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Pb, Cd, and As in soils and yerba mate branches from different cultivation areas

Pb, Cd y As en suelos y ramas de yerba mate de diferentes orígenes geográficos

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Abstract

Yerba mate is cultivated in northeastern Argentina, southern Brazil, and southeastern Paraguay. Agricultural technology, industrial pollution, geological sources, and food processing are the most prominent sources of food contamination by toxic elements, including heavy metals. The objective of this work was to evaluate the influence of soil acidity and fertilization practices in Misiones on Pb, Cd, and As content in soil samples and yerba mate plantations. Chemical analyses were performed by ICP-MS, after microwave acid digestion. Determinations made according to soil acidity indicate that there are differences between areas and between plant fractions on Pb, and Cd content of plantations. Determinations made according to fertilization system, areas and level of fertilization do not have a significant effect on Pb, Cd, and As plantations content. Given that these elements are toxic and that maximum contents in yerba mate are regulated, it is important to study mitigation measures so that plants do not accumulate them in excess in their tissues.

Keywords: Ilex paraguariensis, cultivation areas, soil, heavy metals.

Resumen

La yerba mate es cultivada en el noreste de Argentina, el sur de Brasil y el sureste de Paraguay. La tecnología agrícola, la contaminación industrial, las fuentes geológicas y el procesamiento de alimentos son las fuentes más destacadas de contaminación de alimentos por elementos tóxicos como los metales pesados.

El objetivo de este trabajo fue evaluar la influencia de la acidez del suelo y tipo de fertilización de la provincia de Misiones sobre el contenido de Pb, Cd y As en muestras de suelos y plantaciones de yerba mate. Los análisis químicos fueron realizados por ICP-MS, previa digestión ácida por microondas.

Las determinaciones realizadas según la acidez del suelo indican que hay diferencias entre las regiones y entre las fracciones de la planta sobre el contenido de Pb y Cd de las plantaciones. Para las determinaciones realizadas según el sistema de fertilización, las regiones y el nivel de fertilización no tienen un efecto significativo sobre el contenido de Pb, Cd y As en las plantaciones.

Dado que estos elementos son tóxicos y que los contenidos máximos en yerba mate se encuentran regulados, resulta importante estudiar medidas de mitigación para que las plantas no los acumulen en exceso en sus tejidos.

Palabras clave: Ilex paraguariensis, regiones de cultivo, suelo, metales pesados.

Introduction

Yerba mate (*Ilex paraguariensis* Saint-Hilaire) is an endemic species of South America, cultivated for commercial purposes only in northeastern Argentina (*Misiones* and northeastern *Corrientes*), in southern Brazil, and southeastern Paraguay. In this region, its processing and consumption have great economic and sociocultural importance [1, 2, 3, 4, 5, 6, 7].

Deep red soils are the most suitable for this crop [8]. These soils stand out for their high acidity, indicating that this species is tolerant to this condition [9]. Iron content can vary from less than 0.1 % to more than 30 %, mainly in oxides and hydroxides form. In addition, these types of soils have different manganese and aluminum contents. The low concentration and solubility of phosphorus make it one of the most limiting nutrients [10]. These soils have low fertility compared to others, so fertilization practices are required [11].

Nutrients are essential for plant growth and their main sources are chemical and organic fertilizers [12, 13]. In addition, pesticides are used on crops to repel, destroy, or control any pest or to regulate plant growth [14]. Agricultural inputs often contain trace elements, such as heavy metals, which are considered harmful to human health and are not essential for plants. As a result, the use of these products may result in metal accumulation in soils and crops, potentially influencing the toxicity of the food chain [13, 15, 16, 17].

The term "heavy metals" lacks a standardized definition in scientific literature, and in the vast majority of instances, the element density is considered as a defining factor [18]. It is generally used to refer to metals and metalloids with atomic number greater than 20 and density greater than 5000 kg m-3, associated with environmental pollution, toxicity, and adverse effects on biota [19]. Heavy metals can be absorbed from soil by plant roots and can also penetrate from atmosphere through the surface of leaves. They are considered important chemical contaminants in food, where they are frequently evaluated due to their ability to accumulate in the food chain [16, 20, 21].

