	2	9	27	18	2	11	12	11.5
Sr	mg/kg	Rock	2	32	47	39.5	2	3	8	5.5
Ba	mg/kg	Rock	2	47	101	74	2	11	62	36.5
Pb	mg/kg	Rock	2	2270	2600	2435	2	5	14	9.5
Th	mg/kg	Rock	2	4.95	9.52	7.235	2	5.26	14.1	9.68
U	mg/kg	Rock	2	1.73	2.05	1.89	2	1.31	2.33	1.82

CEC: Cation exchange capacity; SB: Sum of bases; OM: Organic matter

Figures 3a, 3b, and 3c illustrate the vertical distribution of Pb, Zn, and Cu concentrations in the rock-soil-plant sequence, with the soil pH value overlaid for each site. A pattern where soil concentration exceeds rock concentrations (Soil>Rock) is observed at sites E1 and E3.

Transfer to plants exhibits contrasting behavior depending on the element: Pb shows higher relative accumulation in plant tissue at lower pH values (Figure 3a), whereas Zn and Cu concentrations in plants remain elevated across all sites regardless of local pH variations (Figures 3b y 3c).

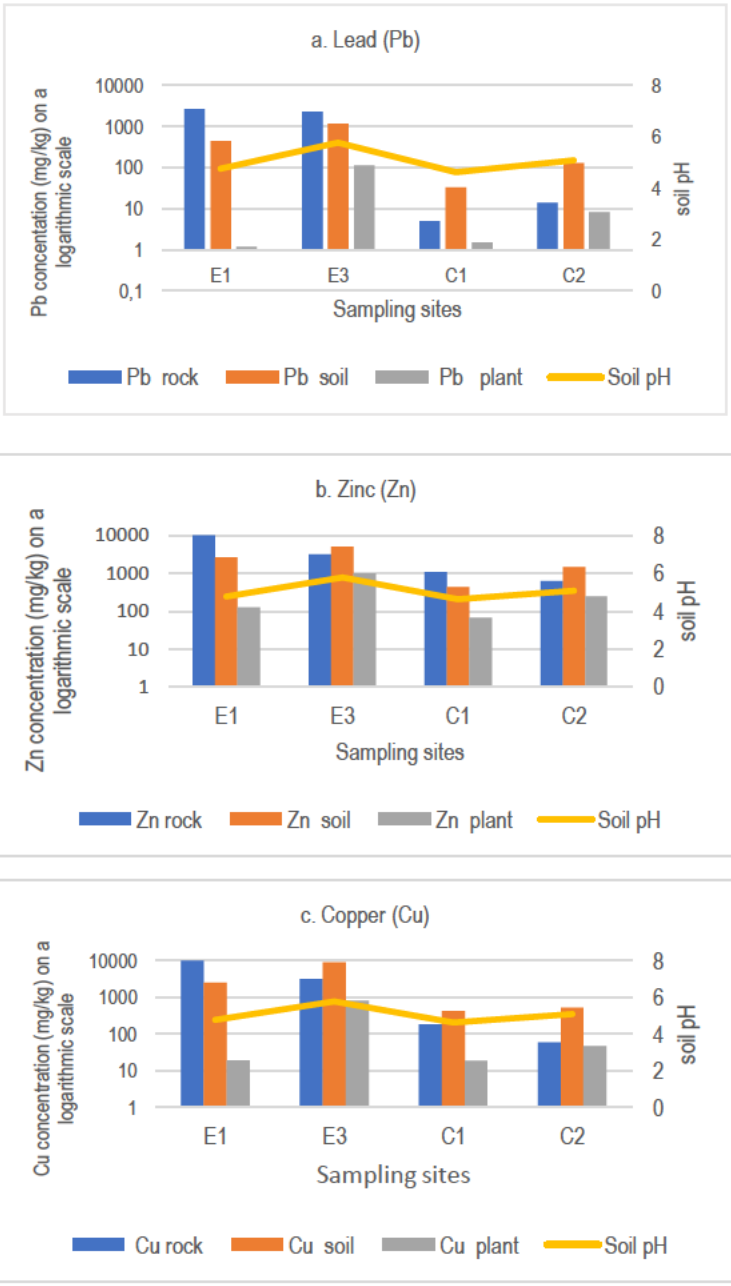

Figure 3. Vertical distribution of lead (Pb), zinc (Zn), and copper (Cu) at the rock-soil-plant interface and their relationship to soil pH, by sampling site

Bars represent individual profile observations (n = 1 per site). Note the logarithmic concentration scale.

