Elemental composition of yerba mate (*Ilex paraguariensis* A.St.-Hil.) under low input systems of southern Brazil

Highlights

- Portions of Fe, Ti, As, Mo, Li, V, and Pb found in yerba mate originate from dust.
- 23% of yerba mate leaves exhibited Cd levels close to or above MAL (0.4 mg kg^{-1}).
- Soil parent material impacted yerba mate foliar elemental composition.
- Yerba mate exhibited a great capacity to extract and accumulate Ca and Mn.

ABSTRACT

Elemental composition of food can be used to determine nutritional potential as well as guiding legislation for establishing maximum acceptable limits (MAL) of metals in consumption products. This study aimed to determine the elemental background levels of yerba mate (*Ilex paraguariensis* A.St.-Hil.) under varied geologic formations in southern Brazil. Mature leaves were randomly collected from four wild-grown plants at thirty native sites in three states and analyzed for 32 elements. Since yerba mate is not washed to obtain the final product, leaves were analyzed with and without washing to assess foliar deposition. Concentration values of As, Ag, Be, Cs, Cr, Li, Se, Tl, U, and V were near detection limits, indicating low potential as a source and/or toxicity to the consumer. Washing decreased concentrations of Fe, Ti, As, Mo, Li, V, and Pb, suggesting atmospheric contributions/dust deposition. Concentrations of Mn (very high), Zn (high), and Ni (high) demonstrated that leaves could be an important source of these elements. Soil parent material affected elemental composition with basalt providing higher concentrations of Mn, P, and Co while Rhyodacite provided higher concentrations of K and Na. All samples exhibited Pb values below the MAL of 0.6 mg kg^{-1}, but 23% of washed leaves and 20% of unwashed leaves had Cd concentrations close to or above the MAL value of 0.4 mg kg^{-1}. Study results indicated that Cd MAL values for yerba mate in southern Brazil should be reassessed.

***Keywords**:* Toxic elements, Heavy metals, ICP-MS, Food security, Legislation.

1. Introduction

Yerba mate (*Ilex paraguariensis* A.St.-Hil.) is a plant native to southern Brazil, Paraguay and northeastern Argentina. Distribution of this species primarily coincides with the subtropical Araucaria forest [*Araucaria angustifolia* (Bertol.) Kuntze] encompassing approximately 540,000 km^2. During pre-Columbian times, many native populations used the leaves and fine branches as an infusion product (Cardozo-Junior and Morand, 2016).

Several cycles of yerba mate exploitation have occurred in the five centuries since European colonization of the region. Yerba mate has played key economic and social roles in many remote communities in Brazil where more than 180 thousand farmers are estimated to be cultivating this species, especially on small farms (Marques, 2014). Also, yerba mate is part of the daily diet for a large portion of populations in Uruguay, Argentina, Paraguay, and Brazil (Marques, 2014). Recently, pharmaceutical, cosmetic, and beverage industries have increased research on potential new products derived from yerba mate (Cardozo-Junior and Morand, 2016).

Yerba mate is not cultivated on a commercial scale elsewhere. Thus, local production has been driven by both internal consumption and exportation. There are two very distinct yerba mate production systems. The first is an agroforestry system (low-input) with spontaneous yerba mate growth under the Araucaria forest canopy without fertilization and liming. The second is monocultures of planted seedlings without forest protection from full sun exposure. However, low-input agroforestry systems have been historically preferred by process industries since they are more lucrative compared to yerba mate monocultures under full sun exposure (Marques, 2014).

Remaining native Araucaria forests can no longer be logged, and yerba mate harvesting and Araucaria seed gathering are the primary uses of these native Araucaria forests (Danner et al., 2012). In the past, different degrees of thinning have been applied to Araucaria forests, especially from logging. These thinning's enabled sunlight to pass through the canopy, allowing the growth of grass for raising cattle, sheep, pigs, and horses (Marques, 2014). By maintaining yerba mate during forest thinning or by natural regeneration, a combination of forest, yerba mate, and pasture has been established and preserved by farmers for generations (Marques, 2014; Pinotti et al., 2018).

Yerba mate is often found on acidic soils under native conditions (pH 3 to 4), and farmers choose acidic soils to plant commercial orchards with low lime application rates (Ca and Mg supply) or with no applied lime (Reissmann et al., 1999). Adaption to acidic soil conditions has been confirmed in a recent study that indicated increased seedling root growth when applying Al to hydroponic solutions (Benedetti, 2012). In this regard, yerba mate displays characteristics similar to tea (*Camellia sinensis* L.) (Fung et al., 2008; Bora et al., 2019).

As result of low soil pH, yerba mate leaves may have Al concentration higher than 1000 mg kg^{-1} (Reissmann et al., 1999) and Mn concentrations higher than 3000 mg kg^{-1} (Fossati, 1997; Jacques et al., 2007). However, these concentrations can vary from site to site as well as within a site (Fossati, 1997). Additionally, soil acidity cannot be the only factor impacting Al uptake by yerba mate since soil exchangeable Al was not directly correlated to Al concentrations found in plants (Fossati, 1997; Reissmann et al., 1999). Researchers have suggested that plant root exudation influences nutrient and toxic element availability in yerba mate (Reissmann et al., 1999; Benedetti, 2012).

Yerba mate samples from marketplaces have been used to study differences in mineral composition between countries (Pozebon et al., 2015; Baran et al., 2018), states (Saidelles et al., 2010; Santos et al., 2017), and municipalities within the same state (Costa et al., 2009; Tatsch et al., 2010; Bragança et al., 2011). However, yerba mate may be transported long distances after drying, and there is no guarantee that processing facilities represent the location of origin. Although the influence of washing tea leaves on metal concentrations has been evaluated (Tsushida and Takeo, 1977; Jin et al., 2005; Han et al., 2006), there is a lack of research on this topic for yerba mate. This aspect of the yerba mate production chain should be investigated since the washing step is omitted during industrial processing (Valduga et al., 2019a).

Recently, highly restrictive legislation for heavy metal allowance in yerba mate was imposed by the Common Market of the South (MERCOSUL), which established concentration limits of 0.60 mg kg^{-1} and 0.40 mg kg^{-1} for Pb and Cd, respectively (ANVISA, 2013). This legislation change has raised many concerns regarding metal contamination. Some investigations have detected Pb and Cd in yerba mate above these limits (Santos et al., 2017; Valduga et al., 2019b). However, no studies have evaluated naturally-occurring toxic element backgrounds under native conditions. Therefore, this study was designed to determine background values of nutrients and trace elements in yerba mate leaves cultivated under native or low anthropic intervention systems. In addition, changes in these values due to leaf washing was investigated.