Lead (Pb) is an environmental contaminant, whose natural sources include volcanic activity and geochemical weathering [22].

However, its ubiquitous occurrence is largely the result of anthropogenic activities such as mining, smelting, and welding, and its use in ammunition, paints, gasoline, and battery and pipe manufacturing [23, 24, 25]. Control measures to regulate or prohibit Pb content in paints, gasoline, food cans, and water pipes significantly reduced levels of this element in the atmosphere [24, 25, 26, 27].

The central nervous system is the main target organ of Pb toxicity. A developing brain is more vulnerable to Pb neurotoxicity than the mature brain and even relatively low levels of exposure can cause severe neurological damage [22, 23, 24, 25, 28]. International Agency for Research on Cancer (IARC) classifies inorganic Pb compounds in Group 2A, as probably carcinogenic to humans [24, 25, 29].

Cadmium (Cd) is a naturally occurring environmental pollutant resulting from volcanic emissions and weathering of rocks [18, 30, 31, 32]. It also arrives from industrial and agricultural sources, including industrial emissions, mining and refining of non-ferrous metals, fossil fuel combustion, incineration and waste disposal, its use in batteries, semiconductors, pigments, enamels and glazes, manufacture and application of phosphate fertilizers and sewage sludge [18, 30, 31, 32, 33, 34].

Cd is mainly toxic to kidneys and can cause kidney failure. It can also cause bone demineralization, either through direct bone damage or indirectly as a result of kidney dysfunction [23, 31, 35, 36]. IARC classifies Cd and Cd compounds in Group 1, as carcinogenic to humans [29, 31, 36].

Arsenic (As) appears naturally in the environment due to volcanic phenomena, rock disintegration and microbial activities [37, 38, 39]. Industrial activities that aggravate pollution are mining, smelting of non-ferrous metals, and energy production from fossil fuels. The As-containing compounds have been used commercially for centuries as agricultural chemicals and wood preservatives [18, 37, 40, 41]. Skin lesions, characterized by hyperkeratosis of the palms of the hands and the soles of the feet, as well as melanosis and leukomelanosis, are some symptoms of chronic intoxication. Hyperkeratosis is painful and can affect daily activities and reduce quality of life [38, 42]. IARC classifies As and inorganic As-compounds in Group 1, as carcinogenic to humans [29, 41, 43].

Dietary intake is the main route of human exposure to heavy metals and long-term consumption of contaminated foods increases the risk of exposure and adverse effects on human health [16, 44, 45].

Resolution 12/11 of Southern Common Market (MERCOSUR, by its name in Spanish *Mercado Común del Sur*), included in the Argentine Food Code (CAA, by its name in Spanish *Código Alimentario Argentino*), establishes the following maximum limits for inorganic contaminants in yerba mate: 0.60 mg kg-1 for lead, 0.40 mg kg-1 for cadmium and 0.60 mg kg-1 for arsenic.

This regulation applies in the territory of MERCOSUR member states, to trade between them and to extra zone imports. In addition, maximum contents apply to solid products (yerba mate) and not to their consumption forms [46].

The objective of this work was to evaluate the influence of soil acidity and fertilization practices in *Misiones* (Argentina) on Pb, Cd, and As content in soil samples and yerba mate plantations.

Materials and methods

Samples

Soil and branch samples were taken from Ilex paraguariensis plantations of different geographical origins between July and August 2021. These commercially exploited plantations were located in the north, centre and south of Misiones, Argentina. Two experiments were carried out: one with different levels of soil acidity (experiment 1) and the other with different levels of fertilisation (experiment 2). The plantations in each geographical region were previously selected using a database available at the Agricultural Experimental Station of the National Institute of Agricultural Technology (INTA) in Cerro Azul.

Experience 1: influence of soil acidity

Three variables were evaluated: cultivation area (3 levels: north, central, and south area), soil acidity (2 levels: acid and very acid), and plant fraction (2 levels: leaves and sticks).

