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Multi-elemental Analysis and Health Risk Assessment of Commercial Yerba Mate from Brazil

Nayara Caroline Majewski Ulbrich[1] · Luciane Lemos do Prado[2] · Julierme Zimmer Barbosa[3] · Eloá Moura Araujo[1] · Giovana Poggere[4] · Antônio Carlos Vargas Motta[1] · Stephen A. Prior[5] · Ederlan Magri[1] · Scott D. Young[6] · Martin R. Broadley[6]

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Abstract

Consumption of yerba mate occurs mostly in the form of hot infusion (*chimarrão*). Water solubility of elements found in commercialized yerba mate is needed to establish nutritional value and risks associated with potentially toxic elements. In this study, yerba mate products marketed in three Brazilian states (*Paraná*, *Santa Catarina*, and *Rio Grande do Sul*) for *chimarrão* were analyzed. Total (dry product) and hot water-soluble concentrations of Al, As, B, Ba, Ca, Cd, Co, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, P, Pb, Rb, S, Se, Sr, Ti, V, and Zn were determined by inductively coupled plasma mass spectroscopy (ICP–MS). Total concentrations of the ten top elements followed the order of K>Ca>Mg>Mn>P>S>Al>Fe>Ba>Zn. The most soluble elements were B, Cs, Ni, Rb, and K, with values greater than 80%. The lowest water-soluble elements were V, Fe, and Ti (values <10%), followed by Ba, Cd, Al, As, Sr, Ca, and Pb with solubility between 10 and 20%. Although total Cd levels in yerba mate products were often above those permitted by South America legislation, estimated daily consumption intake indicated no risk associated with the *chimarrão* beverage. Manganese was the micronutrient with the highest total and soluble levels in yerba mate, which surpassed recommended daily intake values when considering a consumption amount of 50 g day^{-1} of yerba mate as *chimarrão*. The consumption of yerba mate is safe and contributes to intake of nutrients. The Cd and Pb reference values of yerba mate products sold in South America should be revised.

Keywords Herbal beverage · Potentially toxic elements · Trace elements · Determination of origin · Dietary intake

✉ Nayara Caroline Majewski Ulbrich
nayaraulbrich@gmail.com

Luciane Lemos do Prado
lucianeprado@ufpr.br

Julierme Zimmer Barbosa
barbosajz@yahoo.com.br

Eloá Moura Araujo
eloamoura@alumni.usp.br

Giovana Poggere
gi.poggere@gmail.com

Antônio Carlos Vargas Motta
mottaacv@ufpr.br

Stephen A. Prior
steve.prior@usda.gov

Ederlan Magri
ederlan.magri@gmail.com

Scott D. Young
scottdy1955@outlook.com

Martin R. Broadley
martin.broadley@nottingham.ac.uk

1 Department of Soils and Agricultural Engineering, Federal University of Paraná (UFPR), Curitiba, Paraná, Brazil

2 Department of Hydraulics and Sanitation, Federal University of Paraná (UFPR), Curitiba, Paraná, Brazil

3 Federal Institute of Southeast of Minas Gerais, Barbacena, Minas Gerais, Brazil

4 Department of Biological and Environmental Sciences, Federal Technological University of Paraná, Medianeira, Paraná, Brazil

5 USDA-ARS National Soil Dynamics Laboratory, 411 South Donahue Drive, Auburn, AL, USA

6 Science School of Biosciences, University of Nottingham, Sutton Bonington Campus, Nottingham, UK

Introduction

Yerba mate (*Ilex paraguariensis* – A. St. Hil.) is a tree species native to some regions in South America, with natural occurrence in Brazil, Argentina, and Paraguay. About 80% of it natural occurrence area is in Brazil, in the states of *Paraná*, *Santa Catarina*, *Rio Grande do Sul*, *Mato Grosso do Sul*, and *São Paulo* [1–3]. In 2019, Brazil produced almost 518 thousand tons of yerba mate (raw material), with 82% of this production occurring in the states of *Rio Grande do Sul* and *Paraná* [4].