2. Material and methods

2.1. Study area

Thirty sites in southern Brazil were selected for sampling yerba mate leaves and soils (Figure 1). Three states in the region (*Paraná* – PR, *Santa Catarina* – SC, and *Rio Grande do Sul* –

RS) have native occurrence of yerba mate and account for more than 99% of commercial yerba mate production in Brazil (IBGE, 2018). Climatic conditions based on Köppen classification were Cfa (Subtropical Humid, without dry season with hot summers) or Cfb (Subtropical Humid without dry season with temperate summers), with an average altitude above 650 m for the region (Alvares et al., 2013). All sites had Mixed Ombrophylous Forest (Araucaria Forest) as native vegetation.

Four criteria were sought when selecting the 30 sites: 1) close to native conditions with no history of chemical fertilizer, lime application, and herbicide use (note that *Barão de Cotegipe* site was an organic farm system that used pig manure); 2) represent major geologic formations where yerba mate occurs naturally; 3) within major areas of commercial production; and 4) large variation in plant genotype (i.e., no established cultivar, no cloning or plant selection). Table S1 shows compiled information about sites and management conditions.

2.2. Leaf and soil sampling

Samples were collected between 03 July and 18 September 2015. This period represents a state in yerba mate growth where all leaf tissues are mature. At the *Itaiópolis* and *Lebon Régis* sites, plants had not been previously harvested, were greater than 15 m in height, and were part of a preserved forest. The *Lebon Régis* forest differed from others sites in the amount of ground residue from the natural senescence of "*taquara*" (*Merostachys multiramea* Hackel). As a member of the Poaceae family, "*taquara"* can dominate the understory canopy by creating dense cane thickets which naturally died 28 years after blooming.

At each site, four plants were randomly selected and 12 branches were cut from each plant from all sides and heights (low, medium, and top) with manual tree pruning shears. The cut branches were placed in paper bags for transport. At the laboratory, leaves were manually removed from branches, mixed, and divided into two portions for each site. One half was placed in labelled paper bags and the other half was placed on a plastic tray. The tray samples were washed twice with tap water and once with purified water by emersion before placement in another labelled paper bag.

Three soil samples were collected from a meter around from each yerba mate plant and mixed to make a composite soil sample from these 12 single site samples. For sampling, a manual soil auger collected samples to a depth of 0–20 cm.

2.3. Leaf analysis

Two paper bags representing washed and unwashed samples, were placed in a forced air oven at 65^{o}C until constant weight. After drying, samples were ground with a Willey mill to pass a 1 mm sieve and placed in plastic containers.

Leaf tissue was analyzed for Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Se, Sr, Ti, Tl, U, V, and Zn. An Ethos 1 Microwave Digester (Milestone SrL, Bergamo, Italy) platform with a capacity to hold 48 vessels was utilized. Multi-elemental analysis was performed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS; Agilent 7500ce, Santa Clara, CA, USA).

Each 48 sample run consisted of 42 ground leaf samples (200 mg), 2 internal standards, 2 tomato leaf standards (NIST Tomato 1573A, National Institute of Standards and Technology, NIST, Gaithersburg, MD, USA), and 2 reagent blanks. Samples were weighed into vessels before adding 2 mL HNO_3 (re-distilled from 69% 'Aristar' grade; VWR Ltd, Lutterworth, UK), 1 mL of 18.2 MΩ cm water, and 1 mL of 30% (100 volumes) hydrogen peroxide (Trace Select Ultra, Fluka, Gillingham, UK). Operational sample blanks were run to determine limit of detection values (LOD; 3*standard deviation, SD) in digested composite samples. Percentage of recovery LOD values are shown in Table S2.

The microwave heating programme was: 10 min at 500 W to 55º C; 3 min at 100 W to 65º C; 14 minutes at 1200 W to 115º C; 20 minutes at 1200 W to 140º C, 35 bar; and cooling for 15 minutes. Under atmospheric pressure, samples were digested in vessels comprised of polytetrafluoroethylene (PTFE) and polyethylethylketone (PEEK) pressure jackets with a safety devices that activate at a pressure of 35 bar. After cooling, contents of each vessel were washed into a tared 15 mL plastic tube (Greiner Bio-One, Stonehouse, UK) for storage. After all samples were digested, 1:5 dilutions were created by transferring 2 mL of sample solution to a bottle and adding 8 mL of Milli-Q H_2O.

2.4. Soil analysis

Samples were air dried and passed through a 2 mm sieve. Soil chemical analysis consisted of: pH-$CaCl_2$ 0.01 M (1:2.5 – soil:solution ratio), soil buffer to pH 7 (H + Al), exchangeable Al, Ca, and Mg (KCl 1 M – extraction), available P, K, Fe, Mn, Zn, and Cu (Mehlich I – extraction), and organic C according to procedures of Marques and Motta (2002). The following instrumentation was used to perform analysis: atomic absorption spectrophotometer for Ca, Mg, Fe, Mn, Zn, and Cu; flame spectrophotometer for K; and UV/Vis spectrophotometer for P. Soil granulometric analysis was performed for clay, silt, and coarse and fine sand, according to Donagema et al. (2011) using pipette methodology. The sum of soil bases (BS = Ca + Mg + K), effective cation exchange capacity (CEC) (CECef = SB + Al), pH 7.0 CEC (CEC pH 7.0 = BS + (H + Al)), percentage of base saturation (V = BS/CEC pH 7.0*100), percentage of Al saturation [m = Al/(BS + Al)*100] were calculated. Soil chemical and physical properties are shown in Table 1. Soil color was determined from 2 mm dried sieved soil samples using a Munsell color chart.

Total soil chemical composition was determined by digesting a 0.2 g soil sample with HNO_3 and $HClO_4$, followed by HF, in duplicate. The final solution was solubilised with HNO_3 and analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500ce, Santa Clara, CA, USA). Montana soil was used in each batch and percentages of recovery were: Na – 89.7; Mg – 77.4; P – 101.3; K – 93.6; Ca – 89.2; Al – 77.4; V – 97.0; Cr – 78.2; Mn – 91.1; Fe – 94.2; Co – 91.5; Ni – 90.2; Cu – 88.7; Zn – 111.6; As – 107.3; Se – 100.0; Rb – 92.9; Sr – 89.5; Mo – 98.8; Ag – 91.2; Cd – 103.7; Cs – 88.9; Ba – 95.0; Ti – 101.1; and U – 91.8.

2.5. Data analysis

Student t-tests between washed and unwashed samples were performed for each element. Correlation among elements was conducted for washed and unwashed samples. A Principal Component Analysis (PCA) with a correlation matrix of total soil elements (data transformed by box-cox and standardized) was performed. Also, a PCA of leaf elemental composition was performed to identify which elements primarily explain data variance (data not shown). For selected elements (Mn, P, Co, Ni, Mg, Al, Fe, K, Na, Ca, and Ba), Discriminant Linear Analysis (LDA) was used to discriminate samples by region and soil parent material. Elements used in LDA were compared according to soil parent material by the Kruskal Wallis test, followed by Dunn's test (when $p<0.05$). Statistical analyses were performed in software R, version 3.6.0 (R Core Team, 2019).