To distinguish the origin of the elements concentrations and distinguish between geogenic and external contributions, the enrichment factor (EF) was calculated. This was determined by comparing the ratio of the concentration of each trace element (TE) to Zr in the soil with the corresponding ratio in the locally analyzed bedrock (geochemical background). Zr was used as the normalizing element because of its low mobility and conservative nature in the exogenic environment. The choice of Zr as the normalizing element was based on its lower coefficient of variation compared with those of other commonly used elements (Al, Mn, Rb, Hf; Barbieri, 2016).

The enrichment factor (EF) was calculated using the equation below:

$$EF = \frac{\left(\frac{TE}{Zr}\right) soil}{\left(\frac{TE}{Zr}\right) rock}$$

where *(TE/Zr) soil* represents the ratio of the trace element to the normalizing element in the soil, and *(TE/Zr) rock* represents that ratio in the locally analyzed bedrock.

The application of the EF allowed for the quantification of soil matrix alteration relative to its parental material. Zirconium (Zr) was used as the normalizer due to its statistical stability (lower CV recorded compared with Al, Mn, and Hf) and its conservative nature. By normalizing to Zr, the EF compensates for mass variations during soil formation, establishing a lithological baseline. Thus, the EF identifies enrichments that exceed this baseline, allowing for the quantification of external inputs to the system, regardless of their incorporation mechanism (Turhan, 2020).

To distinguish the origin of the elements, the criterion proposed by Zhang and Liu (2002) was adopted, which states that EF values in the range of 0.5 to 1.5 suggest a predominantly lithogenic or crustal origin. In contrast, an EF > 1.5 indicates that a significant fraction of the trace elements comes from non-cortical sources, such as anthropogenic inputs. As can be seen in Figure 4, the obtained values consistently fall above this threshold, allowing for the identification of a clear influence of external inputs on the baseline soil composition at the analyzed sites.

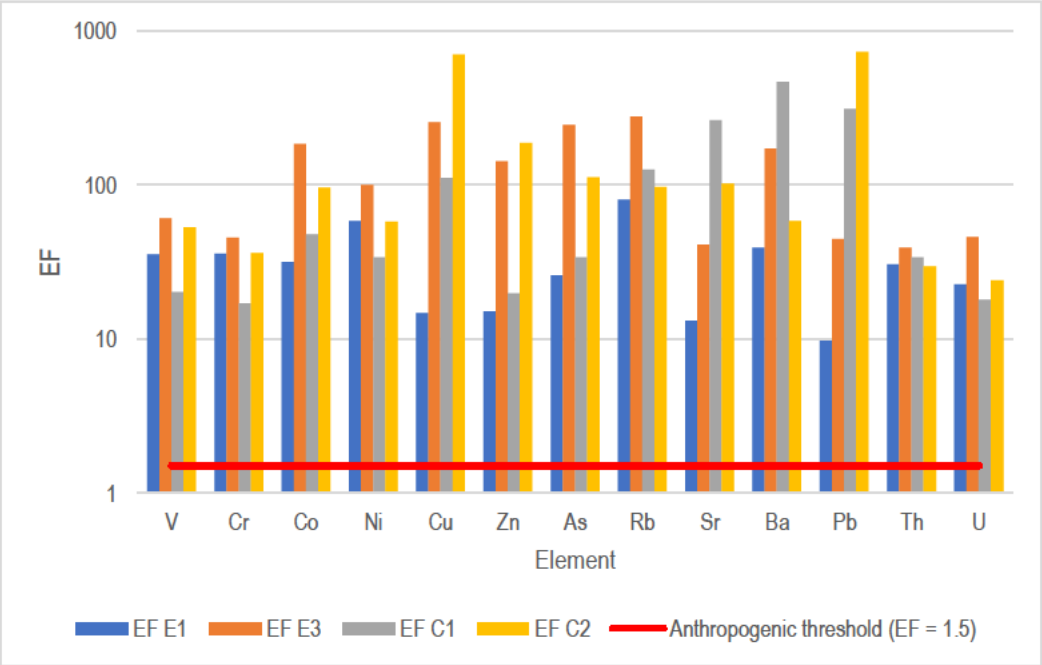

Figure 4. Enrichment factor (EF) by element and by site, normalized to zirconium (Zr)

The EF values are plotted on a logarithmic scale to facilitate the visualization of anomalies.

