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Elemental Composition of *Ilex paraguariensis* Grown in the Brazil–Paraguay Border Region

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Abstract

The mineral composition of *Ilex paraguariensis* is strongly shaped by the physicochemical characteristics and natural fertility of the soils in which it is cultivated. This study evaluated macro- and microelement concentrations in fresh leaves from fourteen rural properties in Mato Grosso do Sul, Brazil, and examined how soil texture, pH, organic matter content, cation exchange capacity (CEC), and aluminum saturation influence nutrient availability and foliar accumulation. Soil, leaf, and environmental data were analyzed using ANOVA, intraclass correlation coefficients, Bayes factors, and principal component analysis (PCA). Sandy and dystrophic soils with low CEC and reduced organic matter showed greater variability in micronutrient retention and favored leaching, resulting in higher fluctuations in foliar Cu, Zn, and Mn. In contrast, clayey eutrophic soils with high CEC and higher organic matter promoted greater nutrient stability and more homogeneous foliar concentrations of K, Mg, and P. PCA confirmed that differences in soil geochemistry, particularly in Se, Cr, Mn, and Zn availability, were reflected in leaf composition. Chromium remained low in leaves despite elevated soil levels, indicating restricted uptake and translocation. Overall, the results demonstrate that edaphic conditions govern the nutritional profile of *I. paraguariensis*, emphasizing the need for region-specific soil management to maintain leaf quality in emerging cultivation areas.

Keywords: yerba mate; mineral composition; soil–plant relationships; Brazil–Paraguay border region

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1. Introduction

Ilex paraguariensis A. St.-Hil., commonly known as yerba mate, is a native arboreal species of South America, widely cultivated in Brazil, Argentina, and Paraguay, where its consumption is deeply rooted in traditional cultural practices [1,2]. In Brazil, yerba mate production is predominantly concentrated in the Southern Region, with well-established commercial-scale cultivation systems in Santa Catarina, Paraná, and Rio Grande do Sul. By contrast, in the border region of Mato Grosso do Sul, cultivation remains limited in scale and is predominantly carried out by smallholder producers under low-input management systems, frequently embedded within traditional or subsistence-based agroecosystems [3–5]. In the Brazil–Paraguay border region, yerba mate plays a relevant socioeconomic role at the local level; nevertheless, growing interest from international

markets in yerba mate–derived products has been observed, driven by their distinctive chemical profile and recognized functional properties [6].

In addition to bioactive compounds such as polyphenols, saponins, and xanthines [7–10], the mineral composition of yerba mate has attracted increasing interest due to its potential contribution to the dietary intake of essential macro- and micronutrients important for human health. Several studies have investigated the mineral composition of *I. paraguariensis*, demonstrating that the elemental profile of this species is influenced by edaphic, climatic, genetic, and management-related factors. Research conducted in southern Brazil has shown that *I. paraguariensis* leaves contain substantial concentrations of calcium (Ca), copper (Cu), iron (Fe), phosphorus (P), magnesium (Mg), manganese (Mn), potassium (K), and zinc (Zn), both in fresh young leaves and in dried yerba mate intended for consumption [1,11]. Additional assessments of commercial products and infusions indicate that a portion of these elements is effectively transferred to the beverage, although with variable efficiency among elements and depending on preparation conditions [11,12].

Motta et al. (2020) [13], in a study evaluating leaves collected directly from plants cultivated under low-input systems in southern Brazil, reported substantial concentrations of macroelements such as K, Ca, Mg, and P, as well as essential micronutrients and potentially toxic elements. These findings reflect both soil fertility status and regional geochemical characteristics. The relationship between edaphoclimatic conditions and foliar mineral composition was further explored by Magri et al. (2022) [14], who assessed *I. paraguariensis* leaves collected from different producing regions in South America, including Brazil, Argentina, and Paraguay. The authors demonstrated that variations in soil texture, acidity, organic matter content, and climatic regime exert a direct influence on the uptake and accumulation of elements such as K, Ca, Mg, Mn, Fe, Zn, and Cu in the leaves, highlighting the importance of soil–plant interactions for understanding the mineral variability in yerba mate. Experimental studies also indicate that fertility management, particularly in acidic soils, can significantly affect plant growth, nutrient uptake, and the accumulation of potentially toxic elements in the leaves [15].

Recent analytical advances have substantially improved the understanding of the elemental profile of yerba mate. The application of multielemental techniques has enabled the identification of geochemical markers associated with the geographical origin of the leaves [16] while also supporting comprehensive health risk assessments related to the consumption of yerba mate commercialized in Brazil by simultaneously addressing essential and potentially toxic elements [17]. In parallel, indirect approaches, including the integration of mid-infrared spectroscopy with machine learning algorithms, have been proposed as promising tools for estimating nutrient contents in yerba mate plant tissues, offering new perspectives for the rapid and non-destructive characterization of mineral composition [18].

Despite the advances highlighted above, the current body of knowledge remains insufficiently explored, particularly with respect to the integrated assessment of soil physicochemical and granulometric attributes and their influence on plant mineral composition. This limitation is especially pronounced in underinvestigated regions such as the state of Mato Grosso do Sul, which, although characterized by traditional yerba mate cultivation systems, presents edaphic and geochemical conditions that differ substantially from those typically reported for southern Brazil. The scarcity of region-specific data constrains a robust understanding of soil–plant interactions, soil productive capacity, and geochemical equilibrium, thereby limiting the assessment of their implications for the nutritional quality of yerba mate intended for human consumption and for the development of value-adding strategies tailored to local conditions.

In this context, the present study aimed to quantify macroelements (K, Mg, and P) and microelements (Cr, Cu, Fe, Mn, Se, and Zn) in leaves of *I. paraguariensis* cultivated in the Brazil–Paraguay border region, in the state of Mato Grosso do Sul, and to characterize the physicochemical properties of soils associated with cultivation. By integrating soil fertility attributes with plant mineral composition, this study seeks to elucidate soil–plant relationships, mineral bioaccumulation patterns in the leaves, and their implications for the potential quality of the final product.

2. Materials and Methods

2.1. Study Area

The study was conducted in 2023, in the southern region of the state of Mato Grosso do Sul, Brazil, an area characterized by subtropical climate and yerba mate (*I. paraguariensis*) cultivation. In total, fourteen rural properties were selected, located in municipalities situated along the Brazil–Paraguay border, including Ponta Porã, Amambai, Antônio João, Coronel Sapucaia, Aral Moreira, Tacuru, Laguna Carapã, Iguatemi, and Paranhos. These properties correspond to registered yerba mate producers officially listed by the Agência de Desenvolvimento Agrário e Extensão Rural (AGRAER, Agricultural Development and Rural Extension Agency of Mato Grosso do Sul, Brazil). Figure 1 illustrates the geographical distribution of the sampled rural properties along the Brazil–Paraguay border. Table 1 provides detailed information on the participating properties, including their respective geographic coordinates.

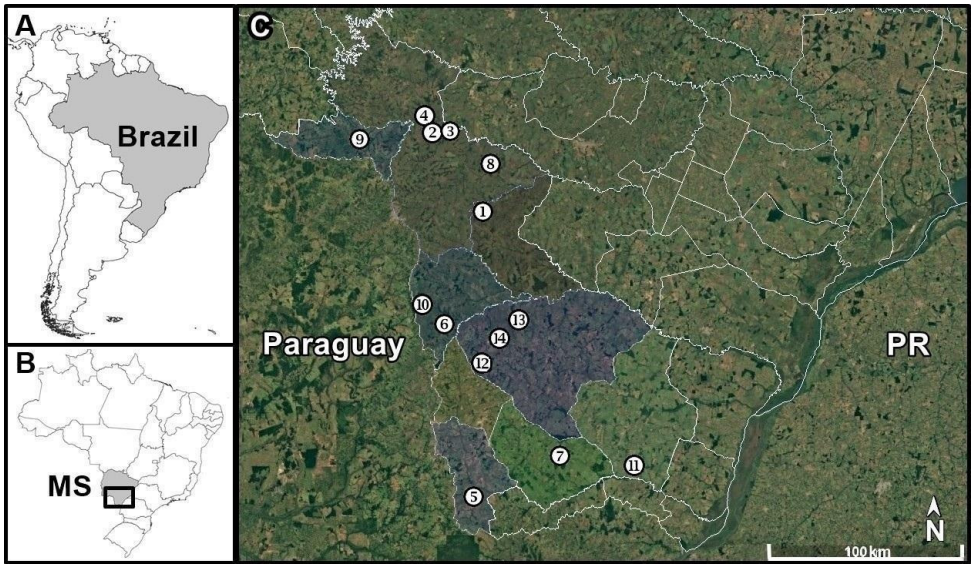


Figure 1. Study area located in the southern region of Mato Grosso do Sul State, Brazil, encompassing the border area with Paraguay. (**A**) Location of Brazil in South America. (**B**) Location of the state of Mato Grosso do Sul (MS) within Brazil. (**C**) Geographical distribution of the sampling sites along the Brazil–Paraguay border; the numbered points indicate the 14 rural properties included in the study.

Table 1. Identification of rural properties producing *I. paraguariensis* in the state of Mato Grosso do Sul, Brazil, with their respective municipalities and geographic coordinates.

Rural Properties	Municipalities	Geographic Coordinates
P1	Laguna Caarapã	22°31′12.0″ S 55°18′56.4″ W
P2	Ponta Porã	22°11′38.5″ S 55°34′40.4″ W
P3	Ponta Porã	22°11′20.4″ S 55°32′54.7″ W
P4	Ponta Porã	22°11′21.5″ S 55°34′49.1″ W

Table 1. *Cont.*

Rural Properties	Municipalities	Geographic Coordinates
P5	Paranhos	23°49′55.4″ S 55°21′30.5″ W
P6	Coronel Sapucaia	23°02′56.2″ S 55°29′21.4″ W
P7	Tacuru	23°38′47.3″ S 54°55′23.7″ W
P8	Ponta Porã	22°22′08.1″ S 55°16′30.5″ W
P9	Antônio João	22°11′46.6″ S 55°56′28.9″ W
P10	Aral Moreira	22°57′16.3″ S 55°37′33.7″ W
P11	Iguatemi	23°41′31.0″ S 54°33′36.7″ W
P12	Amambai	23°12′26.9″ S 55°18′51.0″ W
P13	Amambai	23°04′01.4″ S 55°07′49.7″ W
P14	Amambai	23°06′15.3″ S 55°13′45.6″ W

2.2. Sample Collection

To analyze soil and leaf properties of *I. paraguariensis* cultivated on rural properties, a systematic grid-based sampling design was adopted to characterize spatial variability under field conditions [19]. Within each property, sampling points were arranged in a grid layout composed of rows and columns with regular spacing, adjusted according to the available cultivated area, with distances between points ranging from 15 to 50 m depending on field size. A total of five sampling points were defined per property and uniformly distributed across the area. This grid-based approach enabled the collection of paired soil and leaf samples at corresponding locations, ensuring spatial representativeness of soil–plant relationships without the application of experimental treatments.

For leaf sampling, five subsamples were collected per point and homogenized to form a composite, representative sample of the area. Samples were packed in clean paper envelopes, properly labeled, and transported to the Laboratory of Mineral Metabolism and Biomaterials at the Federal University of Mato Grosso do Sul (UFMS).

Fresh leaves were selected for analysis because they reflect the current physiological uptake and accumulation of elements from the soil, allowing for a direct assessment of soil–plant transfer processes. The use of fresh, non-processed material avoids potential alterations in elemental composition associated with industrial processing, storage, blending, or commercial handling of yerba mate products, thereby providing a more accurate evaluation of macro- and microelement relationships under field conditions.