3. Results and Discussion

3.1. Elemental composition

Levels of many elements were close to or below detection limits (Table S2). Among analysed elements (Table 2), Ag and U were below detection limits in both unwashed and washed samples. For As, Co, Cr, Mo, Na, Ni, Pb, Se, Tl, and V, values were close to or below detection limits. Note that the observed low value of Se is similar to findings of Marcos et al. (1998) and Nookabkaew et al. (2006) for Camellia tea, which is another common infusion product. Although Se is essential for animal nutrition, both yerba mate and Camellia tea are low potential Se sources for human consumption.

The established allowance limit for As is 0.6 mg kg^{-1} (ANVISA, 2013), but there is no established allowance limit for Cr in yerba mate in South America. Camellia tea is another common infusion product; by comparison, Chinese legislation sets allowance limits for Cr at 5.0 mg kg^{-1} and As at 2.0 mg kg^{-1} (Bugang and Woolsey, 2010). Our observed values (Table 2) for both of these elements were below allowance values. Pozebon et al. (2015) reported maximum values of 0.70 (Cr) and 0.06 (As) mg kg^{-1} for 54 processed commercial yerba mate samples from four South American countries. Low values of Cr from native samples observed in our study (Table 2), as well as commercial yerba mate values reported by Pozebon et al. (2015), indicate no contamination from soil or from yerba mate commercial processing. In general, observed Cr and As values for yerba mate leaves (Table 2) and commercial yerba mate samples (Pozebon et al., 2015) were lower than for tea (Zheng et al., 2014; Moreda-Piñeiro et al., 2003; Zhong et al., 2015; Seenivasan et al., 2008; Marcos et al., 1998; Brzezicha-Cirocka et al., 2016; Han et al., 2005).

Lead average levels for yerba mate leaves (Table 2) were lower than the Pb allowance concentration of 0.6 mg kg^{-1} adopted by Mercosul for yerba mate (ANVISA, 2013) and far below the 5.0 mg kg^{-1} level for tea from China (Bugang and Woolsey, 2010). However, some of our yerba mate samples had concentrations above 0.6 mg kg^{-1}. In other words, yerba mate can have natural leaf Pb concentrations above the limit established by Mercosul legislation. Corroborating results of our study, values below the allowance were observed by others for yerba mate commercial samples (Pozebon et al., 2015; Saidelles et al., 2010; Heinrichs and

Malavolta 2001). These yerba mate observations suggest that variation in soil parent material, management practices, and commercial processing has low impact on Pb levels.

Many samples had Cd values above the Mercosul allowance level of 0.4 mg kg^{-1} (Table 2). Five sites had concentrations above that allowed by legislation and two other sites were near the limit (Table S3). Since 29 sites did not receive fertilizer or other manufactured agricultural products that could account for Cd contributions, these observed values represent background concentrations under natural conditions. The *Barão do Cotegipe* site that received lime and pig manure had values of 0.34 mg kg^{-1} (Table S3). Given this noted background level, the 0.4 mg kg^{-1} limit adopted by Mercosul is a very restrictive value since natural concentrations in yerba mate leaves are often very close to or higher than this value. If the adopted limit was 1.0 mg kg^{-1} for yerba mate, all samples sites would be below this limit since the highest value of washed samples was 0.475 mg kg^{-1} (Table 2). Overall, the general mean value of Cd (0.27 mg kg^{-1}) was below those for Brazilian, Uruguayan, and Argentinian commercial yerba mate reported by Pozebon et al. (2015) and were within the 0.35 to 1.21 mg kg^{-1} commercial yerba mate range observed by Saidelles et al. (2010) for three southern Brazilians states used in our study. If the established MRV was closer to natural background, 23% of washed leaves and 20% unwashed leaves would still exceed the standard.

Commercial yerba mate products and leaves used in our study generally had higher Cd concentrations than those reported for tea (Han et al., 2005; Marcos et al., 1998; Tsushida and Taeko, 1997; Seenivasan et al., 2008; Zhong et al., 2015; Brzezicha-Cirocka et al., 2016). Only Zheng et al. (2014) reported Cd in Camellia tea above our average value. On the other hand, Pb concentrations in our study were generally lower than for tea (Zheng et al., 2014; Moreda-Piñeiro et al., 2003; Zhong et al., 2015; Seenivasan et al., 2008; Marcos et al., 1998; Han et al., 2006; Tsushida and Taeko, 1977; Brzezicha-Cirocka et al., 2016, Chen et al., 2010). Thus, soil, climate, or specific plant characteristic could influence differences in toxic metal concentrations for tea and yerba mate. It is important to highlight that observed natural concentrations of Pb and Cd in yerba mate leaves attained levels that could compromise the production chain under current legislation.

We observed means and ranges for Rb (46.4; 14.1 to 132.3 mg kg^{-1}) and Sr (44.1; 15.0 to 88.9 mg kg^{-1}) that were higher than those reported by Pozebon et al. (2015), but similar to their Ba values (64.4; 32.5 to 97.5 mg kg^{-1}). Marcos et al. (1998) observed similar values for Rb (58.8; 23.1 to 114.6 mg kg^{-1}) and smaller values for Sr (18.5; 5.3 to 43.3 mg kg^{-1}) and Ba (27.5; 5.0 to 57.7 mg kg^{-1}) in tea. Despite differences, observed values may have little effect on infusion quality. There are no allowance values for these elements in yerba mate and tea, and observed levels were similar to other plant part levels (Kabata-Pendias, 2011).

Supporting findings of other studies (Giulian et al., 2007; Toppel et al., 2018), Al concentrations in yerba mate leaves were high (Table 2) due to low pH of most evaluated soils (Table 1). However, the *Barão de Cotegipe* soil had almost no exchangeable Al (Table 1) but had high levels in plant tissues. This illustrates the difficulty of associating soil Al availability with leaf concentration (Fossati, 1997; Reissmann et al., 1999), and may suggest that root exudation plays an important role in rhizospheric change and elemental uptake by yerba mate. Although Al values of yerba mate leaves can be considered high, mean values failed to reach the 1000 mg kg^{-1} reported by Fossati (1997) and Reissmann et al. (1999). Also, Al values were lower than those found in commercial tea (Marcos et al., 1998; Fernandez-Caceres et al., 2001; Nookabkaew et al., 2006) and mature tea leaves (Fung et al., 2009; Ruan et al., 2006; Zhong-lei et al., 2001).