3.2 Mobility of Elements at the Soil-Plant Interface

To quantify the mobility of trace elements from soil to plants, the Logarithmic Normalized Transfer Coefficient (NTF log) was calculated according to the following equation:

NTF log = log10 (C plant/C soil)

Where C plant and C soil represent the trace element concentration (mg/kg) in plant tissues and soil, respectively. Values to NTFlog > 0 indicate an active accumulation or preferential transfer of the element to plant tissues (C plant > C soil), whereas values of NTFlog < 0 reflect restricted elemental uptake or exclusion mechanisms by the plant (C plant < C soil). The statistical results for this coefficient are presented in Table 3.

Table 3. Descriptive statistics for NTFlog for the trace elements analyzed

	Minimum	Maximum	Median	Mean	SD	Q1	Q3
NTF(log) V	−1.330	−0.690	−1.226	−1.066	0.296	−1.304	−0.747
NTF(log)Cr	−1.210	−0.768	−1.166	−1.044	0.252	−1.255	−0.773
NTF(log)Mn	−1.080	−0.194	−0.609	−0.628	0.331	−0.926	−0.340
NTF (log)Fe	−2.100	−0.997	−1.655	−1.543	0.454	−1.947	−1.084
NTF (log)Co	−2.040	−0.877	−1.370	−1.360	0.463	−1.778	−0.936
NTF (log)Al	−1.960	−0.419	−1.412	−1.329	0.630	−1.898	−0.718
NTF(log)Cu	−1.780	−0.485	−0.692	−0.990	0.570	−1.591	−0.538
NTF (log)Zn	−0.970	−0.020	−0.342	−0.470	0.401	−0.887	−0.117
NTF (log)Pb	−2.250	−0.610	−1.279	−1.245	0.675	−1.847	−0.627
NTF (log)B	0.790	1.680	1.177	1.269	0.349	0.977	1.608
NTF(log)As	−0.560	0.820	−0.071	0.066	0.559	−0.428	0.629
NTF (log)Ni	−0.280	0.140	−0.188	−0.154	0.173	−0.274	−0.018
NTF(log)Th	−1.800	−0.480	−1.258	−1.237	0.509	−1.691	−0.771
NTF (log)U	−1.710	−0.530	−1.319	−1.222	0.494	−1.668	−0.728
NTF (log)Rb	−0.730	0.270	−0.090	−0.203	0.389	−0.582	0.119
NTF (log)Sr	0.520	1.450	1.057	0.991	0.343	0.677	1.271
NTF (log)Ba	−0.040	1.030	0.431	0.442	0.415	0.065	0.824

Considering the results obtained, transfer was generally low for most elements, as evidenced by the consistently negative NTFlog values, indicating that the concentration of these elements in the soil is higher than that observed in the plant. However, certain differences in the magnitude of transfer were observed, as described below.

Three elements showed positive NTFlog medians, indicating that their concentration in plant tissue was, on average, higher than the concentration in the underlying soil. The elements with this characteristic are Ba (median = +0.43092083), Sr (median = +1.05749055), and B (median = +1.17705529). The next elements with the highest transfer (least negative median values) were Zn (median = −0.34243426), As (median = −0.07135591), and Rb (median = −0.08994684), followed by Mn (median = −0.60876409) and Cu (median = −0.69212686). In contrast, Fe, Al, and Co showed the lowest transfer, with the lowest FTNlog medians (−1.65493249, −1.41151282, and −1.37035649, respectively).

3.3 Geochemical Control of Transfer

To identify the geochemical factors that determine the transfer observed in Section 3.2, the correlation between the median NTFlog values of trace elements and soil properties (Table 2) was evaluated using Kendall's correlation coefficient τ (Table 4). These results showed that mobility is controlled by a complex interaction between retention capacity (cation exchange capacity and clay content) and organic matter.

With regard to soil pH, no negative correlations were observed between this property and cation transfer, which is typically associated with acidic soils. However, the presence of positive correlations suggests that, in this case, an increase in pH toward more neutral values may be promoting the mobility of certain elements. This could indicate that acidity is not the factor that triggers transfer, but rather that other mechanisms (cationic competition or saturation of sites in the CEC) become more important as pH rises.