Yerba mate is primarily used for human consumption. Ground leaves and thin branches are used in *chimarrão* (hot infusion) and *tererê* (cold infusion), corresponding to 96% of yerba mate consumption [5]. Yerba mate has also been used in food, phytopharmaceuticals, and cosmetic industries [6]. Regarding health, yerba mate is a central nervous system stimulant and diuretic with antioxidative effects that has been shown to influence hypocholesterolemia and hepatoprotection; these characteristics are due to the presence of polyphenols, flavonoids, caffeine, theobromine, amino acids, vitamins, and nutrients [2, 3].

To evaluate benefits and risk of yerba mate consumption, total elemental concentration in yerba mate leaves and commercial products (i.e., dry products) has focused on N, P, K, Ca, Mg, S, B, Cu, Fe, Mn, Ni, Zn, Al, Cd, Co, Cr, Na, Pb, and Ba [7–10]. Among these elements, high concentrations of K, Mg, Mn, Ca, P, S, Fe, and Al stand out [11]. However, concentrations of these elements show significant variation depending on soil nutrient availability, genetic variations, leaf age, type of planting, and soil parent material [11–14].

The National Health Surveillance Agency (ANVISA) of Brazil regulates the maximum limits of total As (0.60 mg kg^{-1}), Cd (0.40 mg kg^{-1}), and Pb (0.60 mg kg^{-1}) for tea, yerba mate, and other vegetable infusion products marketed in Mercosul [15] which represents all South American countries. Based on this legislation, several studies have evaluated concentrations of As, Cd, and Pb in yerba mate leaves and products [9, 11, 12, 16–19]. [11] found that As concentration is very low (from 0.014 to 0.056 mg kg^{-1}); but in many cases, the concentration of Cd and Pb can be higher than the regulated limit set by Mercosul legislation [18].

Since yerba mate consumption occurs as a beverage from hot infusion, total elemental concentrations of dry material may not represent the best means of evaluating potential nutritional benefits and/or health risks [20]. Knowledge regarding hot infusion concentrations and beverage consumption amounts can be used to determine daily elemental intake [21, 22]. However, little is known about elemental solubility of yerba mate. Previous studies reported high levels of K, Mg, Ca, P, Mn, and Zn in yerba mate infusions [16, 20]. Determining the percentage of trace elements that are hot water soluble (e.g., As, Cd, Cr, and Pb) can be difficult given that the very low concentrations in infusion solutions can be below detection limits of modern instruments [7, 23]. Also, reported elemental values for hot water solubility of commercial yerba mate are variable. [24] found respective mean percentages of 2.8, 7.0, and 3.5 for Cd, Cr, and Pb, respectively, while [9] found percentages of 53, 26, and 75 for these same elements. Analysis of yerba mate leaves by [20] revealed water-soluble values above 40, 50, and 30 % for Cd, Cr, and Pb, respectively. Due to the variability in findings, more research is necessary to determine the water solubility of elements in yerba mate solutions.

Considering that legislation is based on total concentration found in dry products and that the main form of yerba mate consumption occurs by *chimarrão* (hot water infusion), concentrations of both total (dry product) and hot water-soluble elements were determined for different commercial yerba mate products sold in three states of southern Brazil. Intake was estimated based on water solubility and compared to recommended levels in order to assess nutritional values and consumer risks associated with potentially toxic elements.

Methodology

Sample Preparation

Thirty-five samples of yerba mate for *chimarrão* were obtained from Brazilian supermarkets in *Santa Catarina* (SC; n = 14), *Rio Grande do Sul* (RS; n = 12), and *Paraná* (PR; n = 9) states in southern Brazil. Samples were homogenized, dried (65°C), and milled (< 1 mm).

Elemental Extraction and Determination

For total elemental extraction, 200 mg of dry samples were digested in perfluoroalkoxy-coated digestion tubes (PFA) using a Multiwave 3000 with an MF50 rotor (Anton Paar GmbH, Graz, Austria). Samples were digested in 2 mL of concentrated nitric acid (HNO_3 65%), 1 mL of ultrapure water (Milli-Q system — resistivity of 18.2 MΩ cm; Fisher Scientific UK Ltd), and 1 mL of concentrated hydrogen peroxide (H_2O_2). Samples were digested for 45 min at 140° C, under a pressure of 20 bars and power output of 1400 W. Each digestion run also included two tubes with reagents only (blank sample) and two tubes with 200 mg of a standard (NIST Tomato 1573A, National Institute of Standards and Technology, NIST, Gaithersburg, MD, USA). After digestion, each tube was brought to a final volume of 15 mL using ultrapure water. Samples were transferred to universal tubes, homogenized, and stored at room temperature prior to analysis.