Yerba mate is well known to accumulate large amounts of Mn in leaves without affecting yield or resulting in toxicity (Fossati, 1997; Jacques et al., 2007; Barbosa et al., 2018). However, the *Lebon Régis*, *Catanduvas*, *Bituruna*, and *Getúlio Vargas* sites had values that exceeded the maximum expected value (3000 mg kg^{-1}) by 1.5 to 3.0 times (Table S3). The highest Mn value was found at the *Lebon Régis* site, which had a unique combination of large litter accumulation from "*taquara"* (*M. multiramea*) and native yerba mate plants that had never been cut. This site also had the lowest soil pH among sampled sites. The fact that plants were never cut indicated that leaves should be old and contain large amounts of Mn, similar to observations for Mn in tea (Ruan et al., 2006). Two other sites with high Mn (*Bituruna* and *Getúlio Vargas*) also had large amounts of decaying residue from recent hand thinning intended to favour yerba mate growth. However, this same thinning practice at the *Ilópolis* site did not result in similar Mn levels. Thus, more research should be conducted to evaluate the influence of organic residue decay on Mn levels in yerba mate. From a nutritional aspect, yerba mate could be an alternative Mn source, but it is unknown if high Mn concentrations could result in oversupply for heavy yerba mate drinkers (Barbosa et al., 2015).

In reviews of this particular aspect, Mn concentrations were noted to be much higher than Fe in yerba mate leaves (Reissmann et al., 1999; Barbosa et al., 2018) and commercial products (Pozebon et al., 2015), with similar results for tea (Dambiec et al., 2013; Marcos et al., 1998; Moreda-Piñeiro et al., 2003; Brzezicha-Cirocka et al., 2016). Since availability of both elements can be related to soil pH and redox potential, it appears that both yerba mate and tea crops are more efficient in the uptake of Mn. This has been observed for hydroponic growth of yerba mate (Benedetti, 2012).

Remarkable concentrations of Zn were observed at many yerba mate sampling sites (Table 2). No Zn was applied at any site, except the organically grown yerba mate at *Barão do Cotegipe*. High Zn concentrations have been previously reported for a field study (Fossati, 1997) and under controlled hydroponic conditions (Benedetti, 2012). However, two sites had values below 20 mg kg^{-1} of Zn, which can be considered low. Jacques et al. (2007) found that low light intensity/shade increases Zn concentration in yerba mate leaves, which could help explain some of our observed values. Another important point to highlight is that many of our soils were basalt derived and acidic, which results in good supply of Zn (Table 1).

Like Zn, the average Ni concentration of 3.6 mg kg^{-1} was considered high. Similar values were observed by others for yerba mate leaves (Toppel et al., 2018; Barbosa et al., 2019) and commercial products (Pozebon et al., 2015). In general, tissue Ni concentration can be below 1 mg kg^{-1} (Kabata-Pendias, 2011) and in our study only two samples were below this value. This characteristic is comparable to commercially cropped tea (Scancar et al., 2013; Moreda-Piñeiro et al., 2003; Brzezicha-Cirocka et al., 2016). Also soil acidity could play an important role in explaining these findings.

In contrast to the wide variation in soil Cu seen in Table 1, foliar concentrations displayed a more narrow range (7.3 to 14.0 mg kg^{-1}). Supporting our findings, Pozebon et al. (2015) and Giulian et al. (2007) reported commercial yerba mate values between 7 to 20 mg kg^{-1} for different soils and climate conditions. A much wider range (2.0 to 447.5 mg kg^{-1}) was reported by Han et al. (2005) for 800 Chinese tea samples, while others found mean values close to 20 mg kg^{-1} (Marcos et al., 1998; Zhong et al., 2015; Seenivasan et al., 2008). Higher levels of Cu in tea could be related to Cu containing chemical products used to control fungal diseases which are not used with yerba mate. However, Tsushida and Takeo (1977) reported a low mean Cu value of 11.4 mg kg^{-1} for 139 Camellia tea samples from Japan.

For B, the range concentration in leaves of 29.4-80.5 mg kg^{-1} was within or above normal levels. Similar values for B have been observed under field (Reissmann et al., 1999) and hydroponic conditions (Benedetti, 2012) suggesting a high absorption capacity for yerba mate. In contrast, the very low Mo concentrations found in leaf tissue confirm previous observations made by Pozebon et al. (2015).

Phosphorous levels presented in Table S3 reflect low soil P availability (Table 1). The majority of foliar samples (19 of 30 sites, Table S3) had values below the critical concentration of 1000 mg kg^{-1}. Other researchers found low values of P in yerba mate leaves (Barbosa et al., 2018) and commercial products (Giulian et al., 2007; 2009), which were far below that found in tea (Brzezicha-Cirocka et al., 2016). As expected, the highest value was observed at *Barão de Cotegipe* (Site 23), which was the only site with very high P availability due to pig manure applications (Table 1). Also, *Barão de Cotegipe* was the only site where P concentration was higher than S (Table 2). This could suggest that the majority of our study sites had low P and high S supply. Assessed soils had an abundance of organic matter as reflected by elevated C concentrations (Table 1) and deep, well defined soil A horizons. High organic matter often indicates an abundant S supply since more than 90% of S was found in organic matter in two soils under subtropical conditions (Paraná state, Brazil) and in 6 soils from the state of Iowa, USA (Neptune et al., 1975). Additionally, the largest S values were found at Site 5 (Table S3) where the soil is derived from black shale parent material and the site is in proximity to black shale industrial mining/exploration; this proximity could indicate a possible atmospheric contribution from these operations.

The lowest K concentration in yerba mate leaves was close to 10,000 mg kg^{-1} (Table S3) and similar to the lowest values reported by Reissmann et al. (1999) and Barbosa et al. (2019) for leaves and Pozebon et al. (2015) for commercial yerba mate. These values can be considered normal and were expected since only two soils had K availability between low to medium, while all others were medium to high. The highest observed value (25,319 mg kg^{-1}) was also close to findings of Reissmann et al. (1999) and could be related to luxury consumption of K due to high soil availability under native conditions. Also, results (Table S3) confirmed that K was by far the most abundant nutrient among those evaluated and that yerba mate can be a good K source for consumers (Barbosa et al., 2015; Giulian et al., 2007; Heinrichs and Malavolta, 2001). Despite this abundance, yerba mate had lower K concentration compared to tea (Dambiec et al., 2013; Chen et al., 2009), which was likely due to tea receiving K fertilizer applications by farmers.