For soil sampling, five subsamples were collected around each sampling point within a 1 m radius and at a depth of 20 cm using a stainless-steel shovel. These subsamples were homogenized to form a composite sample representative of each point.

Additionally, a botanical specimen containing vegetative and reproductive structures (leaves, stems, flowers, and fruits) was collected and deposited in the CGMS Herbarium of the Institute of Biosciences at UFMS for taxonomic identification, being confirmed as *Ilex paraguariensis* under a specific registration protocol.

2.3. Drying and Digestion Procedure for I. paraguariensis Leaf and Soil Samples

Plant samples collected from various properties in Mato Grosso do Sul were dried in an oven with forced air circulation at approximately 56 °C for a period of 60 min (Alfa Mare, Minas Gerais, Brazil). After drying, the samples were ground in a mill with stainless steel blades, transferred to universal collection flasks, and stored at room temperature in a dry place until digestion. A mass of 250 mg of each leaf sample was weighed into a borosilicate tube, and 2 mL of 65% of nitric acid (HNO_3, Merck, ultrapure, Darmstadt, Germany), 2 mL of 30% of hydrogen peroxide (H_2O_2, Merck, ultrapure, Darmstadt, Germany), and 1 mL of ultrapure water with a resistivity of 18.2 MΩ.cm (Purelab Option-Q, Elga Veolia—Lane End, Buckinghamshire, UK) were added. The tubes were then homogenized using a QL-901

vortex mixer (Biomixer, QL-901, 167, São Paulo, Brazil) and incubated in a digestion block (Tecnal, model TE-041/25, Piracicaba, São Paulo, Brazil) under optimized temperature and time conditions: 100 °C for 60 min, 120 °C for 90 min, 150 °C for 60 min, and 180 °C for 30 min. After digestion, the samples were filtered and diluted to a final volume of 20 mL with ultrapure water (Purelab Option-Q, Elga Veolia—Lane End, Buckinghamshire, UK).

For soil digestion, 500 mg of each sample was weighed, and 5 mL of nitric acid (HNO_3, 65%; Merck, Darmstadt, Germany), 2 mL of hydrogen peroxide (H_2O_2, 30%; Merck, Darmstadt, Germany), and 1 mL of ultrapure water (Purelab Option-Q, Elga Veolia—Lane End, Buckinghamshire, UK) were added to a borosilicate tube. The tubes were fitted with cold-finger condensers to minimize the loss of volatile elements during the pre-digestion step by promoting the condensation and reflux of acid vapors back into the reaction vessel. The samples were then left at room temperature (23–25 °C) overnight to ensure controlled and efficient pre-digestion.

After pre-digestion, the tubes were homogenized using a vortex mixer (Biomixer, QL-901, 167, São Paulo, Brazil) and then heated in a digestion block (Tecnal, model TE-041/25, Piracicaba, São Paulo, Brazil) under the following temperature program: 90 °C for 60 min, 120 °C for 90 min, and 130 °C for 120 min. Following digestion, the samples were filtered through 70 mm filter paper and diluted to a final volume of 30 mL with ultrapure water (Purelab Option-Q, Elga Veolia—Lane End, Buckinghamshire, UK).

The entire digestion process was performed in triplicate for blank, *I. paraguariensis*, and soil samples. A spike recovery test was also carried out in triplicate to assess method accuracy by adding 0.5 mg/kg of each analyzed element to one *I. paraguariensis* sample prior to digestion.

2.4. Quantification of Macro- and Microelements by ICP OES

The quantification of macro- and microelements (Cr, Cu, Fe, K, Mg, Mn, P, Se, and Zn) in soil and leaf samples was carried out using Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES, iCAP 6300 Duo, Thermo Fisher Scientific, Waltham, MA, USA). The operating conditions were optimized to ensure the maximum sensitivity and stability of the plasma, with the following parameter described in Table 2.

Table 2. Instrumental parameters used in ICP OES.

Instrument Parameter	Setting
RF Power	1250 W
Sample Flow	0.45 L/min
Plasma Flow Rate	12 L/min
Integration Time	5 s
Settling Time	20 s
Nebulization Pressure	30 psi
Analytes	Cr; Cu; Fe; K; Mg; Mn; P; Se; Zn
Nebulizer concentric	concentric
Number of replicates	3

In addition, one calibration curve was prepared from a stock standard solution containing 100 mg/L of each element, using concentrations of 0.05 mg/L, 0.1 mg/L, 0.25 mg/L, 0.5 mg/L, 1.0 mg/L, and 2 mg/L. The curve was constructed for the elements Cu, Fe, K, Mn, P, Se, and Zn. The readings for Cu, Fe, K, and Mn were performed in radial view mode, while the other elements were read in axial view mode.

The limit of detection (LOD) was calculated as three times the standard deviation of the blank divided by the slope of the calibration curve. The limit of quantification (LOQ) was determined as ten times the standard deviation of the blank divided by the slope of

the curve [20]. Table 3 presents the LOD, LOQ, and the coefficient of determination (R^2) for each analyzed element. The LOD and LOQ values for the elements ranged from 0.0003 to 0.5441 and from 0.0038 to 1.8136, respectively. The R^2 of the calibration curves ranged from 0.9959 to 0.9999.

Table 3. Elements, limits of detection (LOD) and quantification (LOQ), wavelength, coefficient of determination obtained from external calibration, and spike recovery percentage.

Elements	LOD (mg/kg)	LOQ (mg/kg)	Wavenumber (nm)	Coefficient of Determination (R^2)	Spike (%)
Cr	0.0012	0.0041	283.563	0.9994	100
Cu	0.0055	0.0184	324.754	0.9982	95
Fe	0.0044	0.0147	259.940	0.9983	90
K	0.5441	1.8136	766.490	0.9979	113
Mg	0.0003	0.0009	279.553	0.9999	98
Mn	0.0003	0.0012	257.610	0.9985	102
P	0.0496	0.1652	177.495	0.9998	97
Se	0.0107	0.0356	196.090	0.9983	99
Zn	0.1765	0.5882	213.856	0.9962	118

The validation of the mineral quantification technique was performed through a spike recovery test by adding 0.5 mg/L of each analyte to the samples. The results demonstrated the precision of the method, with recovery percentages ranging from 92% to 118% (Table 3), values that are in accordance with the criteria established by the International Union of Pure and Applied Chemistry (IUPAC) [21]. No systematic errors or significant losses of elements were observed during the acid digestion process, indicating the robustness and reliability of the analytical procedure.

All plastic and glassware used for sample processing in the mineral analysis were pre-cleaned by immersion in a 10% nitric acid solution (HNO_3, 65%, Merck, Darmstadt, Germany) for at least 24 h to eliminate any residual metal contamination. Afterwards, the materials were thoroughly rinsed with ultrapure water and air-dried at room temperature.

2.5. Determining Soil Characteristics

Soil samples were oven-dried at 105 °C until constant mass, mechanically disaggregated, and sieved through a 2 mm mesh. For all analyses, the air-dried fine earth fraction (<2 mm) was used.

Particle-size distribution was determined after chemical dispersion in an aqueous medium using a dispersing agent to ensure complete separation of primary mineral particles. The sand, silt, and clay fractions were separated based on the differential sedimentation of particles in suspension, according to Stokes' Law, using the pipette method, which is recognized as the reference method for soil texture determination in Brazil. Clay was defined as particles with diameters < 0.002 mm, silt as particles between 0.002 and 0.05 mm, and sand as particles between 0.05 and 2.0 mm. Results were expressed as mass percentages of the fine earth fraction [22–24].

Soil chemical analyses were performed following the procedures described in the Embrapa Manual of Soil Analysis Methods [23]. Soil pH was measured in a soil-to-solution suspension using distilled water or 0.01 mol/L calcium chloride ($CaCl_2$; Merck, Darmstadt, Germany). Exchangeable Ca^{2+}, Mg^{2+}, and Al^{3+} were extracted with 1 mol/L potassium chloride (KCl; Merck, Darmstadt, Germany), whereas exchangeable K^+ and Na^+ were extracted using the Mehlich-1 solution. Based on these results, the sum of exchangeable bases (SB), cation exchange capacity (CEC), base saturation (V%), and aluminum saturation (m%) were calculated. Soil organic matter (OM) content was determined by chemical oxidation of organic carbon using the Walkley–Black method, with subsequent conversion

to organic matter content. Micronutrients (Fe, Mn, Zn, and Cu) were extracted using the Mehlich-1 solution.

Based on the particle-size distribution results, soils were classified into types defined for the Brazilian Agricultural Climate Risk Zoning, according to Normative Instruction SPA/MAPA No. 2 of 9 November 2021 [25]. This classification is primarily based on clay content of the fine earth fraction due to its direct influence on soil water-holding capacity. Accordingly, Type 1 soils present clay contents < 15% and low water retention; Type 2 soils contain 15–35% clay and exhibit intermediate physical behavior; and Type 3 soils present clay contents > 35% and higher water retention capacity [25].

The quantification of Cr, Cu, Fe, K, Mg, Mn, P, Se, and Zn in soil samples was performed by inductively coupled plasma optical emission spectrometry (ICP OES), as described in Section 2.4.

2.6. Bioaccumulation Factor (BAC)

The bioaccumulation factor (BAC) for elements in soil and fresh leaf samples of *I. paraguariensis* was calculated using Equation (1) [26]:

$$BAC = C_{plant}/C_{soil} \quad (1)$$

where C_{plant} (mg/kg) represents the concentration of the element in the aerial plant tissues, and C_{soil} (mg/kg) corresponds to the concentration of the element available in the soil. A BAF value ≤ 1 indicates that the plant absorbs but does not accumulate the element, whereas BAF values > 1 indicate the ability of the plant to accumulate elements from the soil. Higher BAF values reflect greater uptake efficiency and may suggest suitability for phytoremediation and phytoextraction processes. Conversely, BAF values < 1 indicate limited bioaccumulation capacity, suggesting that the species does not exhibit characteristics typical of hyperaccumulator plants [26].

2.7. Statistical Analysis

All statistical analyses were performed using R software (version 4.4.1; R Core Team, 2024). Initially, descriptive statistics were used to assess the distribution of and variability in elemental concentrations across the sampled properties.

Differences among properties were evaluated using a one-way Analysis of Variance (ANOVA). Prior to the analysis, the assumptions of normality and homogeneity of variances were assessed using the Shapiro–Wilk and Levene tests, respectively. In cases where the assumption of homogeneity of variances was violated, Welch's ANOVA, which is robust to unequal variances, was applied.

The magnitude of group differences was quantified using the omega-squared effect size (ω^2), which estimates the proportion of total variance attributable to differences among properties. In addition, the intraclass correlation coefficient (ICC) was calculated to assess within-group consistency and between-group variability in elemental concentrations across properties. To complement the frequentist framework, Bayesian analysis was conducted using Bayes factors to compare competing hypotheses, and a permutation-based approach (99.999 resamplings) was employed to evaluate the robustness of the inferential results. Statistical significance was set at $p < 0.05$.

In addition, Spearman's rank correlation analysis was performed using paired soil and fresh leaf elemental concentrations to evaluate soil–plant relationships in *I. paraguariensis*. This nonparametric method was selected because it does not assume data normality and is suitable for environmental datasets that may exhibit heteroscedasticity or non-linear responses. For each element, the Spearman correlation coefficient (ρ) was calculated to quantify the strength and direction of the monotonic association between elemental

concentrations measured in soil and in leaf tissues, with ρ values ranging from −1 (perfect negative association) to +1 (perfect positive association).