For elemental determinations, samples were diluted 1:5 with ultrapure water. Concentrations of Al, As, B, Ba, Ca, Cd, Co, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, P, Pb, Rb, S, Se, Sr, Ti, V, and Zn were determined by inductively coupled plasma mass spectrometry (ICP–MS; Thermo Fisher Scientific iCAPQ, Thermo Fisher Scientific, Bremen, Germany). Samples were introduced into auto amplifier incorporating an ASXpress™ fast absorption module (Cetac ASX-520, Teledyne Technologies Inc., Omaha, NE, USA) through a PEEK nebulizer (Burgener Mira Mist, Mississauga, Burgener Research Inc., Canada). Elemental recovery values (%) of the standard sample were: Al (73), As (152), B (89), Ba (107), Ca (97), Cd (98), Co (91), Cs (103), Cu (77), Fe (98), K (98), Mg (84), Mn (91), Mo (98), Ni (92), P (104), Rb (103), S (102), Se (156), Sr (110), V (84), and Zn (86).

Elemental water solubility was obtained according to [9]. Approximately 500 mg of sample was weighed and transferred to a polypropylene bottle. Then, 20 mL of ultrapure water (at 100°C) was added, and the sample remained under infusion for five min. After cooling, the suspension was filtered, diluted ten times with 5% (v/v) nitric acid, transferred to a universal tube, and stored at room temperature. Concentrations of Al, As, B, Ba, Ca, Cd, Co, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, P, Pb, Rb, S, Se, Sr, Ti, V, and Zn were also determined with ICP–MS.

Calculation of Element Intake via Infusion

Water solubility of elements was estimated based on total and water-soluble concentrations. That is, water solubility (%) = mass of elements found in hot infusion × 100/total amount found in the yerba mate dry product sample. Five groups of elemental hot water solubility were established: high (81–100%); medium (51–80%); low (21–50%); very low (10–20%), and extremely low solubility (<10%) (Tables 1 and 2).

To calculate the estimated intake of elements by consumption of yerba mate, we adopted values related to *chimarrão*, which is the main consumption form of yerba mate in Brazil [5]. For *chimarrão* preparation, dry leaves (about 50 g) are packed into a gourd, and hot water is poured over them; this is then repeated multiple times, with as much as half to 1 L of water [2]. Estimates of daily intake of elements by a *chimarrão* consumer were based on 50 g of yerba mate and previously determined water-soluble concentrations. Daily intake values were compared with intake indices to determine the contribution of *chimarrão* consumption to the diet of adult humans (70 kg body weight) (Table 3). The indices used were recommended dietary allowance (RDA), the average daily dietary intake level, sufficient to meet the nutrient requirements of nearly all (97–98%) healthy individuals in a group [29], and tolerance upper intake (TUI), the level of daily element intake that likely presents no health risk effects for most people [28]. For elements that did not have values for either of these two indices, the maximum daily intake value (DI) was adopted

Data Analysis

Data were submitted to the residue normality test (Shapiro-Wilk) and, when necessary, transformed using Box-Cox transformation to reach normality. Pearson correlation was applied to total and water-soluble concentrations. Principal component analysis (PCA) was performed from the correlation matrix of normality and standardized data to select variables that best explain data variability. These selected variables were used in linear discriminant analysis to attest the possibility of classifying samples according to their geographical origin. All analyses were performed using the statistical software R [33].

Results and Discussion

Total Concentration of Dry Product

Major elements of yerba mate samples from the three locations showed the following order of total concentration: K > Ca > Mg > Mn > P > S > Al > Fe > Ba > Zn > Sr > B > Rb > Cu > Ti > Ni > other elements (Table 1). The only difference was that B > Sr in the *Paraná* state samples. It was not possible to determine a concentration pattern for occurrence of other elements. [7, 23] found similar concentrations and order of occurrence.