The observed concentration of Mg (Table S3) was close to the 3600 – 7800 mg kg^{-1} found by Reissmann et al. (1999) in yerba mate leaves, and close to 4041 - 5574 mg kg^{-1} found in commercial yerba mate (Pozebon et al., 2015). Benedetti (2012) reported foliar concentrations of 4550 - 5880 mg kg^{-1} Mg for leaves of yerba mate grown in hydroponic solution. Thus, the Mg range observed in this study (Table 2) can possibly be normal. These findings are impressive considering that 25 sites had 0.6 cmol$_c$ dm^{-3} or less exchangeable Mg, indicative of low or very low availability (Table 1). Yerba mate appears to have a high capacity for extracting less exchangeable Mg from soil. Also, our results indicated that yerba mate has more Mg than tea. The concentration of Mg in tea has been shown to be below 3000 mg kg^{-1} for leaves of plants grown in hydroponic solution (Fung et al. 2008) and in commercial tea (Dambiec et al., 2013; Modera-Pineiro et al., 2003; Brzezicha-Cirocka et al., 2016).

Although exchangeable Ca availability was low in 8 soils (Table 1), most leaf Ca values (Table 2) fell within the 2600 - 8759 mg kg^{-1} range for yerba mate leaves and products reported by others (Reissmann et al., 1999; Giulian et al., 2007; Pozebon et al., 2015; Toppel et al., 2018; Barbosa et a., 2019). Our values were also higher than observed in tea products. Additionally, yerba mate appears to have a high capacity for Ca uptake from poor soils.

3.2. Washing effect on elemental composition

Leaf washing had a major impact on Fe, Ti, As, V, Pb, Li, Mo, and Al by decreasing average, minimum, and maximum concentrations (Table 2 and Figure 2). In addition, determined coefficients between washed and unwashed for Fe, Ti, As, and V had low values, suggesting this influence increased variability among samples (Figure 4).

Dust deposition on leaf surfaces may have been responsible for variation in two sample groups related to soil material from nearby roads, tillage activities, and possible atmospheric deposition from fields at greater distances. Mineral contamination from soil has been related to dust deposited on leaf surfaces and soil/plant element ratio related to harvest contamination (Mayland and Sneva, 1983). Although Si, along with Fe, Al, and Ti, are major constituents of all soil types (Kabata-Pendias, 2011), relatively low concentrations were observed in non-washed yerba mate leaves (Table 2). However, high soil/plant ratios for Fe, Al, and Ti, indicate that soil had a large influence on plant concentration as a contaminant in our study. Many soils in this study (Table 1) also had a high degree of weathering, which increases concentrations of Fe, Ti, and Al and reduces concentrations of K, Ca, Mg, and P. Soil/plant ratios of K, Ca, Mg, and P that were close to or smaller than one could possibly explain the lack of influence from washing. Additionally, soils originating from basalt (many soils in our study), have high concentrations of Fe, Ti, and V (Mineropar, 2005), which increases the chance of contaminating plant tissue concentrations.

Hoog (1981) analysed soil from Araucarian forests sites in Brazil (major yerba mate ecosystem), and found the following range concentrations (mg kg^{-1}): 34250 - 122889, Fe; 60750 - 112571, Al; 850 - 4957, K; 250 - 1057, Ca; trace - 889, Mg; 214 - 689, P; and 125 - 789, Mn. These values were similar to those observed in our study. Additionally, the smallest and highest reported values for total Fe were related to sandstone and basalt parent material, respectively. *Paraná* state soil survey reported the following minimum, maximum, and average concentrations: 6156, 32176, and 15726 mg kg^{-1} for Ti; 81, 856, and 370 mg kg^{-1} for V; 15, 45, and 23 mg kg^{-1} for Pb; 2.40, 29.4, and 7.25 mg kg^{-1} for As; and 0.048, 0.457, and 0.187 for Cd (Mineropar, 2005). Soil concentrations were clearly much higher for Fe, Ti, and Al or higher for V and As than corresponding concentrations found in yerba mate leaves, while soil K, Ca, Mg, P, Mn, and Cd had similar or lower concentrations than plant leaves.

In this study, the high concentrations of Mn and Al found in yerba mate leaves (Table S3) eliminate or reduced the possibility of plant contamination. Also, it is important to highlight that Al, unlike Fe, Ti, and Mn, was found in soil as aluminium silicate that may not be solubilised by plant tissue acids.

The average Fe concentration for unwashed samples was 50% higher than for washed (Figure 2), suggesting a large portion of Fe found in commercial yerba mate comes from external deposition of soil particles. In our study cut branches were placed into bags with minimal soil contact. Our samples may have had less Fe contamination than commercial products since their field handling, transportation, and loading procedures were likely avenues of soil contamination. This could explain the large values observed for commercial yerba mate samples reported by Pozebon et al. (2015) and Giulian et al. (2007; 2009).

Although the majority of collection sites had low industrial activity and were far from major road traffic, washing influence on Pb concentration suggested that atmospheric deposition may contribute to small increases. Many instances of atmospheric contributions of Pb have been reported for tea (Han et al., 2006; Tsushida and Takeo, 1977; Jin et al., 2005).

3.3. Soil parent material effect on elemental composition

Considering washed leaf concentrations of Mn, P, Co, Ni, Mg, Al, Fe, K, Na, Ca, and Ba according to sample region, there was no effective discrimination of groups (84 % precision in LDA), primarily confusing samples from *Paraná* with north of *Santa Catarina*, as well north of *Rio Grande do Sul* with west of *Santa Catarina* (Figure 3A). On the other hand, when discriminating samples according to soil parent material there was better discrimination (94 % precision – Figure 3B). This result indicates that the confusion generated in attempting to separate observations by sample region was linked to the effect of soil parent material. In others words, yerba mate composition (Mn, P, Co, Ni, Mg, Al, Fe, K, Na, Ca, and Ba) was dependent on soil parent material, with high values of Mn, P, Co, Ni, and Ba in basalt soils, Ni, Mg, Al, and Fe in sedimentary soils, and Fe, K, Na, Ca, and Ba in Rhyolite/Rhyodacite soils (Table 3). Some of these elements also presented differences according to Kruskal Wallis test, followed by Dunn's Test. Additionally, Table 3 shows that the yerba mate leaf concentration often followed total soil concentration (Table S5).

Therefore, differences in elemental composition of yerba mate reported as geographical differences (countries, states, or municipality) (Pozebon et al., 2015; Baran et al., 2018; Kahmann et al. 2017; Saidelles et al., 2010; Bragança et al., 2011; Costa et al., 2009; Tatsch et al., 2010) were probably linked to the soil parent material where the species was cultivated.

3.4. Correlation among plant elements

Correlations between K and Rb (0.73 and 0.73), Ca and Mg (0.55 and 0.54), Ca and Ba (0.66 and 0.59), Mg and Sr (0.54 and 0.54), Mg and Ba (0.54 and 0.56), and P and Mo (0.51 and 0.52) were observed in both washed and unwashed samples (Figure 4), respectively. The monovalent cations K and Rb have similar hydrate size and consequently exhibit similar behaviour during plant uptake, allowing Rb isotopes to be used as substitutes for K in uptake studies (Broadley, 2012). Additionally, total soil concentrations displayed similar distribution patterns in a geologic survey of *Paraná* state (Mineropar, 2005). The two anions of P and Mo can present synergic interactions. The same value or small differences in coefficient of correlation confirmed a low or no influence of dust deposition on values and relationships.

