

# SOIL CHEMICAL ATTRIBUTES AND THEIR INFLUENCE ON ELEMENTAL COMPOSITION OF YERBA MATE LEAVES

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## Abstract

Yerba mate (*Ilex paraguariensis* St. Hil.) is a raw material used in making a beverage whose chemical composition can be altered by the growing environment and the management adopted during its cultivation. Thus, it is essential that scientific studies are undertaken to understand the chemical composition of yerba mate related to its growing environment. The aim of this work was to determine the elemental composition in the leaves of yerba mate from native cultivations that had never received fertilization and liming, from the Southern Region of the state of Paraná, Brazil. Soil and leaf samples were collected at 11 sites located in the municipalities of São Mateus do Sul, Mallet, São João do Triunfo, and Lapa. Leaf analyzes were performed in an Optical Emission Spectrometer with Inductively Coupled Plasma. The mean concentrations observed (mg kg<sup>-1</sup>), in decreasing order, were: Ca – 7880; K – 7310; Mn – 2418; - Mg – 820; P – 720; Al – 474; Fe – 231; B – 78; Zn – 62; Ba – 62; Cu – 8.9; Ni – 5.6; Cr – 0.82; V – 0.53; Co – 0.17. The Mn concentrations were directly correlated with Al<sup>3+</sup> saturation and inversely correlated with base saturation, pH, and the available Ca<sup>2+</sup>, demonstrating that changes among these soil components can significantly modify the Mn concentrations in the yerba mate leaves. The high concentrations of Mn and Al in the leaves of yerba mate demonstrate the adaptation of this species to acidic soils with high saturation of Al<sup>3+</sup>.

**Keywords:** *Ilex paraguariensis*, trace elements, mineral nutrition, soil fertility.

## Resumo

*Influência das propriedades químicas do solo na composição elementar das folhas de erva-mate.* A erva-mate (*Ilex paraguariensis* St. Hil.) é matéria prima de bebidas cuja composição química pode vir a ser alterada de acordo com o ambiente de cultivo e manejo adotados, tornando-se fundamental trabalhos que discutam a composição química de suas folhas. O objetivo deste trabalho foi determinar a composição elementar de folhas de erva-mate de ervais nativos, que nunca receberam adubação e calagem na região Sul do estado do Paraná. Amostras de solo e folhas de erva-mate *in natura* foram coletadas em 11 propriedades nos municípios de São Mateus do Sul, Mallet, São João do Triunfo e Lapa. As análises das folhas foram efetuadas em ICP-OES. As concentrações médias observadas em ordem decrescentes em mg kg<sup>-1</sup> foram: Ca – 7880; K – 7310; Mn – 2418; - Mg – 820; P – 720; Al – 474; Fe – 231; B – 78; Zn – 62; Ba 62; Cu – 8,9; Ni – 5,6; Cr – 0,82; V – 0,53; Co – 0,17. Os teores de Mn mostraram-se diretamente correlacionado com a saturação por Al<sup>3+</sup> e inversamente correlacionado com a saturação por base, pH e Ca<sup>2+</sup> disponível no solo, demonstrando que alterações entre estes componentes do solo pode modificar significativamente os teores de Mn nas folhas de erva-mate. Os elevados teores de Mn e Al nas folhas de erva-mate demonstram a adaptação desta espécie para solos ácidos e com elevada saturação por Al<sup>3+</sup>.

**Palavra-chave:** *Ilex paraguariensis*, elementos-traço, nutrição mineral, fertilidade do solo.

## INTRODUCTION

Yerba mate (*Ilex paraguariensis* St. Hil.) is a tree species from the Aquifoliaceae family that occurs in the Mixed Ombrophilous Forest, principally between the latitudes 21° S and 30° S and longitudes 48° 30' W and 56° 10' W, cultivated extensively in specific regions of Brazil, Argentina, and Paraguay (HAO *et al.*, 2013). In

Brazil, this species naturally occurs in an estimated area of 450,000 km<sup>2</sup> (TATSCH *et al.*, 2010), mainly in the states of Paraná, Rio Grande do Sul, Santa Catarina, and Mato Grosso do Sul.