Table 4. Kendall's τ correlations for soil properties and NTFlog values of trace elements

Soil properties	Pb	Co	Cu	Cr	V	Mn	Zn	Fe	Al	Ni	As	B	Th	U	Rb	Sr	Ba
CEC	−0.6	−0.6	−0.2	−0.2	−0.4	0	0	−0.2	0	0.2	0	−0.2	0	0.4	−0.2	−0.2	0
pH	0.4	0	0	0.2	0.4	0	0.2	0.2	0.4	0.4	0.2	0.4	0	0.6	0.2	0	0.2
%OM	−0.2	0.2	0.4	−0.4	−0.2	0	0.2	−0.4	−0.6	0.2	0.4	0.4	0	0.4	−0.4	−0.2	−0.4
SB	0.2	0.2	0.2	0.4	0.2	0.2	0.2	0.2	0.4	0.2	0.2	−0.2	0.2	0.2	0	0.2	0.4
Clay	−0.60	−0.6	−0.2	0	−0.2	0	0	−0.2	−0.4	−0.4	−0.4	−0.2	−0.2	−0.2	−0.4	−0.4	−0.4
Silt	−0.20	−0.2	0	0	0	0.2	0	−0.2	0	0	0	0	−0.2	0	0	0	0
Sand	0.40	0.4	0	0	0	0.2	0	0.4	0.2	0.4	0.4	0.2	0.4	0.2	0.2	0.4	0.4
%Fe	0.80	0.6	0	0.8	0.8	0.2	0	0.6	0.2	−0.6	−0.8	−0.8	0.8	0.8	0	−0.6	−0.6
%Al	0.00	0.4	0.6	0	0	0.2	0.6	0.4	0.4	0.2	0.2	0.4	0	0	0	0.4	0.4
%P	0.40	0.2	−0.4	0.2	0.2	0	−0.4	0.6	0.2	−0.6	−0.4	−0.4	0.2	0.2	0	−0.4	−0.4

CEC: cationic exchange capacity; SB: sum of bases; OM: organic matter.



Values represent Kendall rank correlation coefficients (τ), calculated using individual sample pairs across all sampling points (N = 5). Total sulfur (S) was excluded from the matrix due to zero variance across all sites (<0.25%).

Cation exchange capacity (CEC) showed a strong negative correlation (τ = -0.60) with the transfer factors of Pb and Co. While a high CEC represents a dynamic reservoir for nutrient exchange (soil fertility), it also acts as a main retention sink for heavy metals. The high availability of negatively charged sites on clays and organic matter binds metal cations tightly, reducing their concentration in the soil solution and consequently limiting plant uptake. For elements such as Mn, Zn, As, Th, and Ba (τ = 0.00), mobility is independent of CEC and likely governed by precipitation or sorption onto Fe/Al oxides.

Soil organic matter (OM) exhibited a distinct dual effect on trace element transfer from soil to plants, heavily regulated by soil pH. A negative correlation with transfer factors was observed for Pb, Cr, V, Fe, Al, Rb, and Ba, indicating that at the prevailing soil pH, OM acts predominantly as an immobilizing sink through precipitation and retention within the humic fraction. Conversely, OM correlated positively with Co, Cu, Zn, Ni, As, B, and U. Under the specific pH conditions of these soils, this positive association is driven by the formation of soluble organo-metallic complexes that facilitate element availability and uptake by plants.

Finally, soil texture analysis revealed a negative correlation between clay content and the majority of the elements analyzed (Pb, Co, Cu, V, Fe, Al, Ni, As, B, Th, U, Rb, Sr, and Ba). This result is highly consistent with the pattern observed for the CEC and suggests that clay particles are providing the most effective adsorption and retention sites for the immobilization of these elements. It is important to note that the correlation was zero for Cr, Mn, and Zn, indicating that their mobility is independent of the clay content.

4. Discussion

To evaluate trace element dynamics, key elements were selected based on their relative abundance across the individual sampling sites (Table 2) and their distribution in the surface layer (0-20 cm). Control sites and waste rock dump sites are evaluated as independent geochemical units to capture site-specific baseline conditions and potential anthropogenic impacts. These surface distribution patterns reveal distinct trends in element mobility, governed primarily by localized soil properties and site-specific conditions.