Correlations between Fe and As (0.70 and 0.76), Fe and V (0.83 and 0.82), As and V (0.78 and 0.76), and Ti and V (0.56 and 0.81) were observed for washed and unwashed samples, respectively (Figure 4). Also, correlations for Fe and Ti (0.67) and As and Ti (0.64) were only seen in unwashed samples. Plant concentrations of Fe, As, V, and Ti appear to follow similar patterns. The influence of dust deposition was indicated by increased correlations including Ti (i.e., presence of Fe and Ti and As and Ti correlations and increased Ti and V correlations). Other correlations were observed between Al and Pb (0.55 and 0.56) for washed and unwashed samples and Pb and As (0.51) for unwashed.

3.5. Total soil concentration

Total soil concentration (Table S5) showed a strong influence of parent material with Fe, V, Ti, Cu, Ni, and Co having high values under basalt, which was expected (Figure 5). Another aspect of basalt derived soils were the high Cu values similar to or greater than Zn, which confirm observations of Motta et al. (2007) who pointed out two to three times higher concentration of Cu vs Zn in basalt derived soils (Table S5). The same can be stated for Co and Ni in some soils of basalt origin. While eruptive acid rocks (Rhyolite/Rhyodacites) can influence K, Rb, Cs, Ba, Na, Li, and Mg (Figure 5). This was especially true for K, Cs, and Rb which exhibit similar characteristics (charge and size) allowing for selective adsorption to 2:1 clay type (Zaunbrecher et al., 2015).

There was no indication that soil Cd and Pb concentrations were above the reference level for southern soils. The mean, minimum, and maximum concentration values for Cd were 0.098, 0.021, 0.285 mg kg^{-1}, and for Pb were 20.89, 7.13, and 33.37 mg kg^{-1}. These values were below the respective 0.59 and 36 mg kg^{-1} values for Cd and Pb in soil derived from basalt reported by Althaus et al. (2018). In addition, they were in the range of 0.36 - 0.42 mg kg^{-1} for Cd and 16 - 27 mg kg^{-1} for Pb in soil derived from other parent material. Thus, obtained values for Cd and Pb in plants were associated with normal soil conditions.

4. Conclusions

Soil analysis confirmed low pH and availability of Ca, Mg, and P as well as abundant exchangeable Al, except in the soil under organic management. Although foliar analysis indicated low leaf Cd background, 23% of washed leaves had values close to or above the 0.4 mg kg^{-1} MAL for Brazil. However, three other potentially toxic elements (Pb, Cr, and As) had low concentrations and were below the established MAL values for Pb and As.

High Mn concentrations reached up to 9000 mg kg^{-1}, which was 3 to 4 folds higher than previously reported. The highest observed value could be related to particular forest conditions where accumulation and decay of "*taquara*" resulted in very high residue amounts under very old yerba mate trees. The Al concentration in yerba mate was high compared to conventional crop species and reached values up to 1000 mg kg^{-1} as noted in other studies. High concentrations of Zn were observed in tissue, primarily related to basalt derived soil and high availability under low soil pH. Yerba mate can possibly be an important supply for Mn and Zn, however the possibility of Mn oversupply from heavy consumption of yerba mate drinks needs further investigation. In contrast, high Cu availability did not result in high foliar concentrations. Despite low soil availability, normal concentrations of Ca and Mg reflect the root systems ability to exploit low availability nutrient forms. However, this was not true for P, which had low tissues concentrations that mirrored low soil P availability.

The washing process showed that dust residue deposition increased Fe, Ti, As, Pb, Li, Mo, and V concentrations of foliar tissue and that Fe, Ti, As, and V might be trace elements from surface deposition of soil dust. This explains higher Fe values found in commercial yerba mate compared to our study. Also, significant correlations between Fe and As and between Fe and V for washed and unwashed samples and between Fe and Ti in unwashed samples confirmed this relationship.

This study clearly shows that washing yerba mate during industrial processing may alleviate some dust contamination issues, but will not reduce levels of some elements (e.g., Cd) below the current MAL. This work provides some suggested background concentration ranges for native yerba mate that could potentially be used as guidelines for setting more realistic levels in future legislations.

Acknowledgments

The authors thank Yerba Mate companies in Brazil for field work support and to University of Nottingham laboratory staff Lolita Wilson and Saul Vazquez Reina for analytical support. Antônio Carlos Vargas Motta is grateful to the National Council for Scientific and Technological Development (CNPq) for financial support (grant numbers 99999.001631/2015-02 and 306908/2016-6) and Coordination for the Improvement of Higher Education Personnel (CAPES) for scholarship support.

References

ANVISA (2013). Resolução - RDC N° 42, de 29 de agosto de 2013. Dispõe sobre o Regulamento Técnico MERCOSUL sobre limites máximos de contaminantes inorgânicos em alimentos., Brasil, DOU p. 1.

Althaus, D., Gianello, C., Tedesco, M.J., Silva, K.J.D., Bissani, C.A., Felisberto, R. 2018. Natural fertility and metals contents in Soils of Rio Grande do Sul (Brazil). Revista Brasileira de Ciência do Solo, 42, 1-15.

Alvares, C.A., Stape, J.L., Sentelhas, P.C., Gonçalves J.L. de M., Sparovek, G. 2013. Köppen’s climate classification map for Brazil. Meteorol. Z. 22, 711-728. https://doi.org/10.1127/0941-2948/2013/0507.

Baran, A., Gruszecka-Kosowska, A., Kołton, A., Jasiewicz, C., Piwowar, P. 2018. Content and health risk assessment of selected elements in the yerba mate (*Ilex paraguariensis*, St. Hil.). Hum. Ecol. Risk Assess. 24(4), 1092-1114.

Barbosa, J.Z., Zambon, L.M., Motta, A.C.V., Wendling, I. 2015. Composition, hot-water solubility of elements and nutritional value of fruits and leaves of yerba-mate. Ciênc. Agrotec. 39(6), 593-603.

Barbosa, J.Z., Motta, A.C., Consalter, R., Poggere, G.C., Santin, D., Wendling, I. 2018. Plant growth, nutrients and potentially toxic elements in leaves of yerba mate clones in response to phosphorus in acid soils. An. Acad. Bras. Ciênc. 90(1), 557-571.