In the northern area, samples corresponding to acid soils were collected in Comandante Andresito municipality (General Manuel Belgrano department) and samples corresponding to very acid soils in Wanda municipality (Iguazú department). In the central zone, both samples corresponding to acid and very acid soils were collected in Jardín América municipality (San Ignacio department). In the southern area, the two samples corresponding to acid and very acid soils were collected in Itacaruaré municipality (San Javier department).

Each soil sample was composed of 4 sub-samples (soils of 4 plants that were later sampled) that were collected from the middle of the street towards the line (external zone of projection of the crown) at a depth of 20 cm [47]. Soil samples were dried in an oven at 103 °C, size was reduced by quartering, and samples were conditioned in double hermetic plastic bags.

To corroborate the acidity of each sample, pH was measured without replicates in 1 N potassium chloride saline solution (pH-KCl), with a soil-solution ratio of 1:2.5. An Oakton model WD-35620 benchtop pH meter was used.

Each branch sample was made up of four sub-samples taken from the middle crown and from all cardinal directions (north, south, east, and west) [48]. Branches were dried in an oven at the temperature of 60 °C, leaves and sticks were separated, fractions size was reduced by quartering, and each fraction was ground separately in a ceramic mortar. Samples of leaves and sticks were conditioned in double hermetic plastic bags.

Soil, leaf, and stick samples were sent to a chemical analysis laboratory, and Pb, Cd and As content was determined without replication.

Experience 2: influence of fertilization level

Two variables were evaluated: cultivation area (3 levels: north, central, and south area) and fertilization system (2 levels: high and low). High fertilization (intensive) corresponded to plantations with amounts of fertilizers greater than 500 kg ha-1 year-1, while low fertilization (non-intensive) corresponded to plantations with amounts of fertilizers lower than 300 kg ha-1 year-1. In the northern area, samples were collected from plantations with high fertilization in Comandante Andresito municipality (General Manuel Belgrano department) and samples from plantations with low fertilization in Wanda municipality (Iguazú department).

In the central zone, both high and low fertilization samples were collected in Santo Pipó municipality (San Ignacio department).

In the southern zone, the two samples corresponding to high and low fertilization were collected in Campo Ramón municipality (Oberá department).

Each branch sample was made up of four sub-samples taken from the middle crown and from all cardinal directions (north, south, east, and west) [48]. The branches were dried in an oven at a temperature of 60 °C, the leaves and sticks were separated, the fractions were reduced in size by quartering and each fraction was ground separately in a ceramic mortar. Mixtures (reconstituted samples) were prepared with a ratio of 80 % ground leaves and 20 % ground sticks and packed in double airtight plastic bags.

These samples were sent to a chemical analysis and Pb, Cd, and As content was determined without replication.

Instrumental

Determinations of Pb, Cd and As content in each sample were carried out using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), before acid digestion in microwaves, at *Centro de Investigación y Asistencia Técnica a la Industria (CIATI AC)*, located in *Villa Regina*, *Río Negro* province, Argentina.

Reagents and solutions

The following reagents and solutions were used:

- Grade I ultrapure water, obtained with Milli-Q® Advantage A10 System (Millipore) water purification system, obtaining a resistivity of 18.2 MΩ cm-1.
- Hydrochloric acid (HCl) and nitric acid (HNO_3) Merk, Suprapur, purified by sub-boiling distillation.
- Multielement calibration standard solution, 100 mg L-1, Scharlau.
- Monoelement solutions grade AA, Merk (Pb Reference No. 1.19776.0500, Cd Reference No. 1.19777.0500, As Reference No. 1.19773.0500).
- Interference Check Solution. Agilent Part Number "A" 5188-6526, "B" 5188-6527.

Microwave acid digestion

Table 1 shows the equipment used to perform microwave acid digestion as well as operating conditions.

Table 1: Microwave equipment and operating conditions.