In addition, a Principal Component Analysis (PCA) was performed to identify patterns of association among the quantified elements (Cr, Cu, Fe, K, Mg, Mn, P, Se, and Zn) and to determine which properties (P1–P14) exhibited the highest overall concentrations or distinctive elemental profiles. The PCA allowed for the visualization of group clustering and the contribution of each element to the total variance, facilitating the interpretation of environmental or compositional similarities among sites.

The results of both analyses were expressed through scree plots providing a graphical understanding of variance distribution and inter-element relationships. All analyses were conducted with a 95% confidence level ($p < 0.05$).

3. Results

3.1. Concentrations of Macro- and Microelements in I. paraguariensis Fresh Leave

The quantitative analysis of macroelements (K, Mg, and P) and microelements (Cr, Cu, Fe, Mn, Se, and Zn) in *I. paraguariensis* leaves collected from 14 rural properties in Mato Grosso do Sul is presented in Tables 4 and 5, while the average concentrations across all sampling sites are shown in Table 6. The quantification of macroelements (Table 4) revealed that K was the most abundant element in the leaves, with concentrations ranging from 5.586 g/kg (P8) to 19.560 g/kg (P11) and an overall mean of 11.660 ± 4.580 g/kg (Table 6). The coefficient of variation (CV) was 39.3% between the areas with the highest accumulation of chemical elements, indicating high heterogeneity between properties such as P1, P6, and P11, and those with reduced concentrations, such as P3, P4, and P8. Mg, in turn, presented values between 0.942 g/kg (P2) and 2.098 g/kg (P9), with an average of 1.490 ± 0.350 g/kg, suggesting a more uniform distribution compared to K. Phosphorus varied from 0.232 g/kg (P7) to 7.313 g/kg (P12), resulting in an average of 3.220 ± 1.660 g/kg and a CV of 51.6%, the highest among the macroelements, evidencing strong variability between properties.

Table 4. Concentration (mean ± standard deviation) of macroelements in fresh leaves of *I. paraguariensis*.

Rural Properties	Macroelements (g/kg)		
	K	Mg	P
P1	18.124 ± 0.430	1.294 ± 0.018	2.614 ± 0.061
P2	14.036 ± 0.264	0.942 ± 0.009	2.030 ± 0.050
P3	6.472 ± 0.073	1.702 ± 0.027	2.302 ± 0.059
P4	5.988 ± 0.093	2.029 ± 0.031	2.807 ± 0.095
P5	10.497 ± 0.295	1.714 ± 0.048	1.727 ± 0.043
P6	17.720 ± 0.313	1.184 ± 0.004	4.803 ± 0.125
P7	7.730 ± 0.062	1.346 ± 0.009	0.232 ± 0.071
P8	5.586 ± 0.114	1.275 ± 0.009	3.881 ± 0.106
P9	10.906 ± 0.021	2.098 ± 0.018	2.979 ± 0.059
P10	14.126 ± 0.308	1.06 ± 0.002	3.374 ± 0.052
P11	19.560 ± 0.394	1.818 ± 0.044	3.010 ± 0.070
P12	16.390 ± 0.404	1.35 ± 0.033	7.313 ± 0.170
P13	9.550 ± 0.219	1.577 ± 0.016	5.360 ± 0.123
P14	8.860 ± 0.237	1.714 ± 0.040	3.643 ± 0.068

Table 5. Concentration (mean ± standard deviation) of microelements in fresh leaves of *I. paraguariensis*.

Rural Properties	Microelements (mg/kg)					
	Cr	**Cu**	**Fe**	**Mn**	**Se**	**Zn**
P1	2.209 ± 0.220	11.350 ± 0.324	62.726 ± 1.986	1888.565 ± 59.090	3.935 ± 0.206	2694.270 ± 45.900
P2	1.714 ± 0.213	11.333 ± 0.310	189.250 ± 4.168	1374.629 ± 48.382	4.228 ± 0.212	8158.806 ± 151.998
P3	2.946 ± 0.201	11.908 ± 0.217	119.544 ± 1.817	915.188 ± 12.706	3.794 ± 0.186	2661.7808 ± 50.207
P4	1.740 ± 0.228	10.600 ± 0.247	136.148 ± 2.885	900.239 ± 15.163	3.978 ± 0.192	1783.612 ± 49.994
P5	0.706 ± 0.163	7.907 ± 0.293	70.460 ± 1.907	671.020 ± 17.937	3.352 ± 0.205	1177.373 ± 26.672
P6	1.394 ± 0.199	8.658 ± 0.307	50.454 ± 1.154	1583.99 ± 35.631	3.995 ± 0.143	4261.794 ± 98.606
P7	1.294 ± 0.195	9.798 ± 0.194	67.170 ± 1.063	1134.131 ± 15.407	3.980 ± 0.224	1403.129 ± 38.443
P8	1.475 ± 0.235	7.607 ± 0.251	146.220 ± 3.493	640.189 ± 13.859	3.703 ± 0.183	1976.855 ± 43.791
P9	4.190 ± 0.179	6.635 ± 0.089	101.466 ± 0.428	2445.080 ± 10.111	5.321 ± 0.107	2318.229 ± 32.960
P10	0.956 ± 0.141	7.677 ± 0.335	33.978 ± 0.919	1230.116 ± 28.982	3.344 ± 0.107	4970.528 ± 63.261
P11	1.147 ± 0.195	11.373 ± 0.270	99.379 ± 2.116	1395.486 ± 43.598	4.107 ± 0.239	1859.124 ± 38.936
P12	1.120 ± 0.225	6.360 ± 0.351	61.158 ± 1.724	1592.115 ± 68.570	4.193 ± 0.230	2501.617 ± 63.204
P13	0.999 ± 0.226	10.776 ± 0.326	62.094 ± 1.652	2224.059 ± 51.171	4.309 ± 0.253	3425.237 ± 81.803
P14	1.000 ± 0.197	8.673 ± 0.410	74.214 ± 2.572	1077.528 ± 30.144	4.122 ± 0.217	2081.391 ± 41.743

Table 6. Mean concentration ± standard deviation of macro- and microelements in *I. paraguariensis* leaves (*n* = 14 rural properties).

	Mean ± SD	Minimum	Maximum
Macroelements (g/kg)			
K	11.660 ± 4.580	5.586 (P8)	19.560 (P11)
Mg	1.490 ± 0.350	0.942 (P2)	2.098 (P9)
P	3.220 ± 1.660	0.232 (P7)	7.313 (P12)
Microelements (mg/kg)			
Cr	1.700 ± 0.830	0.706 (P5)	4.190 (P9)
Cu	9.460 ± 1.640	6.360 (P12)	11.908 (P3)
Fe	93.060 ± 39.370	33.978 (P10)	189.250 (P2)
Mn	1389.860 ± 508.120	640.189 (P8)	2445.080 (P9)
Se	4.060 ± 0.510	3.344 (P10)	5.321 (P9)
Zn	3206.790 ± 1873.560	1177.373 (P5)	8158.806 (P2)

Among the microelements (Table 5), Cr concentrations ranged from 0.706 mg/kg (P5) to 4.190 mg/kg (P9), with an average of 1.700 ± 0.830 mg/kg (Table 6), reflecting a highly irregular distribution across the sampled properties. Copper concentrations ranged from 6.360 mg/kg (P12) to 11.908 mg/kg (P3), with a mean value of 9.460 ± 1.640 mg/kg and a CV of 17.3%, indicating relatively homogeneous distribution among the sampling sites.

The chemical element iron exhibited a high concentration, ranging from 33.978 mg/kg (P10) to 189.250 mg/kg (P2), with an average of 93.060 ± 39.370 mg/kg. This result demonstrates a strong unevenness in distribution, with P2, P3, P4, and P8 showing the highest values, while P6, P10, and P12 presented the lowest. Manganese was the microelement found in the highest concentration, with average values between 640.189 mg/kg (P8) and 2445.080 mg/kg (P9), presenting an average of 1389.860 ± 508.120 mg/kg and a coefficient of variation of 36.6%. Despite the high concentration, the distribution showed an intermediate pattern, with properties such as P1, P9, and P13 standing out in relation to P5 and P8.

Regarding the other elements, Se exhibited the lowest relative variation in concentration, ranging from 3.344 mg/kg (P10) to 5.321 mg/kg (P9), with an average of 4.060 ± 0.510 mg/kg and a CV of only 12.6%, representing the most uniform distribution among the analyzed elements. In contrast, Zn showed the widest range among the microelements, varying from 1177.373 mg/kg (P5) to 8158.806 mg/kg (P2), with an average of 3206.790 ± 1873.560 mg/kg and a CV of 58.4%, revealing a marked discrepancy between properties and indicating substantial accumulation of this nutrient in specific locations.

The comparative analysis of elemental concentrations (Table 7) revealed the predominance of macronutrients K and P over the micronutrients, with K consistently being the most abundant element. Among the micronutrients, Mn and Zn were the most representative, whereas Cr and Se were detected at lower and more stable concentrations. Overall, elements with lower CV (Mg, Cu, and Se) showed a more homogeneous distribution among properties, while those with higher CV values (P, Cr, Fe, and Zn) exhibited greater spatial variability.

Table 7. Concentration of macro- and microelements quantified in the leaves of the plants in decreasing order.

Rural Properties	Concentration of Macro- and Microelements in Decreasing Order
P1	K > Zn > P > Mn > Mg > Fe > Cu > Se > Cr
P2	K > Zn > P > Mn > Mg > Fe > Cu > Se > Cr
P3	K > Zn > P > Mg > Mn > Fe > Cu > Se > Cr
P4	K > P > Mg > Zn > Mn > Fe > Cu > Se > Cr
P5	K > P > Mg > Zn > Mn > Fe > Cu > Se > Cr

Table 7. *Cont.*

Rural Properties	Concentration of Macro- and Microelements in Decreasing Order
P6	K > P > Zn > Mn > Mg > Fe > Cu > Se > Cr
P7	K > P > Zn > Mg > Mn > Fe > Cu > Se > Cr
P8	K > P > Zn > Mg > Mn > Fe > Cu > Se > Cr
P9	K > P > Mn > Zn > Mg > Fe > Cu > Se > Cr
P10	K > Zn > P > Mn > Mg > Fe > Cu > Se > Cr
P11	K > P > Zn > Mg > Mn > Fe > Cu > Se > Cr
P12	K > P > Zn > Mn > Mg > Fe > Cu > Se > Cr
P13	K > P > Zn > Mn > Mg > Fe > Cu > Se > Cr
P14	K > P > Mg > Zn > Mn > Fe > Cu > Se > Cr

The results presented in Tables 4 and 5 were organized in descending order and are summarized in Table 7.

The statistical evaluation was based on the data presented in Tables 4 and 5. Descriptive and assumption analyses were first performed to verify data normality and homogeneity of variances. A one-way analysis of variance (ANOVA) was then applied to evaluate differences in the concentrations of Cr, Cu, Fe, K, Mg, Mn, P, Se, and Zn among the sampling sites (P1–P14). The ANOVA revealed statistically significant differences among the mean concentrations ($F(8.117) = 61.83$; $p = 1.875 \times 10^{-8}$), indicating that the distribution of elements varied substantially across properties. The proportion of variance explained was high ($\omega^2 = 0.7943$), and the intraclass correlation coefficient (ICC = 0.8129) confirmed strong within-group consistency.

As Levene's test indicated heterogeneity of variances ($p < 0.001$), a Welch's ANOVA robust to unequal variances was used, confirming significant differences among the properties ($F = 89.01$; $df = 45.52$; $p = 3.382 \times 10^{-25}$). The Bayes factor ($BF = 1.904 \times 10^{35}$) provided decisive evidence supporting the hypothesis of unequal means, while the permutation test ($n = 99.999$) confirmed the robustness of these findings ($p = 1.0 \times 10^{-5}$).