4.1 Analysis of the Rock-Soil-Plant Transfer Pathway and Effect of pH

4.1.1 Lead

As shown in Figure 3a, at the waste dump sites (E1 and E3), the concentration of Pb is higher in the rock compared to the soil. This phenomenon is due to the fact that the element comes directly from the parental material (geogenic origin), transferring a direct geochemical inheritance from the bedrock to the soil matrix. According to the conventional pattern in pedogenesis (McBride, 1994), Pb tends to concentrate in the soil relative to the bedrock, due to its low mobility and high affinity for organic matter. Added to this retention mechanism is the influence of phosphorus (P) present in the soil. The P contents recorded in the soils (470-650 mg/kg) are consistent with the ranges reported by Cotter-Howells (1996) for promoting the precipitation of insoluble Pb phosphates. This mineralogical stability could enhance the immobilization of the element, limiting its availability to vegetation, even under acidic pH conditions.

However, this pattern is reversed at the waste rock dump sites. This discrepancy suggests that the system is under the influence of primary mineralization, whose geogenic input into the bedrock exceeds, thus far, the accumulation capacity of soil-forming processes. In contrast, control sites (C1 and C2) show higher Pb concentrations in topsoil than in bedrock. This is consistent with the conventional pedogenic pattern described by McBride (1994), which is characterized by surface enrichment of Pb relative to bedrock due to its low geochemical mobility and strong retention by organic matter in the upper soil horizons. Given the steep topography of

these control sites and the absence of agricultural management, this surface retention appears to be driven primarily by natural pedogenic processes and interactions with organic matter.

At waste rock dump sites, lower pH values are recorded, a condition that generally increases the solubility and potential bioavailability of the element in the soil solution (Zhou et al., 2018). However, analysis of the plant phase shows that this potential mobility does not translate into widespread uptake across all studied species. Regarding transfer to plant material, Figure 3a shows that the Pb concentration in *Blepharocalyx salicifolius* (E1 and C1) behaves similarly at both sites, despite the markedly higher soil Pb concentration at E1. This observation aligns with the findings of Kabata-Pendias (2011), who described root cell wall retention as a general physiological exclusion mechanism in plants, where Pb is bound in root tissues, thereby limiting its movement to aerial parts. In contrast, *Plantago brasiliensis* at E3 exhibits a higher Pb concentration, which suggests –as noted by Bekteshi and Bara (2013) and Levei et al. (2018)– that this species may possess specific tolerance mechanisms to soils with elevated metal concentrations. Finally, *Nierembergia ericoides* (C2) displays a slight increase in Pb concentration compared to C1, supporting the concept that species-specific physiology plays a key role in governing element transfer, interacting alongside soil physicochemical properties.

4.1.2 Zinc

At sites E1 and C1, the concentration of Zn in the bedrock is higher than in the overlying soil (Figure 3b). Unlike immobile elements that readily accumulate in topsoils, Zn distribution is strongly governed by parent material composition and its relative geochemical mobility during weathering, making it susceptible to leaching under acidic conditions (Kabata-Pendias, 2011). Thus, the higher bedrock values at E1 and C1 likely reflect local lithological inputs combined with elemental mobility in the upper soil profile. In contrast, at sites E3 and C2, Zn concentration in the soil exceeds that of the underlying bedrock, which aligns with typical topsoil retention mediated by organic matter binding and clay adsorption in less acidic environments (Kabata-Pendias, 2011; McBride, 1994).

Regarding the plant phase, Zn exhibits a notably more active transfer dynamic toward the aboveground tissues compared to Pb, consistent with its physiological role as an essential micronutrient. The highest accumulation in plant was recorded in *Plantago brasiliensis* at site E3, co-occurring with the highest soil Zn concentration and a moderately less acidic soil pH, which may favor plant availability without triggering physiological toxicity thresholds. Although Zn is generally more soluble at low pH, it has been reported that its availability can be influenced by the formation of complexes with organic matter within certain acidity ranges (Kabata-Pendias, 2011).

A comparison between E1 and C1 (*Blepharocalyx salicifolius*) suggests that the plant regulates its uptake regardless of the metal concentration in the soil. Although the soil at E1 has a higher Zn concentration than that at C1, the levels in plant tissues are similar at both sites. This behavior indicates that species identity, metabolic regulation, and specific nutrient requirements act as determining factors in bioaccumulation (Bekteshi & Bara, 2013; Marschner, 2012).