Parameter	Description
Microwave equipment	CEM, MARS 6 240/50
Microwave power	600-1800 W
Mode	Standard
Stages	3
Time ramp	5-15 minutes
Maintenance time	10-15 minutes
Digestion temperature	180-240 °C

Determination of Pb, Cd, and As content by ICP-MS

Table 2 shows data from instruments used to determine Pb, Cd, and As content in samples, as well as operating conditions.

Table 2: ICP-MS equipment and operating conditions.

Parameter	Description
ICP-MS equipment	Agilent, 7700x
RF power	1550 W
Mode	He
Nebulizer	Agilent, MicroMist nebulizer
Spray chamber	Agilent, quartz double pass chamber
Torch	Agilent, 2.5 mm internal diameter quartz torch
Cones	Nickel sampler cone and skimmer cone
Plasma	Argon gas (99.99 %)
Gas flow rate	Plasma gas: 15.01 L min-1 Auxiliary gas: 0.9 L min-1 Nebulizer gas: 0.99 L min-1
Isotopes	208Pb, 111Cd, 75As
Calibration type	External

Quality parameters

Calibration standards were prepared from a multi-element solution, diluted with a 1 % (v/v) HNO3 solution, purified by sub-boiling distillation. The concentrations of the calibration solutions for these elements were:

Pb: 0 - 0.04 - 0.1 - 1 - 10 - 100 - 500 ug kg-1

Cd: 0 - 0.04 - 0.1 - 1 - 10 - 100 - 500 ug kg-1

As: 0 - 0.2 - 0.5 - 1 - 10 - 100 - 500 ug kg-1

Calibration curves followed a linear behavior ($R^2 >$ 0.995). Terbium (Tb) was used as the internal calibration standard for Pb and Cd and germanium (Ge) was used as the internal calibration standard for As.

Control solutions were prepared from solutions different from those used in the calibration curve. Every 20 samples were introduced into the equipment as a control to check the curve and the signal throughout the batch. Solutions A and B (Interference Check Solution) were used to verify polyatomic interferences. The limits of detection (LOD) were calculated as 3 times the noise signal, while limits of quantification (LOQ) were calculated as 10 times the noise signal. Table 3 presents reported LOD and LOQ values for Pb, Cd, and As in each type of sample tested.

Table 3: LOD and LOQ values reported for Pb, Cd, and As in each type of sample.

Sample	**Pb** (mg kg-1)	**Cd** (mg kg-1)	**As** (mg kg-1)			
	LOD	**LOQ**	**LOD**	**LOQ**	**LOD**	**LOQ**
Leaves and sticks	0,01	0,03	0,01	0,03	0,01	0,03
Soils	2	5	0,3	1	1	3

Analytical methods

The analytical methods followed were AOAC 2015.01 for the determination of Pb, Cd and As by ICP-MS, with prior microwave acid digestion, in food and beverage samples [49], EPA 3051A for microwave acid digestion of soil samples [50] and EPA 6020A for the determination of Pb, Cd and As by ICP-MS in soil samples [51].

Statistical analysis

Statistical analyses of the data obtained were carried out with the STATGRAPHICS® Centurion XVI software [52].

Results and Discussion

Experience 1: influence of soil acidity

Values of pH-KCl measured in acid soil samples were between 3.9 and 4.7, while in very acid soil samples were between 3.6 and 3.9.

Figure 1 shows the Pb, Cd and As content in soils of yerba mate plantations, located in the northern, central and southern areas of Misiones, considering different levels of soil acidity.

In all the cases, it was possible to quantify Pb content (between 19.9 and 27.0 mg kg-1) and As content (between 12.6 and 17.3 mg kg-1). Cd content was not detected in any of the samples.

In Argentina, Regulatory Decree 831/93 of Law 24.051 on hazardous waste presents quality guide levels for agricultural soils, establishing a maximum of 375 mg kg-1 for Pb, 3 mg kg-1 for Cd and 20 mg kg-1 for As [53]. However, Resolution 264/2011 of the National Agri-Food Health and Quality Service (SENASA) establishes maximum permissible limits in soils of 50 mg kg-1 for Pb and 1 mg kg-1 for Cd. This regulation does not establish maximum limits for As in soils [54].