Barbosa, J.Z., Motta, A.C.V., Reis, A.R., Corrêa, R.S., Prior, S.A. 2019. Spatial distribution of structural elements in leaves of *Ilex paraguariensis*: physiological and ecological implications. Trees 34, 101-110. https://doi.org/10.1007/s00468-019-01900-y

Benedetti, E.L. 2012. Tolerância da erva mate (*Ilex paraguariensis* St. Hil.) ao alumínio. 72 p. Tese (Doutorado em Solos e Nutrição de Plantas), Universidade Federal de Viçosa, Viçosa.

Bora, K., Sarkar, D., Konwar, K., Payeng, B., Sood, K., Paul, R.K., Datta, R., Das, S., Khare, P., Karak, T. 2019. Disentanglement of the secrets of aluminium in acidophilic tea plant (*Camellia sinensis* L.) influenced by organic and inorganic amendments. Food Res. Int. 120, 851-864. https://doi.org/10.1016/j.foodres.2018.11.049.

Bragança, V.L.C., Melnikov, P., Zanoni, L.Z. 2011. Trace elements in different brands of yerba mate tea. Biol. Trace Elem. Res. 144, 1197–1204.

Broadley, M., Brown, P., Cakmak, I., Rengel, Z., Zhao, F. 2012. Function of nutrients: micronutrients. In: Marschner's mineral nutrition of higher plants. Academic Press, p. 191-248.

Brzezicha-Cirocka, J., Grembecka, M., Szefer, P. 2016. Monitoring of essential and heavy metals in green tea from different geographical origins. Environ. Monit. Assess. 188 (3), 183. https://doi.org/10.1007/s10661-016-5157-y.

Bugang, W., Woolsey, M. 2010. National food safety standard-maximum levels of contaminants in food. People’s Republic of china. Gain Report Number-CH10000.

Cardozo-Junior, E.L., Morand, C. 2016. Interest of mate (*Ilex paraguariensis* A. St. Hil.) as a new natural functional food to preserve human cardiovascular health-A review. J. Funct. Foods 21, 440-454.

Chen, Y., Yu, M., Xu, J., Chen, X., Shia, J. 2009. Differentiation of eight tea (*Camellia sinensis*) cultivars in China by elemental fingerprint of their leaves. J. Sci. Food Agric. 89, 2350-2355.

Chen, Y, Xu, J. Yu, M., Chen, X, Shi, J. 2010. Lead contamination in different varieties of tea plant (*Camellia sinensis* L.) and factors affecting lead bioavailability. J. Sci. Food Agric. 90, 1501-1507.

Costa, A.M.G. da, Nogami, E.M., Visentainer, J.V., Souza, N.E. de, Garcia, E.E. 2009. Fractionation of aluminum in commercial green and roasted yerba mate samples (*Ilex paraguariensis* St. Hil.) and in their infusions. J. Agric. Food Chem. 57, 196–200.

Dambiec, M., Polechonska, L., Klink, A. 2013. Levels of essential and non-essential elements in black teas commercialized in Poland and their transfer to tea infusion. J. Food Compos. Anal. 31, 62–66.

Donagema, G.K., de Campos, D.B., Calderano, S.B., Teixeira, W.G., Viana, J.M. 2011. Manual de métodos de análise de solo. Embrapa Solos-Documentos (INFOTECA-E).

Danner, M. A., Zanette, F., Ribeiro, J.Z. 2012. O cultivo da araucária para produção de pinhões como ferramenta para a conservação. Pesquisa Florestal Brasileira 32 (72), 441-451.

Fernandez-Caceres, P.L., Martin, M.J., Pablos, F., Gonzalez, A.G. 2001. Differentiation of tea (*Camellia sinensis*) varieties and their geographical origin according to their metal content. J. Agric. Food Chem. 49, 4775-4779.

Fossati, L.C. 1997. Avaliação do estado nutricional e da produtividade de erva-mate (*Ilex paraguariensis* St. Hil.), em função do sítio e da dioicia. 126 pg.

Fung, K. F., Carr, H. P., Zhang, J., Wong, M.H. 2008. Growth and nutrient uptake of tea under different aluminium concentrations. J. Sci. Food Agric. 88, 1582–1591.

Fung, K.F., Carr, H.P., Poon, B.H.T., Wong, M.H. 2009. A comparison of aluminum levels in tea products from Hong Kong markets and in varieties of tea plants from Hong Kong and India. Chemosphere 75, 955–962.

Giulian, R., Santos, C.E.I. dos, Shubeita, S. de M., Silva, L.M. da, Dias, J.F., Yoneama, M.L. 2007. Elemental characterization of commercial mate tea leaves (*Ilex paraguariensis* A. St.-Hil.) before and after hot water infusion using ion beam techniques. J. Agric. Food Chem. 55, 741-746.

Giulian, R., Santos, C.E.I. dos, Shubeita, S. de M., Silva, L.M. da, Yoneama, M.L., Dias, J.F. 2009. The study of the influence of industrial processing on the elemental composition of mate tealeaves (*Ilex paraguariensis*) using the PIXE technique. Food Sci. Technol. 42, 74-80.

Han, W.Y., Zhao, F.J., Shi, Y.Z., Ma, L.F., Ruan, J.Y. 2006. Scale and causes of lead contamination in Chinese tea. Environ. Pollut. 139, 125-132.

Han, W.Y., Shi, Y.Z., Ma, L.F., Ruan, J.Y. 2005. Arsenic, Cadmium, Chromium, Cobalt, and Copper in Different Types of Chinese Tea. Bull. Environ. Contam. Toxicol. 75, 272–277.

He, H., Bleby, T.M., Veneklaas, E.J., Lambers, H., Kuo, J. 2012. Precipitation of calcium, magnesium, strontium and barium in tissues of four *Acacia* species (Leguminosae: Mimosoideae*). PLoS one, 7(7).*

Heinrichs, R., Malavolta, E. 2001.Mineral composition of a commercial product from mate-herb (*Ilex paraguariensis* St. Hil.). Ciênc. Rural 31, (5), 781-785.

Hoog, R.J. de. 1981. Site-nutrition-growth relationships of *Araucaria angustifolia* (Bert.) O. Ktze. in Southern Brazil. Freiburg: Universidade de Freiburg, 161 p. (Doctoral Thesis).

IBGE. 2018. Instituto Brasileiro de Geografia E Estatística. Produção Agrícola Municipal (PAM), Erva-mate (ano base 2016), IBGE.

Jacques, R.A., Arruda, E.J., Oliveira, L.C.S. de., Oliveira, A.P. de., Dariva, C., Oliveira, J.V. de, Carama, E.B. 2007. Influence of agronomic variables on the macronutrient and micronutrient contents and thermal behavior of mate tea leaves (*Ilex paraguariensis*). J. Agric. Food Chem. 55, 7510-7516.