The annual production of native yerba mate in Brazil was 346.9 thousand tons, resulting in R\$ 398.8 million, of which the state of Paraná is responsible for 80%. The municipality of São Mateus do Sul (state of Paraná) is the largest producer in Brazil, producing approximately 65,000 tons a year (IBGE, 2016).

The leaves and small branches (diameter < 3 mm) of the yerba mate have been used mainly to make an infusion known as *chimarrão* or *tererê*. Berté *et al.* (2011) have shown that the leaves of the yerba mate have properties useful to humans, similar to that of caffeine, theobromine, and theophylline. On the other hand, the infusion of yerba mate leaves can be a source of nutrients, although potentially toxic elements were found in very low concentrations (REISSMANN *et al.*, 1999; BARBOSA *et al.*, 2015).

A number of factors control the elemental composition of yerba mate leaves, for instance, the genetics (BENEDETTI *et al.*, 2017; BARBOSA *et al.*, 2018), leaf age, time between harvesting, index of light (JACQUES *et al.*, 2007), variation between leaves and fruits (BARBOSA *et al.*, 2015), and soil attributes (REISSMANN *et al.*, 1999; REISSMANN; CARNEIRO, 2004; BARBOSA *et al.*, 2018). Considering that yerba mate leaves are meant for human consumption, it is necessary to identify its elemental composition and its relationship with soil properties, because the soil chemistry can determine the elemental composition and consequently the raw material quality. Thus, the aim of this study undertaken in the Southern part of the state of Paraná was to first, evaluate the elemental composition in yerba mate leaves derived from productive systems that have never received either fertilization or liming. Second, the study aimed to determine if these were correlated with the soil chemistry.

## MATERIAL AND METHODS

Samples of soil and yerba mate leaves were collected in September and October 2013 from 11 farms, located in the Southern part of the state of Paraná. This region experiences temperate climate, classified as Cfb according to Köppen classification, with annual average temperature of 17.1 °C, and annual average precipitation of 1,494 mm.

The sampling sites were spread across four municipalities: São Mateus do Sul (samples 1, 2, and 3), Mallet (samples 4, 5, and 6), São João do Triunfo (samples 7, 8, and 9), and Lapa (samples 10 and 11). In each farm, we collected two samples from plantations that had no history of fertilization and liming.

Soil samples were collected from 0 to 20 cm depth with Dutch augers, below the crown of the sampled plants. The samples were air dried, subsequently ground, and sieved in a 2 mm aperture sieve. The soil attributes that were determined were: pH in 0.01 mol dm<sup>-3</sup> CaCl<sub>2</sub>, Al<sup>3+</sup>, (H + Al), Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, P, and organic C (Table 1), according to the method described by Marques and Motta (2003). The elements P and K were extracted with Mehlich-1 extractor. For quantification of exchangeable Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Al<sup>3+</sup>, 1 mol dm<sup>-3</sup> KCl was used. The base saturation (V%) and Al saturation (m%) based on the CEC pH 7 e effective CEC were calculated.

Table 1. Chemical analysis of the soil of 11 sample units from the Southern region of the state of Paraná. The results of each sampling unit represent the average of both collections carried out in each field.

Tabela 1. Análise química do solo das 11 unidades amostrais da região Sul do estado do Paraná. Os resultados de cada unidade amostral representam a média das duas coletas efetuadas em cada talhão.