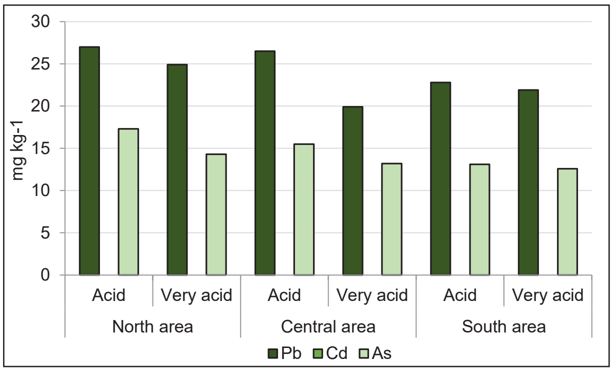

Figure 1: Pb, Cd, and As in yerba mate plantations soils according to acidity.

Values that were quantified in soil samples were below the guide levels and the maximum permitted limits, complying with quality for soils for agricultural use.

Figure 2 shows Pb, Cd and As content in yerba mate leaves and sticks, located in the north, central and south areas of *Misiones*, considering different levels of soil acidity.

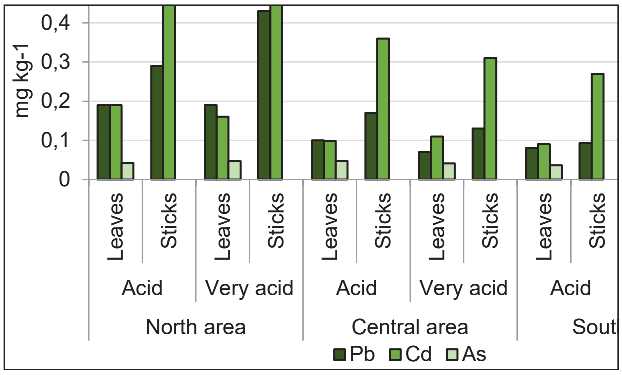

Figure 2: Pb, Cd and As content in yerba mate leaves and sticks according to acidity.

In all cases, Pb content (between 0.070 and 0.190 mg kg-1 in leaves and between 0.093 and 0.430 mg kg-1 in sticks) and Cd content (between 0.090 and 0.190 mg kg-1 in leaves and between 0.270 and 0.530 mg kg-1 in sticks) could be quantified. In leaf samples, it was possible to quantify As content (between 0.034 and 0.048 mg kg-1); however, in stick samples this element could be detected, but in no case could be quantified (< LOQ). Stick samples of the north area yerba mate exceeded the maximum limit allowed for Cd. In all samples, Pb and Cd content were higher in sticks than in leaves.

A multifactorial analysis of variance (ANOVA) was performed to determine which factors had a statistically significant effect on Pb and As content in yerba mate plantation soils (dependent variables). Two factors were evaluated: cultivation area (3 levels: north, central, and south area) and soil acidity (2 levels: acid and very acid). Results showed that none of the factors had a statistically significant effect on Pb and As content in soils, for a confidence level of 95 %. Since Cd could not be detected in soil samples, statistical analyses for this element were not performed.

In addition, a multifactorial ANOVA was performed to determine which factors had a statistically significant effect on Pb and Cd content in yerba mate (dependent variables).

Three factors were evaluated: cultivation area (3 levels: north, central, and south area), soil acidity (2 levels: acid and very acid), and plant fraction (2 levels: leaves and sticks). Results showed that cultivation area and plant fraction had a statistically significant effect on Pb and Cd content in plantations, for a confidence level of 95 %. However, soil acidity did not have a statistically significant effect on Pb and Cd content in plantations. Yerba mate plantations sampled, for different levels of soil acidity, were previously selected from an INTA database. In some cases, the pH of acid soil did not differ widely from the pH of very acid soil, which could have influenced the results. Since As content in stick samples could not be quantified, statistical analyses for this element were not performed.