Among micronutrients, Mn showed the highest concentration that ranged between 523 and 2475 mg kg^{-1} (Table 1). According to [34], normal levels of Mn in plants differ greatly among species (30–500 mg kg^{-1}). However, yerba mate displays a different Mn accumulation pattern. Studies have shown that yerba mate has an average of 3000 mg kg^{-1}, with maximum values close to 10,000 mg kg^{-1} [11, 35]. [14] found that yerba mate can accumulate high levels of Mn in the leaves (~10,000 mg kg^{-1}) without growth impairment.

In general, total concentrations of As, Cd, and Pb were below maximum limits established by legislation (0.60, 0.40, and 0.60 mg kg^{-1}, respectively) [15], with exception of an average 0.66 mg kg^{-1} Cd in samples from *Rio Grande do Sul* (Table 1). Past studies indicate that Cd is frequently found in concentrations above values established by legislation [11, 17, 18, 36]. Based on these findings, [11, 18] indicate a need to revise established limits since these concentrations can be considered natural.

Hot Water Solubility

Elements were classified according to solubility percentage in hot water (Fig. 1): K > Rb > Ni > Cs > B (81–100%), high; Mg > Cu > S > P > Mn (51–80%), medium; Zn > Li > Mo > Se (21–50%), low; Ca > As > Pb > Sr > Al > Ba and Cd (10–20%), very low; and Ti > Fe > V (< 10%), extremely low.

Table 1 Elemental composition of commercial yerba mate products, used for *chimarrão* (hot infusion), sold in supermarkets in three states of southern Brazil (*Paraná*, *Santa Catarina*, and *Rio Grande do Sul*)

	Paraná					*Santa Catarina*					*Rio Grande do Sul*				
	$\overline{\mathbf{M}}$[1]	M_d	Min.	Max.	SD	$\overline{\mathbf{M}}$	M_d	Min.	Max.	SD	$\overline{\mathbf{M}}$	M_d	Min.	Max.	SD
	g kg^{-1}														
Ca	6.76	7.01	5.62	7.27	0.54	7.2	7.44	6.08	8.05	0.67	7.07	7.18	5.45	8.34	0.75
K	11.97	12.43	9.24	13.27	1.19	12.43	12.30	10.54	13.78	0.90	14.06	14.22	11.71	15.84	1.43
Mg	4.19	4.37	3.24	5.09	0.61	4.71	4.98	3.59	5.82	0.72	4.53	4.29	3.21	6.41	0.90
S	0.93	0.96	0.79	1.03	0.08	1.01	1.03	0.73	1.12	0.10	1.01	1.01	0.91	1.12	0.07
P	1.02	0.96	0.75	1.28	0.21	1.07	1.10	0.93	1.19	0.09	1.26	1.24	0.96	1.63	0.18
	mg kg^{-1}														
Al	378	368	174	548	113	332	331	211	434	56	336	329	165	623	115
As	0.04	0.03	0.01	0.08	0.02	0.03	0.03	0.02	0.04	0.01	0.04	0.04	0.02	0.08	0.02
B	35	37	27	42	5	39	40	27	50	6	38	35	26	54	8
Ba	66	69	52	78	9	68	68	56	85	8	69	65	51	102	13
Cd	0.40	0.37	0.27	0.63	0.13	0.47	0.50	0.23	0.66	0.13	0.66	0.70	0.30	1.08	0.21
Co	0.21	0.19	0.10	0.41	0.09	0.27	0.28	0.10	0.34	0.06	0.28	0.20	0.09	0.79	0.21
Cs	0.53	0.51	0.26	0.81	0.19	0.39	0.32	0.17	0.92	0.21	0.26	0.23	0.13	0.50	0.11
Cu	9.22	9.38	7.27	10.79	0.95	9.79	9.71	8.41	11.29	0.73	9.18	8.55	7.39	11.71	1.48
Fe	280	164	94	773	221	197	169	124	404	76	248	175	78	1033	259
Li	0.11	0.08	0.04	0.20	0.06	0.07	0.06	0.05	0.11	0.02	0.10	0.08	0.06	0.26	0.06
Mn	1313	1377	523	2282	592	1439	1474	649	1772	282	1334	1266	676	2475	430
Mo	0.05	0.05	0.03	0.07	0.02	0.05	0.05	0.03	0.09	0.02	0.10	0.09	0.05	0.16	0.03
Ni	2.19	2.26	1.06	2.77	0.55	3.00	2.99	1.98	3.60	0.43	2.19	1.90	0.99	4.10	1.03
Pb	0.28	0.26	0.12	0.47	0.12	0.21	0.18	0.10	0.45	0.11	0.26	0.24	0.12	0.46	0.11
Rb	32	32	22	43	6	28	26	19	49	9	33	34	18	5	11
Se	0.03	0.02	0.01	0.07	0.02	0.02	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.03	0.01
Sr	35	35	31	41	4	31	29	24	44	5	33	34	26	37	3
Ti	7.63	5.97	3.54	16.05	4.16	5.53	5.37	3.59	6.76	0.99	5.42	4.54	2.46	10.74	2.64
V	0.83	0.56	0.29	2.26	0.67	0.57	0.61	0.23	0.84	0.18	0.61	0.40	0.14	2.10	0.57
Zn	55	49	39	79	13	654.68	71	34	95	18	68	71	46	104	19