	pH	Al <sup>3+</sup>	H+Al	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	CEC pH 7	P	C	V	m
Site	(CaCl <sub>2</sub> )	-----		cmol <sub>c</sub> dm <sup>-3</sup>	-----			mg dm <sup>-3</sup>	g dm <sup>-3</sup>	%	%
1	3.85	3.7	10.90	0.5	0.3	0.11	11.76	1.5	22	7.5	81
2	3.80	2.3	9.05	0.2	0.4	0.24	9.79	1.1	31	7.5	76
3	3.75	3.8	13.55	0.2	0.1	0.07	13.47	0.7	17	2.5	91
4	3.45	8.4	21.20	0.2	0.3	0.16	21.76	1.1	22	2.5	94
5	3.65	6.6	19.00	0.4	0.4	0.20	19.95	1.1	26	5.0	87
6	3.45	7.8	21.20	0.1	0.2	0.13	21.63	1.4	14	2.0	95
7	3.65	6.1	19.00	1.4	0.5	0.16	20.96	1.1	24	9.5	76
8	3.75	3.5	15.85	0.5	0.5	0.16	16.91	0.5	19	6.5	77

<b>9</b>	3.70	7.2	20.40	0.7	0.4	0.18	21.63	1.7	27	5.5	86
<b>10</b>	3.70	3.1	12.60	0.2	0.2	0.08	12.98	0.5	18	3.0	89
<b>11</b>	3.80	3.4	14.65	0.6	0.5	0.12	15.82	3.7	20	7.5	75

Soil and plant samples were collected simultaneously. Mature leaves of 20 plants were collected from the middle portion of the crown, in north exposition. The samples were dried in a microwave oven. Leaves were not washed, following the same procedure adopted by the industry during the beneficiation. In order to avoid contamination with the metal mill, the samples were ground in a stone agate mortar, until particle sizes were smaller than 2 mm.

The digestion of leaves was done by a dry process, incinerated in a furnace at 500 °C for a period of 3 h and solubilized by HCl. The extract obtained were used to determine Ca, K, Mg, P, Mn, Fe, B, Zn, Cu, Ni, Co, Ba, V, Cr, and Al in an Optical Emission Spectrometer with Inductively Coupled Plasma (ICP-OES; Varian, 720-ES). These analyzes were run in duplicate.

All results represent the average of each site, taking into consideration the two samples collected at each site. The resulting data was subjected to cluster analysis and Pearson's correlation. The statistical analyzes were performed using the software R, version 3.4.2.

## RESULTS

### Elemental composition

The descriptive statistics for the analyzed elements in the native yerba mate leaves from the Southern region of the state of Paraná are presented in Table 2. The obtained concentrations, in decreasing order, were Ca > K > Mn > Mg > P > Al > Fe > B > Zn > Ba > Cu > Ni > Cr > V > Co.

The fifteen elements analyzed form five groups (Figure 1) according to their respective concentrations in the leaf tissues: 1 – Mg, Al, and P; 2 – Mn, Ca, and K; 3 – Cr, Co, and V; 4 – Cu and Ni; 5 – Fe, Zn, B, and Ba. These results highlight many interesting aspects, such as the proximity between Ca and K concentrations, and the high Mn and Al concentrations, which grouped with the macronutrients Ca, K, Mg and P, respectively.

Table 2. Descriptive statistics of the elemental composition in yerba mate leaves from 11 non-fertilized sites in the Southern region of the state of Paraná, Brazil.

Tabela 2. Estatística descritiva dos teores elementares de folhas de erva-mate *in natura* de 11 ervais não adubados da região Sul do estado do Paraná.

	Minimum	Maximum	Average	S*
	----- g kg <sup>-1</sup> -----			
<b>Ca</b>	5.83	9.92	7.88	1.11
<b>K</b>	5.22	9.39	7.31	1.09
<b>Mg</b>	0.77	0.86	0.82	0.02
<b>P</b>	0.45	0.99	0.72	0.14
	----- mg kg <sup>-1</sup> -----			
<b>Mn</b>	1164	3672	2418	710
<b>Al</b>	335	612	474	73
<b>Fe</b>	62	364	213	65
<b>B</b>	54	102	78	15
<b>Zn</b>	16	108	62	23
<b>Cu</b>	6.24	11.54	8.89	1.50
<b>Ba</b>	47	76	62	12
<b>Co</b>	0.13	0.20	0.17	0.03
<b>Cr</b>	0.63	1.00	0.82	0.22
<b>Ni</b>	3.89	7.33	5.61	1.26
<b>V</b>	0.27	0.79	0.53	0.13

\* Standard derivation.