4.1.3 Copper

As for Cu (Figure 3c), point E1 follows the pattern observed for the previous elements, where the concentration in the rock is higher than that in the soil. This relationship indicates incipient pedogenesis, in which the inheritance of parental material predominates over secondary accumulation processes (Huot et al., 2015). However, at points E3, C1, and C2, a change in trend is observed: the soil shows enrichment relative to the bedrock, consistent with conventional pedogenesis processes (McBride, 1994). At points C1 and C2, the high organic matter content (7.9% and 8.3%) acts as the primary retention factor. Copper is known to have a strong affinity for organic colloids, with soil organic matter frequently reported as the main driver for Cu retention in surface horizons through stable complexation mechanisms (Oorts, 2013). In contrast, at E1, the higher acidity recorded

(pH 4.75) compared with the other points on the waste dump, combined with the substrate instability, favors metal mobilization. This localized acidity can promote Cu desorption into the soil solution (Oorts, 2013), while high water erosion rates and the continuous removal of fine particles prevent profile maturation and impair the overall retention capacity of the matrix (Huot et al., 2015; Kabata-Pendias, 2011).

Regarding vegetation, the marked increase in Cu in E3 (*Plantago brasiliensis*) suggests high phytoavailability of the metal at this site, given that Cu availability is not a function of its total concentration but rather of its chemical speciation, which is controlled by pH and organic matter (Kabata-Pendias, 2011). At this point, the less acidic pH (5.77) favors the formation of soluble organic complexes with dissolved organic matter (DOM), which has a high affinity for Cu and inhibits its sorption onto the soil solid matrix (Kabata-Pendias, 2011; McBride, 1994). These mobile complexes facilitate the migration of the metal toward the root and its subsequent absorption (McBride, 1994). Likewise, this pH closer to neutrality optimizes the activity of root transporters by reducing physiological stress caused by extreme acidity (Marschner, 2012). Conversely, at points C1 and C2, the high levels of organic matter (7.9% and 8.3%) favor the retention of the metal in the solid phase of the soil. The formation of highly stable, low-lability organic complexes in the soil matrix restricts the solubility of Cu (McBride, 1994), which explains the limited transfer to plant tissues despite its abundance in the soil (Kabata-Pendias, 2011).

Finally, at E1 and C1 (*Blepharocalyx salicifolius*), low uptake persists regardless of soil concentration –a pattern also observed for other metals in the same species–, reinforcing the hypothesis of strict metabolic control by the plant (Marschner, 2012).

4.2 Enrichment Factor (EF) Analysis

Given the direct association between the sampling points and the plant species studied, the EF analysis was conducted on a site-by-site basis to illustrate environmental heterogeneity (Figure 4). Based on the classification proposed by Sutherland (2000) and validated by Barbieri (2016) and Loska and Wiechula (2003), two main patterns emerged:

There is a contrast in the levels of V and Cr, as these elements show a notable variation among the evaluated points. While at C1 the values are moderate (EF V = 20.07 and EF Cr = 16.92), at points such as E3 the values increase to 60.81 for V and 45.39 for Cr. According to Sutherland's scale (2000), this places them in the extremely high enrichment category (EF > 40) at this specific point. This variation suggests that, on a regional geogenic basis, there are localized areas where exogenous accumulation exceeds the local background (Barbieri, 2016).

Regarding Pb, Cu, and Zn, the results show that, regardless of the sampling site, these metals have EF values that far exceed the threshold of 40 proposed by Sutherland (2000), with peak values of 731.4 for Pb, 705.3 for Cu, and 188.4 for Zn at site C2. Although the mining nature of the area explains the presence of these elements, the high EF values allow the quantification of the degree of enrichment above bedrock levels. This constant magnitude indicates a dispersion of extracted materials that has homogenized surface enrichment, exceeding the soil's natural buffering capacity (Barbieri, 2016; Loska & Wiechula, 2003; Sutherland, 2000).