[1] $\overline{\mathbf{M}}$, mean; M_d, median; Min., minimum value; Max, maximum value. *SD* standard deviation.

Solubility percentage did not follow the same order as concentration found in the infusion, which occurred in the following order: K > Mg > Ca > Mn > P > S > Al > Zn > Rb > B > Ba > Cu > Sr > Fe > Ni > others (Table 1S).

Pearson's correlation coefficient between total and soluble levels showed a very strong correlation ($1.0 \geq r > 0.9$) for the elements Mn, Mo, and Ni; strong correlation for K, Mg, Ca, P, B, Zn, Se, and Co ($0.9 \geq r > 0.7$); moderate correlation for Cu ($r = 0.68$); and weak correlation for S and Fe ($0.5 \geq r > 0.3$). Solubility percentage of the elements is associated with factors such as nature of the chemical element, plant abundance, compounds containing the element, extraction temperature, and pH of extraction solution [37].

Potassium was the macronutrient found in greatest concentration in dry product and had the highest solubility percentage (92 ± 7.1%) (Fig. 1). Most K in plants is in the soluble form and is very permeable to the plasmatic membrane when not part of organic compound [38]. For this reason, K is highly soluble in yerba mate leaves and products (Table 2) similar to tea. The macronutrients Mg, S, and P showed average solubilities of 68, 57, and 58%, respectively (Fig. 1). Plant Mg is primarily found in soluble and diffusible forms, is associated with organic and inorganic anions (e.g., malate and citrate), and is a constituent of chlorophyll molecules [39]. Sulfur in plants is predominantly found in proteins or in the form of $BaSO_4$ [9]. Since the concentration of Ba in this study was 10 times less than observed S concentration, S in protein forms was of major importance. Phosphorus in plant tissues is also found in organic (phospholipids, phytin, and nucleic acids) and inorganic forms. In plants, these macronutrients are considered mobile, which can also facilitate their solubilization in hot water [38]. Conversely, Ca in plants is usually

Table 2 Hot water solubility (%) of elements in yerba mate products evaluated in this study and values found in the literature for yerba mate, *Camellia sinensis*, and other herbs used as infusions drink