Figure 3 shows mean graphs for Pb and Cd content in yerba mate, according to cultivation area (factor with significant influence).

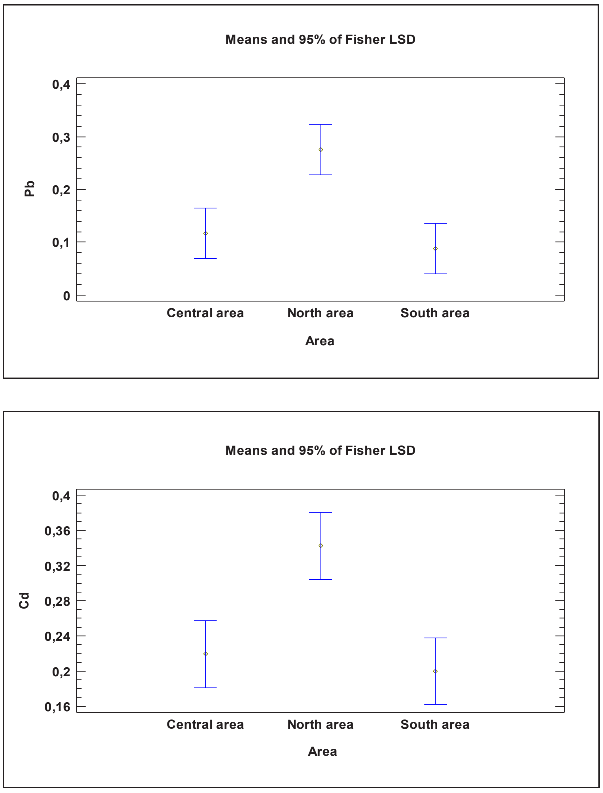

Figure 3: Mean graphs for Pb (left) and Cd (right) content in yerba mate according to area.

In yerba mate, Pb and Cd mean content in the north area showed significant differences with Pb and Cd mean content in yerba mate from the other two areas. North area plantations presented maximum Pb and Cd content. These differences could be influenced by soil-specific characteristics, relief and rainfall regimes of each sampled place.

Figure 4 shows mean graphs for Pb and Cd content in yerba mate, according to plant fraction (another factor with significant influence).

Pb and Cd mean content in yerba mate leaves showed significant differences with Pb and Cd mean content in yerba mate sticks. Sticks presented maximum Pb and Cd content.

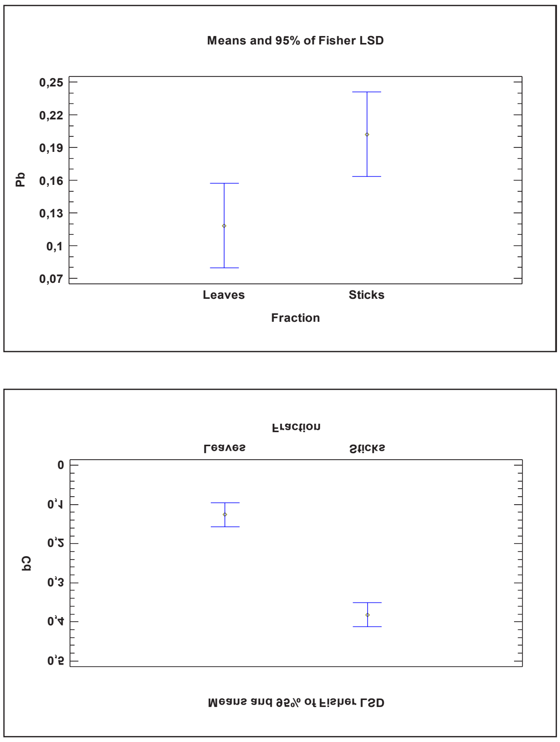

Figure 4: Mean graphs for Pb (left) and Cd (right) content in yerba mate according to plant fraction.