Subsequent pairwise multiple comparisons among the elements demonstrated that most pairs exhibited highly significant differences ($p < 0.001$), reflecting strong heterogeneity in elemental composition across the 14 properties. Elements such as Cr, Cu, Fe, K, Mg, Mn, and Zn displayed clear and consistent variations ($p = 7.47 \times 10^{-6}$) among sites, whereas Mn and P showed non-significant differences ($p > 0.05$) in some comparisons, suggesting possible chemical or environmental associations between these elements.

These results demonstrate that elemental distributions vary significantly among the sampled properties and that the observed inter-element differences are statistically robust, reflecting distinct soil–plant interactions and environmental conditions influencing metal accumulation.

The data presented in Tables 4–7 can be more comprehensively interpreted through a Principal Component Analysis (PCA), illustrated in the two-dimensional diagram shown in the biplot (Figure 2). This biplot displays the distribution of properties (P1–P14) based on the normalized concentrations of the nine analyzed elements. The first two components jointly explain 52.9% of the total variance (PC1 = 27.22%; PC2 = 25.70%).

According to the PCA, PC1 is strongly influenced by Se, Cr, Mn, and Mg, which exhibit high positive loadings. Properties with higher scores along PC1, particularly P9, followed by P13, P1, P12, and P11, indicate greater accumulation of these elements. In contrast, PC2 mainly reflects variations associated with K and P (positive loadings) and inversely with Fe and Mg (negative loadings). Consequently, P12 and P6 stand out with higher PC2 scores, showing relatively elevated levels of K and P, whereas P3, P4, and P8 show the opposite trend, dominated by Fe and Mg.

The dispersion of points in the biplot reveals that P9 behaves as an outlier along the PC1 axis, suggesting a distinct mineral composition characterized by elevated Se and Cr concentrations. Conversely, P5, P7, and P10 display negative scores in both components, indicating lower overall concentrations of the evaluated elements.

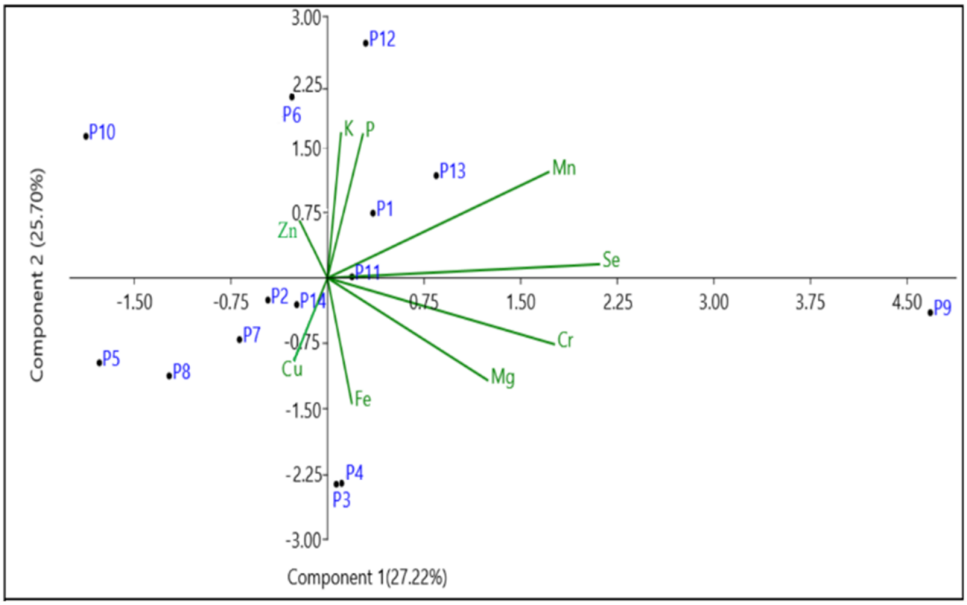


Figure 2. Biplot of the Principal Component Analysis (PCA) showing the distribution of sampling sites (P1–P14) and the contribution of each quantified element (Cr, Cu, Fe, K, Mg, Mn, P, Se, and Zn) in leaf samples.

3.2. Characterization of the Soils of the I. paraguariensis-Producing Regions of Mato Grosso do Sul, Brazil

The data obtained from the characterization of soils in *I. paraguariensis* production areas are presented in Tables 8–11. The clay fraction showed wide variability, ranging from 103 g/kg at rural property P11 to 679 g/kg at P7, indicating soils that vary from extremely sandy to loamy clay. In contrast, total sand values ranged from 130 g/kg (P7) to 864 g/kg (P11), while silt content varied between 10 g/kg (P4) and 241 g/kg (P3). The coefficient of variation was 47.5%, highlighting the pronounced granulometric heterogeneity among properties. This variability directly influenced soil classification according to Normative Instruction No. 2/2008 of the Brazilian Ministry of Agriculture, Livestock, and Food Supply [27], allowing the soils to be grouped into three main categories: Type 1 (P4, P6, P8, P9, and P11), characterized by low water retention capacity; Type 2 (P5 and P10), with intermediate retention; and Type 3 (P1, P2, P3, P7, P12, P13, and P14), with higher clay content and consequently greater water-holding capacity.

Table 8. Physical properties and classification of soils from *I. paraguariensis*-producing regions in Mato Grosso do Sul, Brazil.

Rural Properties	Granulometry Results			Solo Type *	Capacity to Retain Water
	Clay (g/kg)	Total Sand (g/kg)	Silt (g/kg)		
P1	546	225	228	Tipo 3	high
P2	597	243	160	Tipo 3	high
P3	628	132	241	Tipo 3	high
P4	164	826	10	Tipo 1	low
P5	267	699	34	Tipo 2	medium
P6	162	801	37	Tipo 1	low

Table 8. *Cont.*

Rural Properties	Granulometry Results			Solo Type *	Capacity to Retain Water
	Clay (g/kg)	Total Sand (g/kg)	Silt (g/kg)		
P7	679	130	192	Tipo 3	high
P8	199	769	32	Tipo 1	low
P9	162	817	21	Tipo 1	low
P10	234	731	35	Tipo 2	medium
P11	103	864	34	Tipo 1	low
P12	581	195	224	Tipo 3	high
P13	600	289	111	Tipo 3	high
P14	654	195	151	Tipo 3	high

* Soil classification according to Normative Instruction No. 2, of 9 November 2021, of the Ministry of Agriculture, Livestock and Supply (MAPA) [25], Brazil.

Table 9. Chemical properties of soils from *I. paraguariensis*-producing regions of Mato Grosso do Sul, Brazil.

Rural Properties	OM (g/dm^3)	OC (%)	pH $CaCl_2$	H + Al	H	Al	SB	V (%)	m (%)
				(mmolc/dm^3)					
P1	21	1.22	5.0	38	36	3	51	57	5
P2	20.1	1.17	4.6	60	51	9	48	44	15
P3	23.3	1.35	4.3	56	46	10	40	42	20
P4	5.3	0.3	4.2	25	20	6	16	39	27
P5	6.9	0.4	4.0	41	26	15	19	32	43
P6	9.5	0.55	4.0	41	25	16	6	12	73
P7	17.4	1.01	4.8	44	32	12	45	50	21
P8	9	0.52	3.8	41	28	13	9	17	60
P9	7.2	0.42	4.4	22	16	5	11	34	32
P10	15.2	0.88	4.0	45	32	13	8	15	62
P11	5.1	0.29	4.9	15	13	2	10	39	19
P12	20.4	1.18	4.5	57	53	4	66	54	6
P13	27.6	1.6	4.2	74	70	4	55	43	7
P14	16.9	0.98	4.0	62	53	9	35	36	21

OM (organic matter); OC (organic carbon); H + Al (total potential acidity); SB (sum of bases); m (Al saturation) and V (base saturation).

Table 10. Cation exchange capacity (CEC) of soils from *I. paraguariensis*-producing regions of Mato Grosso do Sul, Brazil.

Rural Properties	(Ca/CEC) (%)	(Mg/CEC) (%)	(K/CEC) (%)	CEC (mmolc/dm^3)
P1	37.1	16.7	3.3	89
P2	30.9	10.7	2.7	108
P3	27.3	12.5	1.8	95
P4	20.7	12.8	5.7	42
P5	21.9	7.3	2.8	60
P6	7.3	3.4	1.6	47
P7	37.5	11.7	1.1	89
P8	9.5	6.5	1.4	49
P9	26.9	6.3	1.1	33
P10	7.9	4.4	2.8	54
P11	29.3	7.5	1.9	25
P12	35.5	14	4.1	124
P13	31.2	8.7	2.6	128
P14	20.4	11.3	4.4	97

CEC (cation exchange capacity).

Table 11. Soil micronutrient contents determined by the Mehlich extraction method in *I. paraguariensis*-producing regions of Mato Grosso do Sul, Brazil.

Rural Properties	Ca	Mg	K	P	Cu	Fe	Zn	Mn
	(mmolc/dm^3)			(mg/dm^3)				
P1	33	15	3	3	3.68	19.55	1.12	16.29
P2	33	12	2.9	14	7.41	19.42	3.1	13.65
P3	26	12	1.7	4	5.09	46.75	0.75	8.84
P4	9	5	2.4	5	1.44	56.47	0.69	7.17
P5	13	4	1.7	5	4.69	24.23	0.47	21.89
P6	3	2	0.7	3	0.87	62.23	0.46	1.66
P7	33	10	1	3	4.47	16.82	0.52	5.14
P8	5	3	0.7	2	0.89	33.28	0.19	3.91
P9	9	2	0.3	3	0.67	8.95	0.15	2.97
P10	4	2	1.5	5	2.17	30.85	1.22	11.32
P11	7	2	0.5	17	0.55	11.76	0.5	8.15
P12	44	17	5	7	7.82	16.73	2.5	40.07
P13	40	11	3.4	3	7.98	24.91	0.53	24.55
P14	20	11	4.3	7	3.32	15.45	0.5	22.18

According to the chemical property analyses presented in Table 9, the OM content ranged from 5.1 g/dm^3 (P11) to 27.6 g/dm^3 (P13), resulting in a CV of 42.6%. This pattern was consistent with the OC concentration, which varied between 0.29% and 1.60%. Additionally, the pH in $CaCl_2$ solution was consistently acidic, ranging from 3.8 (P8) to 5.0 (P1), with an overall mean of approximately 4.4 across the sampled properties, indicating soils with moderate to high acidity.

Potential acidity ($H^+ + Al^{3+}$) and base saturation (V%) stood out among the main indicators of soil fertility (Table 9). Rural property P13 exhibited the highest potential acidity value (74 mmolc/dm^3), whereas rural property P11 showed the lowest (15 mmolc/dm^3), directly influencing the variation in base saturation, which ranged from 12% in rural property P6 to 57% in rural property P1. In addition, Al saturation (m%) showed high values in some rural properties, such as P6 (73%) and P8 (60%), in contrast to the lower levels observed in rural properties P1 (5%), P12 (6%), and P13 (7%).

According to Table 10, the CEC values ranged from 25 mmolc/dm^3 (P11) to 128 mmolc/dm^3 (P13), resulting in a coefficient of variation of 36.2%. The relative participation of cations showed a predominance of Ca^{2+} in all study areas (Properties P1–P14), varying from only 7.3% (P6) to 37.5% (P7). The chemical element Mg^{2+} contributed from 3.4% (P6) to 16.7% (P1), while K^+ maintained reduced levels, such as 1.1% (P7 and P9) to 5.7% (P4).