Element	This study Yerba mate Products	Pozebon et al. (2015) [9] Yerba mate Products	Heinrichs and Malavolta (2001) [7] Yerba mate Products	Giulian et al. (2007) [8] Yerba mate Products	Barbosa et al. (2015) [20] Yerba mate Leaves	Dalipi et al. (2018) [25] Tea Products	Pohl et al. (2018) [26] Several herbs Products/others[1]	Gezgin et al. (2006) [27] Green tea Products
Al	15	1	12	-	18	-	14	15
As	18	48	-	-	49	-	22	55
B	81	-	99	-	-	-	24	43
Ba	12	9	-	-	8	12	17	-
Ca	17	22	10	<1	12	19	29	3
Cd	13	53	-	-	55	-	20	-
Co	62	65	-	-	86	-	21	-
Cs	87	-	-	-	-	-	-	-
Cu	65	42	45	20	64	29	31	-
Fe	2	15	3	20	6	8	22	0.3
K	92	59	75	90	80	82	48	64
Li	40	83	-	-	-	-	33	33
Mg	67	46	55	52	74	-	33	22
Mn	53	53	55	30	28	34	54	9
Mo	30	50	-	-	57	-	4	-
Ni	90	60	-	-	88	82	38	46
P	57	51	65	48	72	-	35	24
Pb	17	75	-	-	44	-	20	5
Rb	91	66	-	16	-	92	19	-
S	59	-	-	-	-	-	42	33
Se	24	-	-	-	-	-	24	24
Sr	17	2	-	-	-	9	26	-
Ti	3	-	-	-	-	32	8	-
V	1	37	-	-	80	-	13	-
Zn	45	32	80	18	34	59	37	2

[1] Primarily leaves but may also contain other plant organs.

found as Ca pectates in cell walls or as insoluble salts such as Ca oxalate [10, 38], which explains the low solubility of this element after infusion (Fig. 1; Table 2).

Manganese was the micronutrient with the highest total concentration in yerba mate dry products (Table 1) and also had the highest concentration in infusions (Table 1S). Solubility percentage was ~53% (Fig. 1), which was similar to reports in previous studies (Table 2). [40] found that 48% of Mn in commercial yerba mate samples was water-soluble, while the percentage varied from 34 to 45% for camellia teas.

None of the potentially toxic elements had high solubility (Fig. 1), which can be considered beneficial for *chimarrão* consumers. Since the incorporation of As, Cd, and Pb into marketing legislation [15], these elements have received more attention in yerba mate elemental composition studies [41]. However, less than 20% of As, Cd, and Pb was found to solubilize in hot water infusions. Other studies have reported solubility values from 44 to 75% for yerba mate and from 20 to 22% for other herbal plants (Table 2).

The high solubility of monovalent Cs and Rb may be due to the physiochemical similarity of these elements with K [42]. With values below 5%, the lowest solubility occurred for Fe, V, and Ti (Fig. 1). Values of 3% for water-soluble Fe were reported by [40] for yerba mate, and values less than 1% were reported by [27] for tea products. Other studies have reported a strong relationship between these elements due to the similarity of their chemistry in plants [12, 42] and due to soil contamination on leaves or other plant parts [11].

Nutritional Value and Risk Assessment

In general, we estimated low contribution of potentially toxic elements via infusion when compared to tolerance upper intake (TUI) levels. These contributions were less than 1% for

Table 3 Daily intake of elements by consumption of yerba mate (50 g day^{-1}) via *chimarrão* and contribution to recommended dietary allowance (RDA), tolerance upper intake (TUI), or maximum daily intake value (DI)

Element	Index	Value (mg day^{-1})	Estimated daily intake via *chimarrão* (mg)			Contribution (%) to RDA, TUI, or DI		
			PR	SC	RS	PR	SC	RS
Al[1]	TUI	65	2.50	2.75	2.62	3.9	4.1	4.0
As[1]	TUI	0.15	0.001	0.001	0.001	0.32	0.32	0.32
B[2]	TUI	20	1.37	1.75	1.50	7.0	8.5	7.5
Ba[3]	TUI	1.3	0.37	0.50	0.50	29.3	34.6	34.8
Ca[2]	RDA	1000	53.5	66.5	63.0	5.3	6.6	6.2
Cd[1]	TUI	0.065	0.002	0.002	0.005	3.8	4.6	6.8
Co[4]	TUI	1.4	0.01	0.01	0.01	0.38	0.63	0.56
Cs[1]	DI	0.075	0.025	0.025	0.0125	26.6	26.6	13.3
Cu[2]	RDA	0.9	0.25	0.37	0.25	32.2	37.7	33.3
Fe[2]	RDA	13	0.25	0.25	0.25	1.87	1.75	1.87
K[2]	RDA	3000	548	573	660	18.2	19.1	22.0
Li[1]	DI	0.1	0.002	0.002	0.002	2.0	2.0	2.0
Mg[2]	RDA	370	134	169	156	36.2	45.6	42.1
Mn[2]	RDA	2	33.2	40.7	36.6	1660	2035	1830
Mn[2]	TUI	11	33.2	40.7	36.6	301	370	332
Mo[2]	RDA	0.045	0.001	0.001	0.002	2.2	2.2	4.5
Ni[2]	TUI	1	0.125	0.125	0.125	10.0	14.0	10.0
P[2]	RDA	700	29.0	30.5	37.5	4.1	4.3	5.3
Pb[1]	TUI	0.25	0.002	0.001	0.001	1.0	0.6	0.6
Rb[1]	DI	7	1.50	1.25	1.50	21.3	18.6	21.3
S[5]	-	-	27.5	30.5	28.5	-	-	-
Se[2]	RDA	0.055	0.001	0	0	0.9	0	0
Sr[6]	TUI	9.1	0.25	0.25	0.25	3.0	3.0	3.1
Ti[7]	TUI	0.3	0	0	0	3.3	3.3	3.3
V[2]	TUI	1.8	0.001	0	0	0.025	0	0
Zn[2]	RDA	9.5	1.1	1.5	1.6	11.5	15.5	16.5