4.3 Analysis of Element Mobility at the Soil-Plant Interface

To evaluate the ability of vegetation to transfer metals from the soil to its aboveground tissues, the logarithmic normalized transfer factors (NTFlog) presented in Table 3 were analyzed. According to Baker's (1981) criteria, the values for Fe and Co suggest that plants may be acting as excluders, maintaining low concentrations of these elements in their leaves regardless of their levels in the soil. In the case of Fe, this restriction is due to root immobilization mechanisms and selective control of internal transport, processes that ensure the protection of

aerial tissues against concentrations that could be harmful (Kabata-Pendias, 2011; Krämer, 2010). Likewise, the low transfer of Co reinforces this defense mechanism, whereby the plant prioritizes maintaining its vitality by limiting the passage of metals to the leaves (Krämer, 2010). This behavior is characteristic of species adapted to substrates with high metal content, where survival depends on the plant's ability to establish effective barriers against the uptake of these elements (Krämer, 2010).

However, the behavior of Al was exceptional in *Plantago brasiliensis* (site E3). While the other species showed marked exclusion (NTFlog values close to −2), *P. brasiliensis* reached an NTFlog value of −0.41, representing superior transfer efficiency. According to Baker's (1981) criteria, this indicates that this species acts as an accumulator, capable of transferring and concentrating high levels of the metal in its aboveground parts. This behavior results in foliar Al concentrations of 5,240 mg/kg. By exceeding the threshold of 1,000 mg/kg proposed by Jansen et al. (2002), the species is classified as a metal accumulator, demonstrating a remarkable capacity to integrate this element into its tissues. The restriction of this species to areas with soil overlying waste rock dumps reinforces its status as a facultative accumulator, according to the criteria of Pollard et al. (2014), suggesting a specific adaptation that enables it to colonize these environments by overcoming the exclusion barriers that limit other species (Krämer, 2010).

4.4 Analysis of the Geochemical Control of Transfer

To identify the edaphic factors that regulate the transfer of trace elements, Kendall correlations analyses were performed using the median of the normalized transfer factors (NTFlog) for each element per site. This approach integrates the plant community's response and highlights the primary geochemical control, minimizing individual biological variability and focusing on the partitioning of metals between the solid phase and the soil solution.

4.4.1 Transfer Dynamics of Pb and Co: Relationship with Cation Exchange Capacity

The transfer dynamics of Pb and Co are strongly regulated by the retention capacity of the soil matrix. A marked negative correlation ($\tau = -0.6$) was observed between CEC and the median of NTFlog, suggesting that the transfer of metals from the soil to the leaves increases when exchange sites are scarce. This inverse relationship demonstrates that, as the density of negative charges in the colloidal fraction decreases (as occurs at site E3), the activity of metals in the solution increases, along with their consequent availability to vegetation (Kabata-Pendias, 2011). As Alloway (2013) points out, when the concentration of a heavy metal exceeds the soil's sorption capacity, the geochemical sink function becomes saturated, favoring direct transfer to the biota.

4.4.2 The Role of Organic Matter: Adsorption vs. Mobility in Solution

With regard to organic matter (OM), the results reveal a dual behavior at the system level. For elements such as Al ($\tau = -0.6$), Cr, and Fe ($\tau = -0.4$), the negative correlation with the median NTFlog indicates that OM acts predominantly as a sink, immobilizing these elements in the solid phase through the formation of stable complexes. Conversely, the positive correlations detected for Cu and U ($\tau = 0.4$) suggest that OM promotes overall mobility of these elements in the study area. This phenomenon is associated with the "carrier effect" described by McBride (1994): although certain metals have a high intrinsic affinity for OM, the formation of dissolved organometallic complexes (mainly associated with fulvic acids) increases their total solubility. According to Weng et al. (2002), dissolved organic matter (DOM) competes for the adsorption sites in the soil matrix, keeping the metal in the soil solution and facilitating its mass transport to the roots. The use of the median of NTFlog confirms that this solubilization process is a determining factor that increases the geochemical supply for the plant community as a whole.

4.4.3 Influence of pH on Systemic Transfer

Soil pH emerges as a relevant factor in the mobilization of various elements, although through different geochemical mechanisms. Positive correlations were observed for Al, Pb, V, and B ($\tau = 0.4$), with a more pronounced relationship noted for U ($\tau = 0.6$).

In the case of Uranium (U), pH acts as a critical regulator of its speciation. Although the oxidation-reduction potential (Eh) is the primary determinant of this element's mobility by controlling its oxidation state and solubility, in the absence of direct Eh measurements, pH allows for an approximation of its geochemical behavior. According to Alloway (2013), the most soluble and available form (uranyl cation) increases its mobility as pH moves away from extreme acidity toward neutrality, a range in which soluble complexes stabilize. For boron (B), the positive correlation suggests an increase in its availability within the studied pH range. Kabata-Pendias (2011) indicates that, in acidic soils, organic matter and Fe and Al oxides act as the main retention sites for this element. A slight increase in pH toward neutrality favors the release of B from the organic fraction or alters its adsorption equilibrium, thereby facilitating its systemic transfer.