Based on the integrated analysis of the physicochemical properties of the soils and considering the mean values obtained for each parameter in the areas classified as Type 1, Type 2, and Type 3 (Figure 3), it was possible to identify clear differences in natural fertility, nutrient availability, and charge retention capacity, reflecting distinct soil quality and productive potential among the studied sites (Figure 1).

Type 1 soils (P4, P6, P8, P9, and P11), which predominate in sandy-textured regions, exhibited low cation exchange capacity (mean = 39 mmolc/dm^3), low organic matter content (7.2 g/dm^3), and high Al saturation (42%), indicating low natural fertility and limited nutrient retention capacity.

Type 2 soils (P5 and P10), characterized by medium texture, presented an intermediate cation exchange capacity (CEC) of 57 mmolc/dm^3, a moderate organic matter content (11 g/dm^3), and a base saturation of 24%. These features indicate dystrophic conditions and moderate fertility, typical of soils that require periodic corrective fertilization to sup-

port optimal growth of yerba mate. In contrast, Type 3 soils (P1, P2, P3, P7, P12, P13 and P14), predominantly clayey, exhibited a high CEC (104 mmolc/dm^3), higher organic matter content (21 g/dm^3), low aluminum saturation (14%), and a base saturation of 47%. These characteristics reflect a greater nutrient retention capacity and generally improved soil fertility.

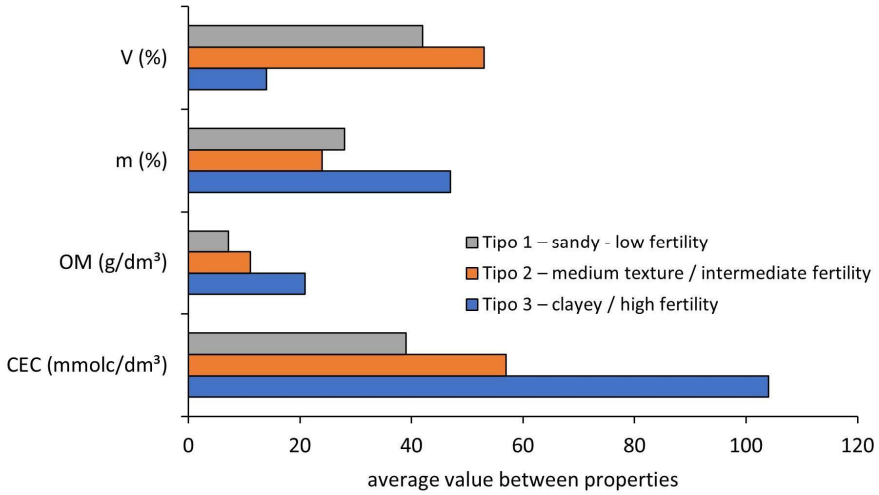


Figure 3. Average value of chemical composition parameters (V, m, OM, and CEC). Classification of soils in *I. paraguariensis*-producing regions in Mato Grosso do Sul according to physical-chemical characteristics and soil fertility. Here, Type 1 is the average of the values of properties P4, P6, P8, P9 and P11; Type 2 is the average of the values of properties P5 and P10; Type 3 is the average of the values of properties P1, P2, P3, P7, P12, P13 and P14, according to data presented in Tables 9 and 10. V—base saturation; m—Al saturation; OM—organic matter; CEC—cation exchange capacity.

The analysis of soil micronutrients using the Mehlich [28] extraction method reinforced the marked heterogeneity observed among the sampled areas (Table 11). Calcium concentrations ranged from 3 mmolc/dm^3 (P6) to 44 mmolc/dm^3 (P12), while Mg varied between 2 mmolc/dm^3 (P9, P10, and P11) and 17 mmolc/dm^3 (P12). Phosphorus showed minimum concentrations ranging from 2 to 7 mg/dm^3, with higher values recorded in P2 (14 mg/dm^3) and P11 (17 mg/dm^3). Potassium remained relatively low across all properties, ranging from 0.3 mmolc/dm^3 (P9) to 5 mmolc/dm^3 (P12).

Manganese exhibited the widest variation, ranging from 1.66 mg/dm^3 (P6) to 40.07 mg/dm^3 (P12), with a coefficient of variation of 81.6%, indicating substantial differences in the availability of this element among properties.

Overall, the soils analyzed demonstrated considerable physicochemical variability, ranging from clayey soils rich in organic matter, with high cation exchange capacity (CEC) and greater nutrient availability, to sandy soils poor in organic matter, characterized by low natural fertility and high Al saturation.

The results obtained from soil elemental quantification by ICP OES (Table 12) revealed a pronounced contrast in the chemical composition of the evaluated rural properties. Regarding iron, a wide difference was observed among sites, with properties P1, P2, and P3 showing high concentrations (above 55.000 mg/kg), whereas P11, P12, and P14 exhibited much lower levels (<4.000 mg/kg). The coefficient of variation exceeded 120%, indicating strong heterogeneity among sampling sites. This contrast suggests that, in certain areas, excessive Fe may compete with the uptake of essential micronutrients such as Zn and Mn, while in others, its availability is limited.

Table 12. Mean concentration ± standard deviation of macro- and microelements in soil (mg/kg) from rural properties producing *I. paraguariensis* in Mato Grosso do Sul, Brazil, determined by ICP OES.

Rural Properties	Concentration (Median ± Standard Deviation) of Macro- and Microelements in Soil (mg/kg)								
	Cr	**Cu**	**F**	**K**	**Mg**	**Mn**	**P**	**Se**	**Zn**
P1	121.276 ± 2.657	58.349 ± 1.338	56,177.425 ± 859.524	7.148 ± 0.024	29.891 ± 0.702	454.962 ± 2.583	631.902 ± 1.726	29.433 ± 0.355	70.185 ± 0.292
P2	177.422 ± 3.099	114.613 ± 0.727	57,708.336 ± 591.475	6.857 ± 0.059	38.668 ± 0.325	377.429 ± 5.469	664.491 ± 2.414	38.793 ± 0.37	96.214 ± 0.676
P3	132.725 ± 2.544	84.401 ± 0.728	55,328.495 ± 232.673	5.241 ± 0.09	26.151 ± 0.384	358.739 ± 4.235	599.945 ± 2.526	45.074 ± 0.287	56.122 ± 0.484
P4	151.816 ± 2.736	42.725 ± 0.64	29,477.779 ± 308.701	2.967 ± 0.046	14.653 ± 0.20	176.055 ± 1.848	328.343 ± 3.916	26.876 ± 1.01	28.292 ± 0.492
P5	32.388 ± 0.08	2.021 ± 0.066	5859.5284 ± 56.378	2.938 ± 0.045	4.262 ± 0.052	42.799 ± 0.458	127.761 ± 0.791	6.34 ± 0.07	6.97 ± 0.086
P6	28.841 ± 0.567	3.771 ± 0.107	6232.232 ± 133.979	4.553 ± 0.077	7.109 ± 0.064	84.022 ± 0.805	132.43 ± 0.354	9.044 ± 0.077	9.078 ± 0.081
P7	33.284 ± 0.266	3.34 ± 0.052	6345.011 ± 13.887	2.586 ± 0.018	3.772 ± 0.045	71.392 ± 0.364	110.886 ± 0.042	5.317 ± 0.053	7.0354 ± 0.051
P8	137.173 ± 1.758	33.12 ± 0.331	26,590.25 ± 19.955	3.279 ± 0.027	14.417 ± 0.051	205.231 ± 1.032	340.65 ± 0.359	37.6 ± 0.327	51.419 ± 0.663
P9	125.662 ± 0.82	47.366 ± 0.398	21,025.448 ± 37.254	3.351 ± 0.017	13.108 ± 0.06	196.458 ± 0.192	264.427 ± 1.455	36.934 ± 0.221	32.494 ± 0.159
P10	104.967 ± 0.672	34.453 ± 0.196	21,570.606 ± 39.323	3.892 ± 0.019	16.02 ± 0.084	347.298 ± 0.542	261.46 ± 0.44	67.148 ± 0.155	56.189 ± 0.287
P11	11.811 ± 0.565	1.121 ± 0.054	2471.836 ± 18.675	2.361 ± 0.028	1.708 ± 0.023	85.566 ± 0.749	80.265 ± 0.4	6.841 ± 0.084	1.998 ± 0.028
P12	19.587 ± 0.079	2.391 ± 0.045	3990.2 ± 14.253	3.331 ± 0.075	4.116 ± 0.074	51.373 ± 0.27	102.678 ± 1.11	15.195 ± 0.103	6.628 ± 0.041
P13	34.107 ± 1.118	11.936 ± 0.467	6296.571 ± 29.7389	2.643 ± 0.031	4.248 ± 0.055	77.799 ± 1.224	128.4 ± 0.286	19.865 ± 0.202	10.632 ± 0.181
P14	19.747 ± 0.362	1.737 ± 0.056	3699.527 ± 16.55	2.44 ± 0.0451	1.834 ± 0.011	20.178 ± 0.11	99.654 ± 0.251	8.964 ± 0.072	3.719 ± 0.06

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Similarly, Cr concentrations showed substantial variation. Property P2 reached 177.422 mg/kg, whereas P11 showed only 11.811 mg/kg. In addition, P1, P3, P4, P8, P9, and P10 displayed concentrations above 100 mg/kg, in contrast to P5, P6, P7, P11, P12, P13, and P14, which remained below 35 mg/kg. The CV, approximately 95%, highlights the influence of soil parent material and pedogenetic processes on the spatial distribution of metallic elements.

According to the results presented in Table 12, rural property P2 showed the highest Cu concentration (114.613 mg/kg), followed by P3 and P1, whereas P5, P6, P7, P11, P12, and P14 recorded much lower values, below 4 mg/kg. The coefficient of variation, approximately 115%, highlights the pronounced heterogeneity among the sampled sites. Since Cu is an essential micronutrient required in small amounts, soils with such low concentrations may impair plant metabolism; however, excessive levels may also pose toxicity risks.

Zinc exhibited a similar pattern to Cu, with the highest concentrations found in P2 (96.214 mg/kg), P1 (70.185 mg/kg), and P10 (56.189 mg/kg), contrasting with the low values measured in P11 (1.998 mg/kg) and P14 (3.719 mg/kg). The CV, close to 90%, confirms substantial spatial variability and indicates the need for site-specific micronutrient management strategies.

Manganese also displayed wide variation, with values of 454.962 and 377.429 mg/kg in P1 and P2, respectively, while P5, P12, and P14 showed concentrations below 55 mg/kg. This variability (CV > 80%) may affect key physiological processes, given the role of Mn in photosynthesis and enzymatic regulation.

Selenium likewise showed a markedly heterogeneous distribution, with P10 recording the highest concentration (67.148 mg/kg), followed by P3, P8, and P9 (36–45 mg/kg). In contrast, P7 showed only 5.317 mg/kg, indicating significant differences in Se availability across the studied soils.

When analyzing macroelements, a distinct pattern emerges. Potassium exhibited consistently low concentrations across all properties, ranging from 2.361 to 7.148 mg/kg, indicating a generalized deficiency of this nutrient in the evaluated soils. In contrast, Mg showed moderate concentrations, with notably higher values in rural properties P2 (38.668 mg/kg) and P1 (29.891 mg/kg), whereas P11 and P14 displayed levels below 2 mg/kg. Phosphorus, in turn, exhibited one of the most pronounced variations among the soils. Properties P1, P2, and P3 showed concentrations above 600 mg/kg, while P11 and P14 had levels below 100 mg/kg. This contrast highlights the coexistence of naturally fertile soils and areas with clear mineral limitations, which may compromise the growth and establishment of *I. paraguariensis*.