[1] [28]
[2] [29]
[3] [30]
[4] [31]
[5] Consumption estimated based on amino acids containing S, not total S.
[6] [26]
[7] [32] Brazilian states: *Paraná* - PR, *Santa Catarina* - SC, and *Rio Grande do Sul* - RS.

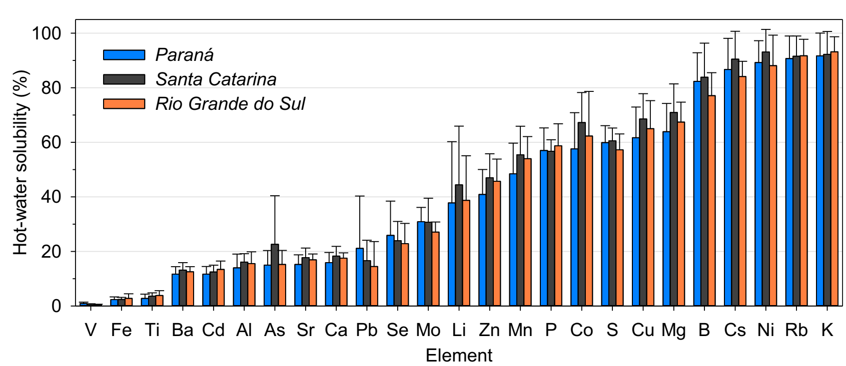

Fig. 1 Hot water solubility (%) of elements in commercial yerba mate products from three states (*Paraná* - PR, *Santa Catarina* - SC, and *Rio Grande do Sul* - RS) of southern Brazil

Pb, Co, As, V, and Se and between 1 and 7% for Cd, Al, Ti, Sr, and Li. Therefore, As, Cd, and Pb in yerba mate infusion does not seem to contribute significantly to the TUI. These results reinforce suggestions of [11, 17, 18] recommending that Cd reference values of yerba mate products sold in Mercosul should be revised. Currently, the reference value is 0.40 mg kg^{-1} [15], but 1 mg kg^{-1} seems to be more consistent with values found in yerba mate under native conditions.

The consumption of *chimarrão* was found to contribute primarily to the intake of Mn, Mg, Ba, and Cu (>25%), as well K, Rb, Zn, and Cs (10–25%) (Table 3). Evaluating only leaves, [20] estimated that the consumption of yerba mate infusions contributed to the intake of K, Mg, P, Mn, and Cu. Intake values of Mn were much higher than RDA and TUI values (Table 3). Other works have reported intakes greater than the TUI from consumption of herbal infusions [43, 44].

Despite high levels of Mn, yerba mate has been consumed for centuries, and no problems related to Mn toxicity due to yerba mate consumption have been reported. In human blood tests from five Brazilian states, [45] found similar levels of Mn in blood from *Rio Grande do Sul* (a state with high rates of *chimarrão* consumption) in comparison to other states that do not share the culture of yerba mate consumption. Thus, despite being ingested in high concentrations, forms of Mn derived from yerba mate may have low bioavailability. In another study evaluating blood Mn levels in consumers and non-consumers, [46] found no relationship with Mn intake via tea (*Camellia sinensis*) despite the greater intake by tea consumers. However, due to Mn being a relevant dietary source via yerba mate infusion, future investigations should be considered in communities with high yerba mate consumption rates.