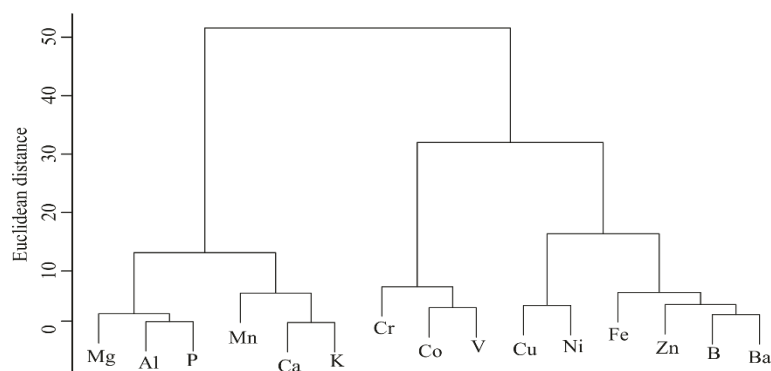


Figure 1. Dendrogram of similarity considering the elemental composition of yerba mate leaves from 11 non-fertilized sites in the Southern region of the state of Paraná, Brazil.

Figura 1. Dendrograma de similaridade considerando a composição elementar de folhas de erva-mate *in natura* de 11 ervais não adubados da região Sul do estado do Paraná.

### Correlation between concentrations of elements in leaves

The correlation between concentrations of elements in yerba mate leaves was determined using Pearson's correlation coefficient (Table 3). The Al concentration in yerba mate leaves showed positive correlation with Fe and Mg, and a negative correlation with Co. Phosphorus presented a positive correlation with Cu and negative correlation with Mn. Additionally, positive correlations occurred between V and Fe, Co and Mn, and Ca and Ba. Negative correlation was observed between K and Ba.

Table 3. Pearson's correlation coefficient between concentration of elements in yerba mate leaves from 11 non-fertilized sites in the Southern region of the state of Paraná, Brazil.

Tabela 3. Coeficiente de correlação de Pearson dos teores foliares de erva-mate proveniente de 11 ervais não adubados, da região Sul do estado do Paraná.

	Al	B	Cu	Fe	Mn	Zn	Ba	Cr	Co	Ni	V	Ca	K	Mg
<b>B</b>	0.08													
<b>Cu</b>	0.24	0.10												
<b>Fe</b>	0.73*	-0.24	0.15											
<b>Mn</b>	-0.32	-0.43*	-0.51*	0.09										
<b>Zn</b>	0.13	-0.23	0.06	0.00	0.09									
<b>Ba</b>	0.46*	-0.04	-0.02	0.49*	0.30	-0.05								
<b>Cr</b>	-0.11	0.44*	-0.41	0.07	0.35	-0.14	0.10							
<b>Co</b>	-0.70*	-0.16	-0.19	-0.44	0.62*	-0.02	-0.09	0.31						
<b>Ni</b>	0.03	0.41	0.47	-0.09	-0.35	-0.53*	0.04	0.06	-0.03					
<b>V</b>	0.36*	-0.14	0.15	0.82*	0.17	-0.24	0.42*	0.24	-0.18	0.06				
<b>Ca</b>	0.11	-0.19	-0.50*	0.27	0.59*	0.23	0.67*	0.18	-0.02	-0.46*	0.20			
<b>K</b>	-0.47*	0.40	0.18	-0.57*	-0.28	0.06	-0.64*	0.07	0.22	0.16	-0.43	-0.54*		
<b>Mg</b>	0.70*	0.27	-0.18	0.57*	-0.07	-0.13	0.54*	0.25	-0.43*	-0.22	0.33	0.33	-0.39	
<b>P</b>	0.42*	-0.01	0.80*	0.09	-0.61*	0.36	-0.12	-0.51*	-0.31	0.16	-0.10	-0.51*	0.07	-0.06

\* p value <0.05.