Experience 2: influence of fertilization level

Figure 5 shows the Pb, Cd, and As content of leaf and stick mixtures from yerba mate plantations in north area, central area and south area of *Misiones*, with different fertilization systems (high and low).

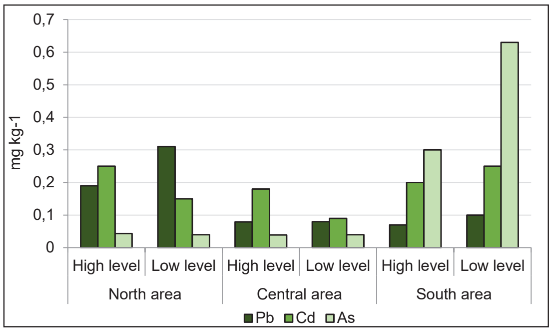

Figure 5: Pb, Cd, and As content in yerba mate according to fertilization level.

In all cases, Pb content (between 0.070 and 0.310 mg kg-1), Cd content (between 0.090 and 0.250 mg kg-1), and As content (between 0.039 and 0.630 mg kg-1) could be quantified. South area yerba mate sample, with low fertilization level, slightly exceeded the maximum limit allowed for As.

Multivariate ANOVA was performed to determine which factors had a statistically significant effect on Pb, Cd, and As content in yerba mate (dependent variables). Two factors were evaluated: cultivation area (3 levels: north, central and south area) and fertilization level (2 levels: high and low). Results showed that none of the factors had a statistically significant effect on Pb, Cd and As content in yerba mate, for a confidence level of 95 %.

In experience 1, the highest Cd contents were found in the stick samples of the north area, and in experience 2, the highest As contents were found in the yerba mate samples of the south area. In both cases, these situations could be due to particular conditions of geographical areas and plantations. Numerous factors influence the absorption of elements by crops.

The distribution and availability of toxic elements in the soil profile are determined by some characteristics such as pH, redox potential, and type and quantity of adsorption components [55, 56]. Types of clay, oxides and hydroxides, and organic matter are part of the soil solid phase and provide permanent and variable charges, responsible for the sorption of many contaminants [55]. Iron, aluminum, and manganese oxides and hydroxides are the main soil constituents involved in the metal specific adsorption as an important retention mechanism [56], being able to be released into the soil solution and absorbed by plants. These are the main characteristics that can be related to values found in this work. Other particular conditions affect the availability and absorption of the elements. In the case of Cd, an important source of this metal is phosphate fertilizers. However, phosphate added to soils can reduce the mobility of Cd [57]. On the other hand, zinc competes with Cd for plant uptake [58]. In As case, its chemical and mineralogical speciation affects its mobility, availability, and toxicity. In addition, phosphate presence competes with As for adsorption sites [56]. Phosphate fertilizers addition to agricultural soils favors As availability in soil solution [59]. Similarly, phosphorus competes with As for plant uptake [60]. However, the soils of the region where yerba mate grows are deficient in phosphorus, and doses of this element added are generally too low to presume that these mechanisms would have a significant influence. The specific soils and plantations of each region need to be characterized in order to propose appropriate management practices.

Results obtained by other authors

Table 4, Table 5 and Table 6 present the main published works on Pb, Cd and As content, respectively, in *Ilex paraguariensis* plantations soils, leaves, and sticks.

Poletti et al. (2014) [61] analysed Pb and Cd content in virgin and organically and chemically fertilised soils in the states of Paraná (PR), Santa Catarina (SC) and Rio Grande do Sul (RS) in Brazil. Average values between 8.23 and 34.20 mg kg-1 for Pb and between 1.76 and 3.53 mg kg-1 for Cd were found. For both metals, concentrations were similar in the PR and SC regions and relatively lower in RS. The virgin soil in RS had a higher Pb concentration than in the other regions and the authors mention soil diversity as a possible explanation.

Table 4: Pb content in soils, leaves and sticks of *Ilex paraguariensis* plantations.