Classification According to Origin

Based on principal component analysis results, the most relevant variable that explained data variability (Fe, Co, V, Al, Ba, Ti, Mo, K, and Cd) was selected. Considering these variables, a linear discriminant analysis (LDA) made it possible to group samples according to the state where yerba mate products were processed (Fig. 2).

Although we cannot definitively say that yerba mate was harvested and processed in the same state, commercial products were likely processed in the state of origin since each producing region has local processing industries [47, 48]. The greater variability for *Rio Grande do Sul* (Fig. 2) may be due to more use of fertilizers since this region has a greater occurrence of commercial yerba mate plantations [18]; this also supports the higher P and K levels in samples from this state (Table 1). However, [11] performed a LDA of yerba mate elemental composition for leaves collected in situ and concluded that grouping by soil parent material was more robust than regional grouping since composition of leaves was dependent on soil proprieties.

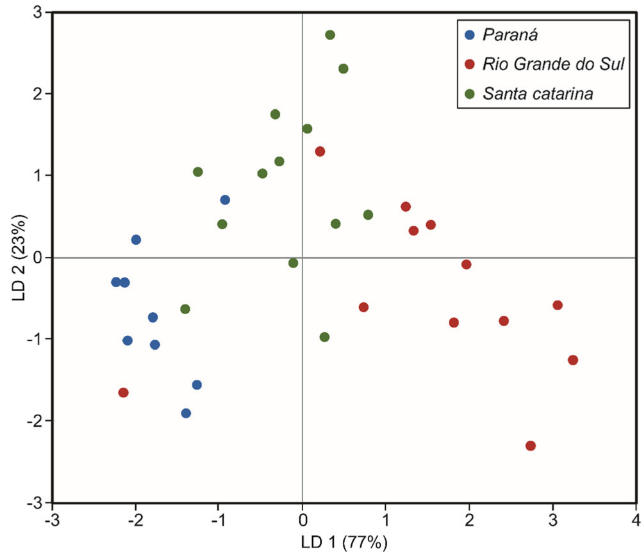

Fig. 2 Discriminant analysis of commercial yerba mate samples used for *chimarrão* (hot infusion) from three states (*Paraná* - PR, *Santa Catarina* - SC, and *Rio Grande do Sul* - RS) of southern Brazil

Conclusion

Yerba mate from southern Brazil had high nutritional value and did not show potential risk for consumers. Values of elements in yerba mate had the following order of occurrence: K > Ca > Mg > Mn > P > S > Al > Fe > Ba > Zn > Sr > B > Rb > Cu > Ti > others. Manganese was in high concentration and had a high solubility percentage (53%), which reinforces that yerba mate has a great capacity to accumulate this element and is a relevant dietary source in consuming regions. The Cd and Pb reference values of yerba mate products sold in Mercosul should be revised. Discrimination analysis made it possible to group samples according to their processing location, indicating that this could be a useful tool for origin certification processes.

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Author Contribution Nayara Caroline Majewski Ulbrich: writing (original draft), conceptualization, methodology, and investigation. Luciane Lemos do Prado: writing (review and editing), conceptualization, methodology, and investigation. Julierme Zimmer Barbosa: writing (review and editing), conceptualization, and investigation. Eloá Moura Araujo: review and editing, software, and formal analysis. Giovana Poggere: writing—review and editing. Antônio Carlos Vargas Motta: writing (review and editing), conceptualization, methodology, and investigation. Stephen A. Prior: writing (review and editing) and investigation. Ederlan Magri: writing (review and editing), conceptualization, methodology, and investigation. Scott D. Young: writing (review and editing) and investigation. Martin R. Broadley: writing (review and editing) and investigation.

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Data Availability All data generated or analyzed during this study are included in this published article (and its supplementary information files).

Code Availability Not applicable.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Conflict of Interest The authors declare no competing interests.

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