The data in Table 12, relating to the chemical composition of the soils, were interpreted using PCA, as shown in Figure 4. The Biplot of the Principal Component Analysis (PCA) illustrates the distribution of rural properties according to the concentrations of macro- and microelements in the soil. The first two principal components together explain 93.96% of the total variance (PC1 = 86.21%; PC2 = 7.75%), demonstrating the strong ability of the model to represent the chemical variability among samples.

The component PC1 (86.21%) represents the main gradient of chemical variation in the soils, largely driven by two contrasting element groups: one associated with K, Mg, P, and Fe and the other characterized by Se, Cr, Mn, and Zn. Soils positioned on the right side of the biplot (higher PC1 scores) show enrichment in Se, Cr, Mn, and Zn, while those on the opposite side (lower PC1 scores) are characterized by higher contents of K, Mg, P, and Fe.

Within this framework, properties P1 and P2 appear on the far right of PC1, reflecting soils with greater accumulation of Se, Cr, and Mn. In contrast, P13, P14, P7, P12, P5, and P6 are grouped on the opposite side, representing soils richer in K, Mg, P, and Fe. Properties

P4, P8, and P9 occupy intermediate positions, indicating a balanced chemical composition between these two element groups.

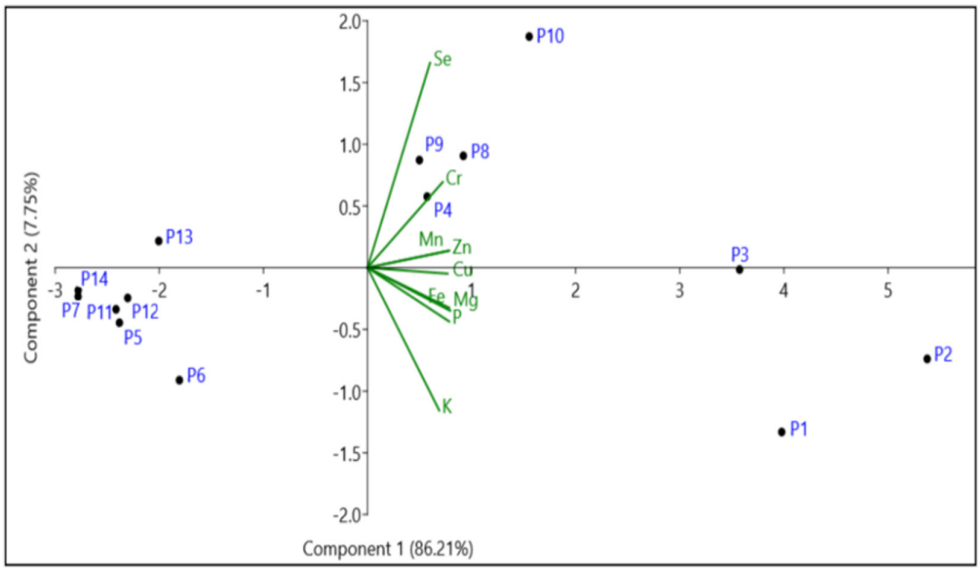


Figure 4. Biplot of the Principal Component Analysis (PCA) showing the distribution of sampling sites (P1–P14) and the contribution of each quantified element (Cr, Cu, Fe, K, Mg, Mn, P, Se, and Zn) in soil samples.

PC2, which accounts for 7.75% of the variance, represents a secondary gradient mainly influenced by Se and K. Properties with higher PC2 scores, such as P10, P8, and P9, are distinguished by increased Se concentrations, whereas those with lower PC2 values, including P1, P2, P5, P6, P12, P13, and P14, show relatively higher contributions of K, suggesting soils dominated by macronutrients.

Spearman correlation analysis was performed using paired soil and leaf elemental concentrations to evaluate soil–plant relationships in *I. paraguariensis* (Table 13). Significant positive correlations were observed for K ($\rho = 0.69$, $p < 0.01$) and Mn ($\rho = 0.82$, $p < 0.001$), indicating a strong to very strong association between soil availability and leaf accumulation. Zinc also showed a significant positive correlation ($\rho = 0.58$, $p = 0.02$), classified as moderate.

Table 13. Spearman correlation between soil and leaf elemental concentrations in *I. paraguariensis*.

Element	Spearman's ρ (Soil × Leaf)	*p*-Value	Interpretation
K	0.69	<0.01	Strong positive correlation
Mg	0.48	0.04	Moderate correlation
P	0.41	0.07	Positive trend
Cr	0.22	0.38	Not significant
Cu	0.36	0.12	Weak correlation
Fe	0.19	0.45	Not significant
Mn	0.82	<0.001	Very strong positive correlation
Se	0.33	0.15	Weak correlation
Zn	0.58	0.02	Moderate correlation

According to Table 13, Mg exhibited a moderate correlation ($\rho = 0.48$, $p = 0.04$), whereas P showed a positive trend ($\rho = 0.41$, $p = 0.07$) that was not statistically significant. No significant correlations were observed for Cr ($\rho = 0.22$, $p = 0.38$), Fe ($\rho = 0.19$, $p = 0.45$), Se ($\rho = 0.33$, $p = 0.15$), or Cu ($\rho = 0.36$, $p = 0.12$), suggesting limited direct soil–leaf coupling for these elements under the studied conditions.

The bioaccumulation factor (BAC), calculated as the ratio between mean elemental concentrations in fresh leaves and the corresponding soil concentrations, revealed pronounced differences in soil–plant transfer among elements and sampling sites (Table 14). Potassium exhibited consistently high BAC values across all properties, ranging from 1234.9 (P3) to 8284.6 (P11), indicating strong accumulation of this macronutrient in *I. paraguariensis* leaves. Magnesium also showed elevated BAC values, particularly at P11 (1064.4) and P14 (934.6), while P displayed moderate to high BAC values, with maxima at P12 (71.2) and P13 (41.7).

Table 14. Bioaccumulation coefficients (BACs) of elements in fresh leaves of *I. paraguariensis*.

Property	K	Mg	P	Cr	Cu	Fe	Mn	Se	Zn
P1	2535.534	43.291	4.137	0.018	0.195	0.001	4.151	0.134	38.388
P2	2046.959	24.361	3.055	0.010	0.099	0.003	3.642	0.109	84.799
P3	1234.879	65.084	3.837	0.022	0.141	0.002	2.551	0.084	47.428
P4	2018.200	138.470	8.549	0.011	0.248	0.005	5.113	0.148	63.043
P5	3572.839	402.159	13.517	0.022	3.912	0.012	15.678	0.529	168.920
P6	3891.939	166.549	36.268	0.048	2.296	0.008	18.852	0.442	469.464
P7	2989.172	356.840	2.092	0.039	2.934	0.011	15.886	0.749	199.438
P8	1703.568	88.437	11.393	0.011	0.230	0.005	3.119	0.098	38.446
P9	3254.551	160.055	11.266	0.033	0.140	0.005	12.446	0.144	71.343
P10	3629.496	66.167	12.904	0.009	0.223	0.002	3.542	0.050	88.461
P11	8284.625	1064.403	37.501	0.097	10.145	0.040	16.309	0.600	930.492
P12	4920.444	327.988	71.223	0.057	2.660	0.015	30.991	0.276	377.432
P13	3613.318	371.234	41.745	0.029	0.903	0.010	28.587	0.217	322.163
P14	3631.148	934.569	36.556	0.051	4.993	0.020	53.401	0.460	559.664

Among the microelements, Mn and Zn presented the highest BAC values, frequently exceeding 10 and reaching up to 53.4 for Mn (P14) and 930.5 for Zn (P11), demonstrating marked accumulation in leaf tissues. Copper showed site-specific accumulation, with BAC values greater than 1 at several properties, notably P11 (10.1) and P14 (5.0). In contrast, Cr, Fe, and Se exhibited consistently low BAC values (generally <0.1 for Cr and Fe, and <1 for Se), indicating restricted soil-to-plant transfer for these elements across the studied sites.

4. Discussion

4.1. Influence of Soil Physicochemical Characteristics and Natural Fertility on the Accumulation of Macro- and Microelements in I. paraguariensis Leaves

The results obtained in this study reveal substantial variability in the mineral composition of *I. paraguariensis* leaves cultivated in the border region between Mato Grosso do Sul, Brazil, and Pedro Juan Caballero, Paraguay. This variability was directly associated with the physicochemical properties and natural fertility of the soils from the production areas (Tables 8–10).

Parameters such as pH, OM content, CEC, and soil texture classification were found to significantly influence soil quality and productive potential, thereby affecting the availability and uptake of macro- and micronutrients by the plants. These findings are consistent with previous studies conducted in southern Brazil and other *I. paraguariensis*-producing regions of South America, which also highlight the strong linkage between soil composition and the nutritional profile of the species [13,14,16,29].

Type 1 soils (P4, P6, P8, P9, and P11), predominantly found in sandy regions (Figure 3), exhibited low cation exchange capacity (CEC: 39 mmolc/dm^3), low OM content (7 g/dm^3), acidic pH (4.3), and high Al saturation (42%). These characteristics are typical of dystrophic soils with low natural fertility and high potential acidity [25]. Under such conditions, the reduced specific surface area of sand particles limits cation adsorption and the formation

of organo-mineral complexes, thereby restricting nutrient and water retention in the root zone [28]. Similar chemical and physical constraints have been reported in Santa Catarina, where soils containing more than 700 g/kg of sand showed lower water- and nutrient-holding capacities, especially under extensive management systems [28], in agreement with the findings of Motta et al. (2020) [13] and Toppel et al. (2018) [29] for sandy soils in southern Brazil. As a consequence, greater micronutrient leaching and significant variation in foliar Cu and Zn contents were observed, a pattern consistent with that reported by Magri et al. (2022) [14] for soils with low natural fertility. Conversely, Naibo et al. (2024) [18] reported organic matter levels ranging from 35 to 50 g/kg in cultivated areas of Paraná in Brazil, contrasting with values below 20 g/kg found in part of the evaluated properties in Mato Grosso do Sul (Table 9).

This difference may explain the high Cu variability observed in this study (CV > 100%), since soils with higher organic matter content tend to have a greater ability to complex and release micronutrients more evenly. Furthermore, recent studies have shown that soils with low CEC and high acidity require continuous corrective management such as liming and periodic fertilization to maintain productivity and the nutritional quality of perennial species [30].

Type 2 soils (P5 and P10), characterized by a medium texture, exhibited an intermediate CEC of 57 mmolc/dm^3, a moderate OM content of 11 g/dm^3, pH around 4.0, and base saturation close to 24%, indicating moderate fertility [25]. Even at intermediate levels, OM contributes to increasing CEC and to the complexation of microelements such as Cu, Zn, Fe, and Mn, acting as an important buffering agent for nutrient availability [28,31]. These soil characteristics in Mato Grosso do Sul are similar to those reported by Santin et al. (2013) [3] and Barbosa et al. (2018) [15], who observed a positive response of yerba mate to corrective fertilization in medium-fertility soils in Paraná (Brazil), with increased absorption of Ca, Mg, and K. The moderate OM content in these soils also helps improve structure and moisture retention capacity, enhancing nutrient dynamics [28]. According to Palavicini et al. (2025) [10], in integrated cropping systems of the Cerrado biome, soils with intermediate levels of OM and CEC display greater biological activity and structural stability, which favor mineralization and nutrient availability to plants.