### Correlation between elements in yerba mate leaves and soil chemical attributes

The Pearson correlation coefficient values between elemental composition in yerba mate leaves and soil chemical attributes are presented in Table 4. The most significant positive correlations were between soil pH and B concentration in leaves,  $\text{Ca}^{2+}$  concentration in soil and P concentration in leaves, and base saturation (V%) with Mn concentration in leaves.

Table 4. Pearson's correlation coefficient between elements in yerba mate leaves and soil chemical attributes from 11 non-fertilized sites in the Southern region of the state of Paraná, Brazil.

Tabela 4. Coeficiente de correlação de Pearson dos teores nutricionais de folhas de erva-mate provenientes de 11 ervais não adubados da região Sul do estado do Paraná, correlacionados com propriedades químicas do solo.

	pH	$\text{Al}^{3+}$	$\text{H} + \text{Al}^{3+}$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{K}^+$	CEC	P	C	V%	m%
<b>Al</b>	-0.05	-0.03	0.19	0.48	0.28	0.00	0.24	0.00	0.09	0.18	-0.24
<b>B</b>	0.65*	-0.63*	-0.43	0.19	0.59*	0.09	-0.38	0.44	0.10	0.56	-0.78*
<b>Cu</b>	0.34	-0.49	-0.39	0.43	0.03	-0.30	-0.35	-0.42	-0.16	0.39	-0.42
<b>Fe</b>	-0.10	-0.16	-0.11	-0.19	-0.36	-0.31	-0.13	-0.31	-0.14	-0.33	0.24
<b>Mn</b>	-0.65*	0.37	0.21	-0.74*	-0.58	-0.06	0.13	0.03	-0.33	-0.71*	0.69*
<b>Zn</b>	-0.46	0.43	0.43	0.15	0.18	0.50	0.45	-0.22	0.19	0.05	0.08
<b>Ba</b>	0.07	-0.33	-0.30	-0.30	-0.04	0.19	-0.30	-0.01	0.22	-0.06	-0.09
<b>Cr</b>	0.01	-0.28	-0.19	-0.70*	-0.17	-0.11	-0.25	0.20	-0.38	-0.39	0.11
<b>Co</b>	-0.29	0.16	0.01	-0.53	-0.40	-0.25	-0.04	0.00	-0.53	-0.39	0.40
<b>Ni</b>	0.56	-0.58*	-0.49	0.04	-0.22	-0.50	-0.51	-0.09	-0.31	0.07	-0.20
<b>V</b>	0.08	-0.32	-0.30	-0.34	-0.46	-0.43	-0.33	-0.30	-0.23	-0.36	0.25
<b>Ca</b>	-0.20	0.11	-0.02	-0.42	-0.04	0.51	-0.03	0.20	0.46	-0.17	0.16
<b>K</b>	0.42	-0.37	-0.37	0.07	0.24	0.01	-0.35	0.06	-0.05	0.40	-0.45
<b>Mg</b>	0.00	-0.09	0.12	0.09	0.43	0.22	0.15	0.29	0.19	0.12	-0.29
<b>P</b>	-0.05	0.01	0.15	0.72*	0.31	-0.03	0.22	-0.35	-0.05	0.44	-0.36

\* p value <0.05.

## DISCUSSION

### Elemental composition

The nutrients Ca and K presented the highest concentrations in yerba mate leaves (Table 2). The soils, in general, presented a low and medium concentration for extractable Ca and K, respectively. This fact suggested a high capacity for Ca uptake by yerba mate. The concentration of Ca in the mate leaves was similar to those observed by Oliva *et al.* (2014) at Barão de Cotegipe municipality (state of Rio Grande do Sul, Brazil) (average of  $7.80 \text{ g kg}^{-1}$ ) but was lower than those in the Ivaí municipality (state of Paraná, Brazil) (average of  $11.20 \text{ g kg}^{-1}$ ). With regards to K, in the same study, the averages were higher than that recorded in our work, with concentrations of  $12.30$  and  $11.90 \text{ g kg}^{-1}$ , respectively at the municipalities of Barão de Cotegipe and Ivaí. It is important to consider that K easily washes off with water, and hence its concentration can be altered with rainfall.