Jin, C.W., He, Y.F., Zhang, K., Zhou, G.D., Shi, J.L., Zheng, S.J. 2005. Lead contamination in tea leaves and non-edaphic factors affecting it. Chemosphere 61, 726–732.

Kabata-Pendias, A. 2011. Trace Elements in Soils and Plants 4th ed. p. 534. CRC Press. Taylor and Francis Group. Boca Raton.

Kahmann, A., Anzanello, M.J., Marcelo, M.C.A., Pozebon, D. 2017. Near infrared spectroscopy and element concentration analysis for assessing yerba mate (*Ilex paraguariensis*) samples according to the country of origin. Computers and Electronics in Agriculture, 140, 348-360.

Marcos, A., Fisher, A., Rea G., Hill, S.J. 1998. Preliminary study using trace element concentrations and a chemometrics approach to determine the geographical origin of tea. J. Anal. Atom. Spectrom. 13, 521–525.

Marques, A. da C. 2014. As paisagens do mate e a conservação socioambiental: um estudo junto aos agricultores familiares do planalto norte catarinense. 434 p. (Tese, curso de Doutorado em Meio Ambiente e Desenvolvimento da Universidade Federal do Paraná).

Mayland. H.F., Sneva, F.A. 1983. Effect of soil contamination on the mineral composition of forage fertilized with nitrogen. J. Range Manage. 38(3), 286-289.

Mineropar, 2005. Geoquímica de solo-Horizonte B. Relatório final de projeto. Curitiba: Mineropar, 2 vol. 453 p.

Moreda-Piñeiro, A., Fisher, A., Hill, S.J. 2003. The classification of tea according to region of origin using pattern recognition techniques and trace metal data. J. Food Compos. Anal. 16, 195–211.

Motta, A.C.V., Serrat, B.M., Reissmann, C.B., Dionisio, J.A. 2007. Micronutrientes na rocha, no solo e na planta. Curitiba: UFPR. 246 p.

Neptune, A.M.L., Tabatabai, M.A., Hanway, J.J. (1975). Sulfur fractions and carbon-nitrogen-phosphorus-sulfur relationships in some Brazilian and Iowa soils. Soil Sci. Soc. Am. J. 39(1), 51-55.

Nookabkaew, S., Rangkadilok, N., Satayavivad, J. 2006. Determination of trace elements in herbal tea products and their infusions consumed in Thailand. J. Agric. Food Chem. 54, 6939-6944.

Pinotti, L.C.A., Hanisch, A.L., Negrelle, R.R.B. 2018. The impact of traditional silvopastoral system on the Mixed Ombrophilous Forest remnants. Floresta Ambient, 25(4), http://dx.doi.org/10.1590/2179-8087.019217

Pozebon, D., Dressler, V.L., Marcelo, M.C.A., Oliveira, T.C. de, Ferrão, M.F. 2015. Toxic and nutrient elements in yerba mate (*Ilex paraguariensis*). Food Addit. Contam. B 8(3), 215-220.http://dx.doi.org/10.1080/19393210.2015.1053420

R Core Team, 2019. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. <https://www.R-project.org/>.

Reissmann, C.B., Radomski, M.I., Quadros, R.M.B. 1999. Chemical composition of *Ilex paraguariensis* St. Hil. under different management conditions in seven localities of Paraná state. Braz. Arch. Biol. Techn. 42, 187-194.

Ruan, J., Ma, L., Shi, Y. 2006. Aluminium in tea plantations: mobility in soils and plants, and the influence of nitrogen fertilization. Environ. Geochem. Health 28, 519–528.

Saidelles, A.P.F., Kirchner, R.M., Santos, N.R.Z. dos, Flores, E.M. de M., Bartz, F.R. 2010. Análise de metais em amostras comerciais de erva-mate do sul do Brasil. Alim. Nutr. 21(2), 259-265.

Santos, L.M.G.D., Neto, V., Alves, S., Iozzi, G., Jacob, S.D.C. 2017. Arsenic, cadmium and lead concentrations in yerba mate commercialized in southern Brazil by inductively coupled plasma mass spectrometry. Ciênc. Rural 47(12). http://dx.doi.org/10.1590/0103-8478cr20170202.

Scancar, J., Zuliani, T., Milacic, R. 2013. Study of nickel content in Ni-rich food products in Slovenia. J. Food Compos. Anal. 32, 83–89.

Seenivasan, S., Manikandan, N., Muraleedharan, N.N., Selvasundaram, R. 2008. Heavy metal content of black teas from south India. Food Control 19, 746–749.

Tatsch, F.R.P., Gonçalves, V.C., Meurer, E.J. 2010. Alumínio total e solúvel em amostras de erva-mate comercializadas no Rio Grande do Sul. Scientia Agraria 11(1), 83-86.

Toppel, F.V., Junior, A.M., Motta, A.C.V., Frigo, C., Magri, E., Barbosa, J.Z. 2018. Soil chemical attributes and their influence on elemental composition of yerba mate leaves. Floresta 48(3), 425-434.

Tsushida, T., Takeo, T. 1977. Zinc, copper, lead and cadmium contents in green tea. J. Sci. Food Agric. 28, 255-258. https://doi.org/10.1002/jsfa.2740280306.

Valduga, A. T., Gonçalves, I. L., Magri, E. 2019a. Analysis of the Presence of Toxic Metals in Yerba Mate Samples: a Case Study from South Brazil. Water Air Soil Pollut. 230(7), 153.

Valduga, A.T., Gonçalves, I.L., Magri, E., Finzer, J.R.D. 2019b. Chemistry, pharmacology and new trends in traditional functional and medicinal beverages. Food Res. Int. 120, 478-503.

Zaunbrecher, L.K., Cygan, R.T., Elliott, W.C. 2015. Molecular models of cesium and rubidium adsorption on weathered micaceous minerals. J. Phys. Chem. *A*, 119(22), 5691-5700.

Zheng, H., Li, J., Li, H., Hu, G. Li, H. 2014. Analysis of trace metals and perfluorinated compounds in 43 representative tea products from South China. J. Food Sci. 79(6), 1123-1129. https://doi.org/10.1111/1750-3841.12470.

Zhong, W., Ren, T., Zhao, L. 2015. Determination of Pb (Lead), Cd (Cadmium), Cr (Chromium), Cu (Copper), and Ni (Nickel) in Chinese tea with high-resolution continuum source graphite furnace atomic absorption spectrometry. J. Food Drug Anal. 4 (1), 46-55. doi: 10.1016/j.jfda.2015.04.010.

Zhong-Lei, X., De-Ming, D., Guo-Zhang, B., Sheg-Tian, W. Yao-Guo, D. Li-Min, Q. 2001. Aluminium content of tea leaves and factors affecting the uptake of aluminium from soil into tea leaves. Chinese Geogr. Sci. 11(1), 87-91.