Type 3 soils, collected from the rural properties P1, P2, P3, P7, P12, P13, and P14, which are predominantly clayey, exhibited a high cation exchange capacity (CEC = 104 mmolc/dm^3), higher OM content (21 g/dm^3), slightly acidic pH (4.5–6.8), and low Al saturation (14%), indicating eutrophic soils with naturally higher fertility and a greater ability to retain and supply nutrients efficiently [25]. Under these conditions, the higher number of negative sites in the exchange complex enhances cation (Ca^{2+}, Mg^{2+}, K^+) retention, reduces leaching losses, and prevents the increased solubility of toxic elements such as Al^{3+} and Mn^{2+} [31–33], providing greater buffering capacity, chemical stability, and less pH fluctuation. Moreover, OM contributes to the formation of stable organo-mineral complexes, regulating the availability of micronutrients and preventing their irreversible fixation [31]. This balance favors efficient nutrient absorption and explains the greater homogeneity in foliar K and Mg concentrations observed in these samples. Similar findings were reported by Magri et al. (2022) [14] and Bastos et al. (2014) [1], who observed that clayey soils in southern Brazil and Paraguay support higher concentrations of macro- and micronutrients in *I. paraguariensis* leaves, reflecting the direct influence of soil fertility and mineral composition on the plant's elemental profile.

In the Type 3 soils from rural properties P1, P2, and P3, CEC values exceeded 80 mmolc/dm^3 and OM contents were around 20 g/dm^3. However, the pH ranged from 4.3 to 5.0 (Table 9). Thus, despite favorable CEC and OM levels, this pH range still includes more acidic conditions, particularly in P2 and P3, which may increase the solubilization of certain micronutrients and the availability of Al compared to higher pH levels. Therefore,

while P1 is closer to equilibrium conditions between adsorption and solubility, P2 and P3 may exhibit greater mobility of elements such as Mn and Al, with direct implications for foliar uptake.

The behavior of Mn, with foliar concentrations ranging from 540 to 2000 mg/kg (Table 4), reflects both the natural availability of this element in the soils analyzed from Mato Grosso do Sul and the high capacity of *I. paraguariensis* to absorb and accumulate it [15,28]. Although Mn is essential for photosynthesis and enzymatic activation in metabolic processes, its excessive accumulation can cause phytotoxic effects [31,33]. This behavior may be associated with the lower pH values and higher Al saturation observed in some properties (Table 9), which favor Mn solubilization and absorption [34]. Indeed, *I. paraguariensis* has the ability to hyperaccumulate Mn in its leaves, resulting in elevated concentrations associated with the occurrence of interveinal chlorosis induced by transient toxicity [34]. This phenomenon occurs when Mn accumulation exceeds the plant's physiological demand, leading to temporary nutritional imbalances [34]. In contrast, studies conducted in Paraná and Santa Catarina, also in Brazil, reported narrower concentration ranges, between 600 and 1200 mg/kg [13], suggesting that the more pronounced acidity and specific edaphic conditions of Mato Grosso do Sul soils promoted greater solubilization and absorption of this element. This characteristic reinforces the importance of monitoring Mn levels in yerba-mate-producing regions, since both deficiency and excess can compromise leaf productivity and quality for consumption.

The results of this study indicate that soils with moderately acidic pH, high CEC, and adequate levels of OM promote greater stability in nutrient availability, resulting in leaves with a more balanced composition of macro- and microelements. In contrast, sandy and dystrophic soils, characterized by low CEC and reduced OM content, limit nutrient absorption and require continuous corrective management, such as liming and periodic fertilization, to maintain the productivity and nutritional quality of yerba mate (*I. paraguariensis*) [30].

The statistical analyses revealed that the concentrations of the chemical elements Cr, Cu, Fe, K, Mg, Mn, P, Se, and Zn varied significantly among the different sampling sites (P1–P14). Initially, the data were tested for normality and homogeneity of variances, followed by a one-way analysis of variance (ANOVA) to compare mean values between groups at a significance level of $p < 0.05$. The ANOVA showed statistically significant differences among the sampling sites, with a high proportion of variance explained, indicating a strong influence of the sampling location on elemental concentrations. This suggests that environmental and edaphic factors such as soil composition, topography, and agricultural management play a decisive role in mineral uptake and accumulation in the leaves.

The intraclass correlation coefficient (ICC) confirmed strong within-site consistency, while Welch's test, applied due to variance heterogeneity, corroborated significant differences across properties. In addition, the Bayes factor and permutation test provided decisive evidence supporting the existence of unequal means, reinforcing the robustness of the findings.

The results indicate that certain sites, particularly P9, P12, P1, and P13, showed higher mean concentrations of elements such as Cr, Fe, Mg, and Se, whereas P5, P7, and P10 displayed lower levels, highlighting marked spatial variation in soil fertility and mineral composition.

Multiple pairwise comparisons among elements revealed that most combinations were highly significant ($p < 0.001$), demonstrating substantial heterogeneity in elemental concentrations. Elements such as Fe, K, Mg, Mn, and Zn exhibited the most pronounced differences across sites, while P and Se showed more homogeneous behavior. Together with the PCA, these results demonstrate that the observed inter-element variations are

not random but reflect site-specific geochemical patterns, with some properties showing higher accumulations of particular elements, likely influenced by soil composition and environmental conditions.

The apparent divergence in the behavior of Mg between soils and leaves may indicate foliar sequestration processes or differential mobilization by the plant under specific soil conditions.

The application of PCA to the soil and leaf data of *I. paraguariensis* confirmed the strong influence of local edaphic factors and plant physiology on mineral absorption and accumulation. In soils, the first two principal components explained more than 93% of the total variance (PC1 = 86.21%; PC2 = 7.75%). PC1 separated soils dominated by Se, Cr, Mn, and Zn (positive loadings) from those enriched in K, Mg, P, and Fe (negative loadings), suggesting geochemical differences associated with the parent material of the soil [31].

In the PCA of leaf samples, the first two axes explained 52.9% of the variance, with PC1 mainly influenced by Se, Cr, Mn, and Mg, while PC2 reflected variations primarily related to K and P (positive loadings) and Fe and Mg (negative loadings). Properties with high PC1 scores (P9, P13) exhibited elevated levels of Se and Cr, indicating that soils with greater availability of these elements promote higher foliar accumulation, even when these are nonessential elements for the plant [31].

The apparent divergence in Mg loadings negative in soils but positive in leaves may indicate foliar sequestration processes or differential mobilization by the plant under specific soil conditions.

From a physiological perspective, the grouping of K, P, and Mg in PC2 of the leaf samples reflects nutritional synergisms associated with photosynthesis, sugar transport, and osmotic regulation [35]. On the other hand, the opposition between Fe and K suggests ionic antagonism in the roots of plants grown in Fe-rich soils.

The relationship between soil and leaf patterns reinforces that *I. paraguariensis* responds in an integrated manner to edaphic variability through selective absorption, retention, or exclusion mechanisms of specific minerals. These processes are linked to ionic competition and are modulated by soil parameters such as pH, texture, and organic matter content [13,31,36]. Studies on *I. paraguariensis* cultivated in different edaphoclimatic regions and under various soil management systems corroborate the patterns of nutritional selectivity and physiological adaptation observed in our research. Among the macronutrients, K, P, and Mg are among the most required by the species and contribute most significantly to the growth of yerba mate. Furthermore, the parent material of the soil directly influences the elemental composition of the leaves [3,13]. Therefore, the mineral composition of *I. paraguariensis* leaves reflects both the geochemical characteristics of the environment and the plant's physiological processes, emphasizing the importance of the soil–plant relationship in assessing the nutritional quality of the final product.

The strong correlations observed for Mn and K reflect their high mobility in soil–plant systems and their essential role in plant metabolism. Conversely, the lack of correlation for Fe and Cr suggests geochemical constraints and plant homeostatic mechanisms that limit foliar accumulation, even under elevated soil concentrations. These findings highlight the importance of considering bioavailability rather than total soil concentrations when assessing elemental uptake.

The Spearman correlation results highlight contrasting soil–plant transfer behaviors among the evaluated elements. The strong to very strong correlations observed for K and Mn indicate that leaf concentrations of these elements are closely linked to their respective soil levels. This finding is consistent with the high mobility of K in the soil–plant system and its essential physiological role, as well as with the known availability of Mn in acidic soils, where its solubility and uptake by plants are enhanced.

The moderate correlation observed for Zn suggests partial dependence on soil availability, potentially influenced by additional factors such as organic matter content, cation exchange capacity, and competitive interactions with other micronutrients. Similarly, the moderate correlation for Mg indicates that soil fertility plays a relevant role in leaf Mg concentrations, although plant physiological regulation and soil chemical interactions may also modulate uptake.

In contrast, the lack of significant correlations for Cr, Fe, Se, and Cu suggests that leaf concentrations of these elements are not directly controlled by total soil concentrations. This behavior may reflect low bioavailability due to strong adsorption to soil mineral phases, complexation with organic matter, or active exclusion mechanisms at the root level. The absence of a significant soil–leaf relationship for Fe, despite its essentiality, is consistent with its limited solubility under oxic conditions and tight physiological regulation in plants.

Therefore, these results indicate that soil properties exert a selective influence on elemental uptake by *I. paraguariensis*, with strong coupling for highly mobile and physiologically demanded elements, while other elements appear to be governed by geochemical constraints and plant regulatory mechanisms rather than by soil concentration alone.

The BAC patterns observed for potassium highlight its consistently strong accumulation in *I. paraguariensis* leaves across all sampled properties, with values ranging from 1234.9 at P3 to 8284.6 at P11. Magnesium followed a similar trend, showing notably elevated BAC values at specific locations, particularly at P11 (1064.4) and P14 (934.6). Phosphorus exhibited intermediate to high BAC values, reaching peak levels at P12 (71.2) and P13 (41.7), suggesting variability in soil–plant transfer efficiency among sites.

Regarding micronutrients, manganese and zinc stood out as the elements with the highest relative accumulation in leaf tissues, with BAC values reaching 53.4 for Mn at P14 and 930.5 for Zn at P11. Copper displayed a more heterogeneous pattern, with BAC values exceeding unity at several properties, especially at P11 (10.1) and P14 (5.0), indicating site-dependent accumulation. Conversely, chromium, iron, and selenium consistently exhibited low BAC values across all properties, generally below 0.1 for Cr and Fe and below 1 for Se, reflecting limited transfer from soil to leaves in the studied areas.

The BAC results provide quantitative evidence of differential soil–plant transfer patterns in *I. paraguariensis*. Consistently elevated BAC values for P can be explained by its relatively high mobility in soils and its essential role in plant physiological processes, including energy metabolism, osmotic regulation, and enzymatic activation, as widely described in plant nutrition and soil science literature [28,37]. Similarly, the high BAC values observed for magnesium (Mg) at several sites indicate efficient uptake relative to soil concentrations, with its accumulation being strongly influenced by site-specific soil fertility conditions, such as cation exchange capacity and base saturation [31].

Manganese and Zn exhibited particularly pronounced bioaccumulation, with BAC values exceeding unity by one to three orders of magnitude. This pattern is consistent with the increased availability of Mn in acidic soils, where Mn^{2+} becomes more soluble and readily absorbed by plant roots [31]. In the case of Zn, elevated BAC values can be attributed to its essential role as a cofactor in numerous metabolic and enzymatic pathways and to its high physiological demand in plants [38,39]. The exceptionally high BAC values for Zn observed at some sites suggest that foliar concentrations in *I. paraguariensis* are highly responsive to variations in soil Zn availability.

Copper showed intermediate and spatially variable BAC values, indicating that its soil–plant transfer is strongly influenced by localized soil chemical properties. In particular, soil organic matter content, cation exchange capacity, and competitive interactions with other metal cations are known to regulate Cu solubility and bioavailability, resulting in heterogeneous accumulation patterns across sites [31,40].