The average concentrations of Mg and P (Table 2) were smaller than those observed in other studies at the state of Paraná, with an average concentrations of Mg and P of  $4.93$  and  $1.17 \text{ g kg}^{-1}$ , respectively, at the municipality of General Carneiro (CALDEIRA *et al.*, 2006), and  $5.80$  and  $11.90 \text{ g kg}^{-1}$ , respectively at the municipality of Ivaí (OLIVA *et al.*, 2014). As described, the sampling sites were never fertilized, nor had lime been applied in order to correct for acidity. Further, the sites had sedimentary rocks as parent material, which had low natural concentrations of essentials nutrients, such as Mg and P.

Although the concentration of Mn was the highest among micronutrients and amongst the analyzed elements, it showed a wide variation in values (Table 2). Our results confirm earlier observations that yerba mate leaves under native conditions presented high Mn concentration (REISSMANN *et al.*, 1999; HEINRICHS; MALAVOLTA, 2001; CALDEIRA *et al.*, 2006). The elevated concentration of Mn in yerba mate leaves necessitates attention because it is a micronutrient and was found in concentrations higher than macronutrients, such as Mg and P. Furthermore, normal concentrations of Mn in leaves differ between species, typically varying between 30 and 500 mg kg<sup>-1</sup>, and concentrations above this range could be toxic to most vegetable species (MILLALEO *et al.*, 2010).

Therefore, the observed concentrations of Mn suggest that yerba mate is a Mn-tolerant species, showing concentrations much higher than what would be considered toxic for majority of crops, reaching values that exceed 3000 mg kg<sup>-1</sup> of Mn in leaves (REISSMANN *et al.*, 1999). Soil acidity, with pH lower than 4.0 that was seen in all our soil samples is a factor that has to be considered to explain the high availability of Mn. However, the variations in pH provided little support for the large variation in the Mn level that was observed. Barbosa *et al.* (2018) reported that elevated concentrations of Mn in leaves were dependent on its availability, as well as the amount of low crystalline compounds containing Mn in the soil.

Manganese is an integral part of superoxide dismutase (SOD) structure, an enzyme that catalyzes the dismutation of O<sup>2</sup> and H<sub>2</sub>O<sub>2</sub> (BARBOSA *et al.*, 2013). These enzymes are responsible for the detoxification of oxygen free radicals (ROS), both in vegetable cells and animal cells. When imbalance occurs in the catalysis of ROS, different alterations occur in the tissues, including the decline in cell functions that can contribute to ageing and degenerative diseases (ENGERS *et al.*, 2007). Thus, the elevated levels of Mn in yerba mate leaves show a pharmacological potential that needs to be explored. In addition, there is also a need to understand the contribution of Mn to the nutritional requirements of the plants (BARBOSA *et al.*, 2015).

The aluminum concentrations found in the yerba mate leaves (Table 2) were similar to those reported in previous studies (REISSMANN *et al.*, 1999; HEINRICHS; MALAVOLTA, 2001; CALDEIRA *et al.*, 2006; OLIVA *et al.*, 2014; BARBOSA *et al.*, 2018). According to Reissmann *et al.* (1999), yerba mate is a species that is Al-tolerant. The adaptation of yerba mate to tolerate Al can be considered an important evolutionary characteristic because its natural area of distribution is in acidic soils with high Al<sup>3+</sup> saturation (REISSMANN *et al.*, 1999), such as in this study where values higher than 75% was observed (Table 1). The Al<sup>3+</sup> in high concentration in soil solutions could provoke root toxicity; however, Benedetti *et al.* (2017) reported that Al stimulates root growth in yerba mate.