Meanwhile, the mobility of vanadium (V) is explained by its predominant chemical form as an anion (vanadate). As pH increases, the adsorption capacity of soil colloids for anions decreases, thereby facilitating its release into solution (Madejón, 2013). As for lead (Pb), its positive correlation suggests mobility mediated by the formation of organometallic complexes. According to Steinnes (2013), in soils with high organic matter content, a major fraction of dissolved Pb is associated with organic ligands. A slight increase in pH within the acidic range facilitates the solubility of these complexes, thereby promoting their uptake by plants.

Finally, the absence of correlation for elements such as Cu, Co, and Th ($\tau = 0$) confirms that their transfer is primarily regulated by other edaphic parameters. In the specific case of copper (Cu), its strong affinity for organic matter is a factor that predominates over the pH variations recorded in the study area, maintaining its availability at an equilibrium that is independent of acidity (Weng et al., 2002).

4.4.4 Influence of Major Soil Constituents (Fe, Al and P) on Transfer Dynamics

To explore potential interactions between major soil constituents and element mobility, total contents of Fe, Al, and P were incorporated into the correlation analysis. Total sulfur (S) was excluded from statistical evaluations as concentrations remained consistently below the analytical detection limit (<0.25%).

Correlations observed for soil Fe and Al suggest distinct geochemical trends within the studied substrates. As documented by Basta et al. (2005), Fe and Al oxides act as key immobilizing phases via surface complexation and adsorption, which is consistent with the negative correlations recorded in this study for elements such as As and B. Conversely, the positive correlations observed for elements like Pb, Cr, and V could suggest spatial co-occurrence in the mine impacted substrate, where site-specific baseline concentrations in the solid phase might influence total element abundance.

The relationships observed with P align with chemical retention and rhizosphere pathways described by Basta et al. (2005). Specifically, negative correlations between soil P and Ni, Cu, and Zn may suggest immobilization mechanisms whereby the evaluated phosphate availability could favor low-solubility metal-phosphate species or enhance competitive sorption. Meanwhile, the positive correlation between P and Fe transfer may be associated with rhizosphere dynamics, where root-induced chemical changes during nutrient uptake could indirectly facilitate iron solubilization and plant uptake in these environments.

5. Conclusions

The concentration of trace elements in the soils of the Mina La Oriental area derives from materials accumulated as a result of base metal mining (Cu, Pb, Zn), although their distribution is heterogeneous. Geochemical evidence indicates that at the waste dump sites, the Pb concentration in the parental material predominates over that in the soil, whereas for Zn and Cu this relationship is only evident at point E1. At the remaining evaluated sites, soil concentrations of Zn and Cu exceed those in the rock, indicating the predominance of surface accumulation processes.

Soils associated with the waste rock dump exhibit higher levels of Pb, Zn, and Cu than the control sites. However, the enrichment factor (EF > 40) showed extremely high values across all sampled points, indicating that metal enrichment in the study area exceeds the site's natural baseline, even at points far from the waste rock deposits. Regarding vegetation, transfer is regulated by plant species identity: *Plantago brasiliensis* was identified as an accumulator (especially of Al and Pb) capable of colonizing mine deposits, unlike *Blepharocalyx salicifolius*, which exhibits exclusionary behavior.

Finally, the transfer of elements is governed by three main geochemical factors: cation exchange capacity (CEC), pH, and organic matter. CEC showed an inverse correlation with the transfer of Pb and Co, suggesting that a shortage of exchange sites favors the availability of these metals to biota. Likewise, pH acted as the main controlling factor for the transfer of V and U, while organic matter conditioned the mobility of Cu and Pb, acting either as a soil retainer or as a facilitator of their uptake by plants, depending on the partitioning between the solid phase and the solution.

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Transparency of Data

Available data: The entire data set that supports the results of this study was published in the article itself.

Author Contribution Statement

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Conceptualization	■	■	■
Formal analysis	■	■	
Investigation	■	■	■
Methodology	■	■	■
Supervision		■	■
Writing – original draft	■		
Writing – review and editing	■	■	■

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