Conversely, the uniformly low BAC values observed for Cr and Fe indicate strong restriction of their transfer from soil to leaves. For Fe, this behavior is consistent with its low solubility under oxic soil conditions and with the tight physiological regulation of Fe uptake and translocation within plants, which limits excessive accumulation in aerial tissues [37]. Chromium, which is not considered essential for plant metabolism, tends to be largely excluded from shoots, with most of the absorbed fraction retained in root tissues, reflecting effective physiological and geochemical barriers to its translocation [41,42].

Overall, the BAC analysis indicates that *I. paraguariensis* efficiently accumulates selected essential macro- and microelements while limiting the transfer of potentially toxic or non-essential elements to its leaves. These findings underscore the importance of integrating soil chemical characterization with plant mineral analysis to improve the interpretation of soil–plant interactions and to assess their implications for the nutritional quality and environmental safety of yerba mate produced in agroecosystems located in sensitive border regions [43].

4.2. Macro- and Microelement Content in Fresh Leaves of I. paraguariensis from Mato Grosso do Sul Compared to Other Producing Regions

The composition of macro- and microelements in the natura leaves of *I. paraguariensis* from Mato Grosso do Sul revealed that the highest concentrations of K and P (Table 4) were consistent across all properties (P1–P14), reflecting the essential physiological roles of these elements in the plant's metabolism, particularly in photosynthetic processes and osmotic transport. The low Mg content observed in some areas, exacerbated by the predominantly acidic pH of the region (Table 9), may negatively affect photosynthesis, considering its central role in the chlorophyll molecule [44]. Studies on yerba mate leaves have confirmed that limited Mg concentrations are associated with reduced growth [13]. When compared with other studies, Motta et al. (2020) [13] reported similar concentrations in *I. paraguariensis* leaves cultivated with no history of chemical fertilizer in southern Brazil, with K from 16.771 g/kg, Mg from 6.506 g/kg, and P from 1.062 g/kg, as determined by ICP-MS in unwashed leaves. Comparable values were also described by Bastos et al. (2014) [1], who found 12.9–19 g/kg of K, 2.7–4.4 g/kg of Mg, and 1.8–2.3 g/kg of P in young leaves collected in Paraná, Brazil. In commercial yerba mate samples from different regions of Brazil, Argentina, and Uruguay, purchased in local markets of Rio Grande do Sul, Caniza et al. (2020) [16] quantified K (13.242 g/kg), Mg (4.615 g/kg) and P (1.1 g/kg) using particle-induced X-ray emission (PIXE).

These findings corroborate and suggest that yerba mate plants from southern Mato Grosso do Sul exhibit a mineral composition comparable to that of traditionally producing regions in southern Brazil, although the variability in P (CV = 51.6%) indicates sensitivity of this element to management practices and soil availability. It is worth noting that significant seasonal variations in foliar k content are associated with the plant's developmental stage, as previously reported by Corrêa et al. (2025) [45].

Among the microelements, Mn and Zn exhibited the highest mean concentrations in the leaves (Table 5), exceeding 1300 mg/kg and 3200 mg/kg, respectively, followed by Fe (93 mg/kg), Cu (9 mg/kg), Cr (1.7 mg/kg), and Se (4 mg/kg). Both Mn and Zn showed wide variation among the sampled properties (Mn: 640–2445 mg/kg; Zn: 1177–8158 mg/kg), indicating a direct influence of soil characteristics and pH on their uptake. Comparable values were reported by Pozebon et al. (2015) [11], who found Mn levels ranging from 730 ± 150 to 1445 ± 167 mg/kg in commercial samples from Brazil, Paraguay, Argentina and Uruguay and Zn concentrations of 44.2 ± 14.7 mg/kg in Brazilian samples and 77.3 ± 25.4 mg/kg in Paraguayan samples. Similarly, Caniza et al. (2020) [16] reported 1983 ± 494 mg/kg of Mn and 69 ± 30 mg/kg of Zn in samples analyzed by particle-induced X-ray emission (PIXE).

Iron showed high variability, with concentrations ranging from 33.978 to 189.250 mg/kg (Table 5), corroborating the findings of Olivari et al. (2020) [12], who recorded mean Fe levels of 14.95 ± 5.695 mg/kg in commercial yerba mate samples from Brazil and 7245 ± 1433 mg/kg in samples from Paraguay. The wide range observed for Fe and Zn in the present study (CV = 39.4% and 58.4%, respectively) reinforces that the accumulation of these elements is strongly influenced by the interaction between soil availability, acidity, and organic matter content [15,29].

Chromium exhibited the lowest variability among the evaluated properties, with an average concentration of 1.7 mg/kg in *I. paraguariensis* leaves (Table 5). This relative stability may be associated with physiological mechanisms that regulate Cr absorption and translocation, as well as its inherently low mobility in soil typical of metals with high affinity for mineral fractions and organic matter [31]. However, seven properties (P1, P2, P3, P4, P8, P9, and P10) showed elevated Cr concentrations in the soil, exceeding 100 mg/kg (Table 12). Notably, properties P2 and P4 surpassed the maximum guideline value for agricultural soils (150 mg/kg) established by Brazilian National Council for the Environment [46]. The discrepancy between high soil concentrations and low foliar levels suggests efficient physiological mechanisms in the plant that restrict Cr uptake and translocation, supporting the findings of Sharma et al. (2020) [47], who reported that Cr transfer from roots to aerial tissues is limited and highly dependent on the chemical form of the element within plant tissues. Studies conducted in other yerba-mate-producing regions have reported very low or even undetectable foliar Cr concentrations. Motta et al. (2020) [13] found levels below 0.936 mg/kg in native crops from Paraná, while Olivari et al. (2020) [12] reported approximately 0.16 mg/kg in Brazilian samples commercialized in Spain. Similarly, Górka et al. (2025) [48] found mean Cr concentrations of 0.319 ± 0.078 mg/kg in commercial yerba mate samples imported to Europe, and Pozebon et al. (2015) [11] observed average concentrations of 0.37 ± 0.19 mg/kg in samples from Brazil. These regional differences likely reflect the influence of soil parent material, as soils derived from mafic and ultramafic rocks tend to naturally accumulate higher Cr contents [31]. Although the foliar Cr levels found in this study fall within the ranges reported in the literature, the presence of elevated concentrations in some soils may represent a potential long-term risk of bioaccumulation, particularly in areas of continuous cultivation or under inadequate management. Therefore, systematic monitoring of this element in both soils and plants is essential to ensure the chemical safety and sanitary quality of yerba mate intended for human consumption.

Although selenium is not classified as an essential element for plants, yerba mate is capable of absorbing and accumulating this element in its tissues, which may enhance the nutritional value of the final product. Recent studies have identified Se as a beneficial component at low concentrations; however, excessive levels may pose toxicity risks for consumers [12,49]. The Se concentrations found in our study (Table 5) contrast with significantly lower average values reported in Paraná (0.02 mg/kg), Santa Catarina, and Rio Grande do Sul (0.01 mg/kg) [17], suggesting a distinctive geochemical feature in the study area.

The correlation between macro- and microelements in *I. paraguariensis* leaves indicated that properties with higher K concentrations generally exhibited higher levels of Zn and Mn, suggesting a possible synergistic relationship in the absorption of these nutrients, likely associated with greater availability of exchangeable cations in the soil [3,15]. Conversely, the stability observed for Mg, Cu, and Se, both in this study and in previous works [11,17], suggests the presence of stricter homeostatic mechanisms regulating their foliar concentrations.

Micronutrients such as Mn, Fe, Cu, and Zn are essential for plant growth, stress resistance, and the biosynthesis and function of different plant biomolecules; however,

both deficiency and excess of these elements may lead to physiological disorders in plants and adverse effects on human health [50]. With the exception of Fe, these elements occur at relatively high concentrations in *I. paraguariensis* leaves; nevertheless, this does not necessarily imply full bioavailability to humans, since consumption occurs through infusion rather than by direct ingestion of the leaves. According to Pozebon et al. (2015) [11], the removal of available nutrients during infusion ranges from 20% to 60%, and extraction efficiency varies according to water temperature, extraction time, particle size, and the amount of infusion consumed per day.

Therefore, the results obtained in Mato Grosso do Sul are consistent with the mineral profile of *I. paraguariensis* cultivated in the main yerba-mate-producing regions of South America. These findings reinforce that soil characteristics and acidity are key determinants of macro- and microelement uptake and accumulation in the leaves. Moreover, they highlight the importance of integrating regional geochemical data into the monitoring of the nutritional and environmental quality of yerba mate, particularly in new cultivation frontiers such as the Brazilian Midwest.

5. Conclusions

The findings of this study demonstrate that the accumulation of macro- and microelements in *I. paraguariensis* leaves is directly governed by the physicochemical properties and natural fertility of soils in Mato Grosso do Sul. Sandy and dystrophic soils characterized by low cation exchange capacity (CEC), low organic matter content, and higher acidity exhibited reduced nutrient retention, enhanced micronutrient mobility, and greater variability in foliar elemental composition. In contrast, clayey and more fertile soils with higher CEC and organic matter provided improved buffering capacity, greater nutrient stabilization, and more consistent leaf concentrations, particularly for K, Mg, and P.

The bioaccumulation coefficient (BAC) analysis provided quantitative evidence of differential soil–plant transfer patterns. Elevated BAC values for P and Mg reflected their high physiological demand and efficient uptake, modulated by site-specific soil fertility conditions. Manganese and Zn showed particularly pronounced bioaccumulation, consistent with increased Mn availability under acidic conditions and the essential metabolic roles of Zn in plant physiology. Conversely, the uniformly low BAC values observed for Cr and Fe indicate strong restrictions on their transfer from soil to leaves, reflecting limited solubility, effective physiological regulation, and exclusion mechanisms that reduce accumulation in aerial tissues.

Multivariate analyses further confirmed that spatial variability in soil fertility and geochemical characteristics is the principal driver of elemental uptake patterns in *I. paraguariensis*, reinforcing the strength of soil–plant interactions. Overall, these results indicate that yerba mate efficiently accumulates essential macro- and microelements while limiting the translocation of potentially toxic or non-essential elements to leaves. This highlights the importance of integrating soil chemical characterization with plant mineral analysis to support sustainable management practices, ensure product quality, and safeguard the environmental and nutritional safety of yerba mate cultivated in sensitive Brazil–Paraguay border agroecosystems.

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Abbreviations

The following abbreviations are used in this manuscript:

IBGE	Brazilian Institute of Geography and Statistics
Ca	cadmium
Mg	magnesium
K	potassium
Fe	iron
Zn	zinc
Cr	chromium
Cu	copper
Mn	manganese
P	phosphorus
Se	selenium
UFMS	Federal University of Mato Grosso do Sul
CGMS	CGMS Herbarium of the Institute of Biosciences at UFMS
ICP OES	Inductively Coupled Plasma Optical Emission Spectroscopy
LOD	limit of detection
LOQ	limit of quantification
R^2	correlation coefficient
IUPAC	International Union of Pure and Applied Chemistry
MAPA	Brazilian Ministry of Agriculture, Livestock, and Food Supply
CEC	cation exchange capacity
AAS	atomic absorption spectrophotometry
IAC	Agronomic Institute of Campinas
AES	atomic emission spectrometry
ANOVA	One-way Analysis of Variance
PCA	Principal Component Analysis
CV	coefficient of variation
PC1	Principal Component 1
PC2	Principal Component 2
OM	Organic matter content
ICC	Intraclass correlation coefficient
PIXE	particle-induced X-ray emission

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