The average concentration of Fe and Zn (Table 2) were higher than that observed by Oliva *et al.* (2014), which were 98.60 and 85.70 mg kg<sup>-1</sup> Fe and 15.30 and 16.50 mg kg<sup>-1</sup> Zn, in samples from the municipalities of Ivaí and Barão de Cotegipe, respectively. The Zn concentrations are consistent with those found by Pandolfo *et al.* (2003) who reported an average concentration of 41 mg kg<sup>-1</sup>. The authors have reported an average Fe concentration of 191 mg kg<sup>-1</sup>.

Regarding the average concentration of B and Cu (Table 2), these were similar to concentrations at the municipality of Barão de Cotegipe, where an average of 85 and 7.70 mg kg<sup>-1</sup>, respectively, was reported (OLIVA *et al.*, 2014). According to the same study, the concentrations recorded in the municipality of Ivaí were higher, at 70 and 11.80 mg kg<sup>-1</sup>, respectively. Reissmann *et al.* (1999) reported B concentrations in yerba mate leaves between 11 and 79 mg kg<sup>-1</sup>, and in plants that were one year old, the concentrations ranged between 20 and 23 mg kg<sup>-1</sup>.

The average concentration of Ni (Table 2) was less than that reported by Heinrichs and Malavolta (2001) for processed yerba mate, but higher than that observed by Barbosa *et al.* (2015) for leaves and fruits of four yerba mate varieties. For V, the concentrations measured were higher than that reported by Barbosa *et al.* (2015) and Barbosa *et al.* (2018). Vanadium has a number of health benefits for humans, such as to control the sugar levels in the blood in diabetic people, anti-tumoral and anti-carcinogenic activity, although high dosages can have negative effects (KORBECKI *et al.*, 2012). These need to be better studied.

Pozebon *et al.* (2015) evaluated the elemental composition of 54 samples of commercial yerba mate from Brazil, Paraguay, Argentina, and Uruguay. Their results indicate that the average concentrations measured for Ca, Fe, Ba, Zn, V, and Co were similar to those obtained in this study (Table 2). However, concentrations of Al, Mn, Cr, and Ni were lower than that observed in our study, while that of K, Mg, P, and Cu were higher. Although these samples were taken from commercial yerba mate, that had been industrially processed and would normally have 30% of finning branches, no significant differences were observed when compared to the non-processed yerba mate that was analyzed in this study.

### Correlation between concentrations of elements in leaves

The strong correlation between Fe and V (Table 3) that we observed was similar to the results of Barbosa *et al.* (2018). In acidic soils, although V is predominant in its ionic form ( $\text{VO}_2^+$ ), it presents a number of oxidation states that have ionic radiuses similar to  $\text{Fe}^{2+}$  (0.74 Å) (KABATA; PENDIAS, 2011). Additionally, the V and Fe can share the same transporter form from the roots to the shoot, because  $\text{Fe}^{2+}$  is transported in complexes, principally with citrate (KOBAYASHI; NISHIZAWA, 2012).

### Correlation between elements in yerba mate leaves and soil chemical attributes

The correlation between V% and Mn suggested that Mn concentrations in yerba mate leaves can be altered with soil base saturation. This conclusion is supported by the finding of Reissmann and Carneiro (2004) who observed a reduction of 807  $\text{mg kg}^{-1}$  in Mn concentration in yerba mate leaves when lime was applied to enhance the V% from 11.6 to 100%.

Significant negative correlations were observed between soil pH and Mn in leaves, soil  $\text{Al}^{3+}$ , and m% with B in leaves, soil Ca with Mn and Cr in leaves, and between V% and Mn in leaves. The B in leaves was found to be positively correlated to the soil pH and negatively correlated to soil  $\text{Al}^{3+}$  and m%, which can be explained by the direct effect that the soil pH has on  $\text{Al}^{3+}$  availability and consequently on the m%, although the availability of  $\text{Al}^{3+}$  is also influenced by mineralogy and soil organic carbon (RABEL *et al.*, 2018).

Additionally, these correlations explained the high variation in the concentration of Mn in yerba mate leaves. The increase in soil pH and the consequent increase in base saturation and decrease in  $\text{Al}^{3+}$  in the soil solution occurred with a proportional decrease in the Mn concentrations in yerba mate leaves (Figure 2). However, the increase in Ca concentration in soil also contributed significantly to the decreased Mn levels.

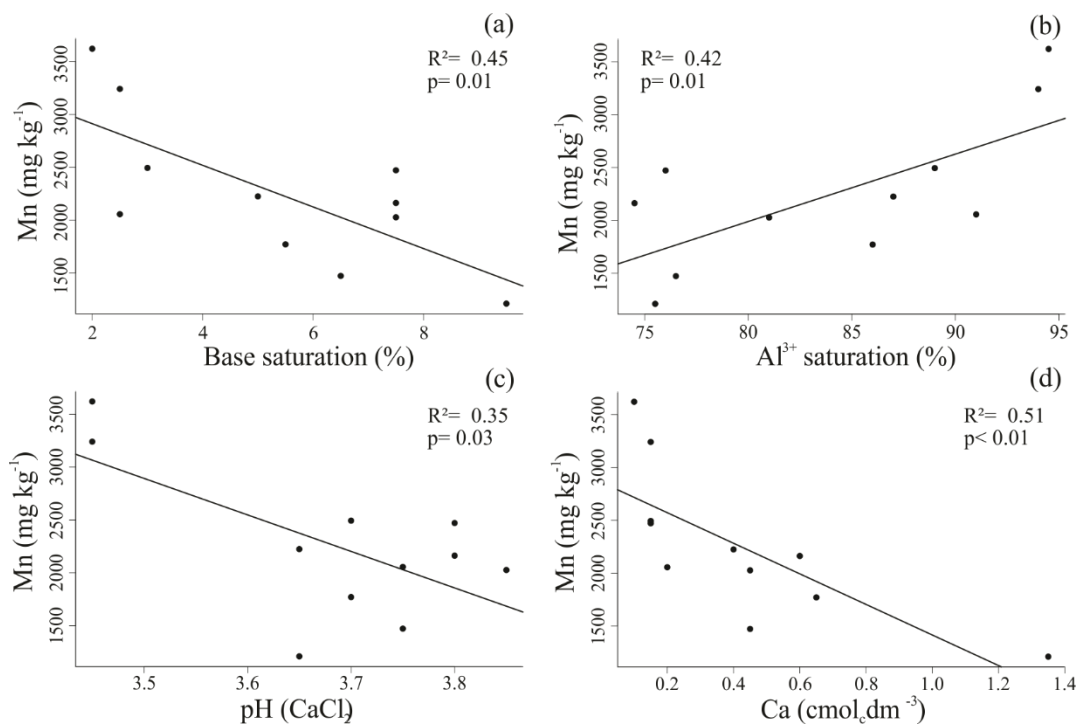


Figure 2. Linear regression analysis between the Mn content of yerba mate leaves with (a) base saturation, (b) saturation by  $\text{Al}^{3+}$ , (c) pH  $\text{CaCl}_2$ , and (d) Ca concentration, from 11 non-fertilized plantations in the Southern region of the state of Paraná, Brazil.

Figura 2. Análise de regressões lineares entre o teor de Mn em folhas de erva-mate com (a) saturação por bases, (b) saturação por  $Al^{3+}$ , (c) pH  $CaCl_2$ , e (d) concentração de Ca, provenientes de 11 ervais não adubados da região Sul do estado do Paraná.

Our results suggest that the adoption of management practices to correct soil acidity, such as the application of lime, can significantly decrease Mn accumulation in yerba mate leaves due to increase in soil pH, V%, and Ca availability, in addition to decreases in m%. As already discussed, yerba mate is a Mn-tolerant species, and neither high or low concentrations of this nutrient affect the development of the plant.

## CONCLUSIONS

- Yerba mate shows high Ca extraction capacity from the soil.
- Yerba mate leaves contain a small amount of V, which was strongly correlated with the Fe concentration.
- Chemical attributes of the soil determine the concentration of elements in yerba mate leaves, especially Mn.
- High concentrations of Mn and Al in the leaves of yerba mate suggest that this species is adapted to acidic soils.

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