Pb (mg kg-1)									
Sample	Parameter	Poletti et al.[1] 2014 [61]	Barbosa et al.[2] 2015 [48]	Magri et al.[3] 2017 [62]	Barbosa et al.[4] 2018 [9]	Barbosa et al. 2020 [63]	Frigo et al.[5] 2020 [64]	Vargas M. et al.[6] 2020 [65]	Magri et al. 2021 [7]
Soils	Instrument	FAAS[7]		ICP-MS[8]			ICP-OES[9]	ICP-MS	ICP-OES
	Min.			6.50 (HC) 7.90 (FS)			14.50 (ER) 13.50 (IL)	7.13	5.80
	Max.			20.63 (HC) 17.94 (FS)			21.20 (ER) 17.20 (IL)	33.37	37.51
	Mean ± SD	24.16 ± 1.59 (PR, VS) 29.57 ± 1.25 (PR, OF) 29.87 ± 3.54 (PR, CF) 27.55 ± 3.00 (SC, VS) 31.01 ± 5.78 (SC, OF) 34.20 ± 4.36 (SC, CF) 16.38 ± 5.58 (RS, VS) 8.23 ± 1.12 (RS, OF) 8.90 ± 0.53 (RS, CF)		14.41 ± 4.51 (HC) 13.06 ± 2.89 (FS)				20.89	
Leaves	Instrument		ICP-OES	ICP-MS	ICP-OES	ICP-OES	ICP-OES	ICP-MS	GF-AAS10
	Min.			0.13 (HC) 0.07 (FS)				< LD (U) < LD (W)	0.11
	Max.			0.47 (HC) 0.58 (FS)				0.602 (U) 0.475 (W)	2.59
	Mean ± SD		0.49 ± 0.02 (C) 0.45 ± 0.16 (I) 0.61 ± 0.18 (QI) 0.56 ± 0.08 (BC)	0.23 ± 0.11 (HC) 0.23 ± 0.13 (FS)	0.54 (C1, -P) 0.44 (C1, +P) 0.40 (C2, -P) 0.38 (C2, +P)	0.21 ± 0.06	0.16 ± 0.11 (NL, ER) 0.22 ± 0.13 (NL, IL) 0.40 ± 0.19 (OL, ER) 0.36 ± 0.13 (OL, IL)	0.257 (U) 0.209 (W)	0.61 ± 0.40
Sticks	Instrument						ICP-OES		
	Min.								
	Max.								
	Mean ± SD						0.17 ± 0.10 (ER) 0.17 ± 0.09 (IL)		

Table 5: Cd content in soils, leaves and sticks of *Ilex paraguariensis* plantations.

Cd (mg kg-1)									
Sample	Parameter	Poletti et al.11 2014 [61]	Barbosa et al.12 2015 [48]	Magri et al.13 2017 [62]	Barbosa et al.14 2018 [9]	Barbosa et al. 2020 [63]	Frigo et al.15 2020 [64]	Vargas M. et al.16 2020 [65]	Magri et al. 2021 [7]
Soils	Instrument	FAAS17		ICP-MS18			ICP-OES19	ICP-MS	ICP-OES
	Min.			0.75 (HC) 0.62 (FS)			0.57 (ER) 0.11 (IL)	0.021	0.11
	Max.			3.61 (HC) 3.20 (FS)			0.85 (ER) 0.25 (IL)	0.285	1.54
	Mean ± SD	3.23 ± 0.30 (PR, VS) 3.53 ± 0.32 (PR, OF) 3.38 ± 0.28 (PR, CF) 2.61 ± 0.38 (SC, VS) 3.23 ± 0.10 (SC, OF) 3.33 ± 0.23 (SC, CF) 1.82 ± 0.15 (RS, VS) 1.83 ± 0.09 (RS, OF) 1.76 ± 0.08 (RS, CF)		1.85 ± 0.85 (HC) 1.75 ± 0.94 (FS)				0.098	
Leaves	Instrument		ICP-OES	ICP-MS	ICP-OES	ICP-OES	ICP-OES	ICP-MS	GF-AAS20
	Min.			0.08 (HC) 0.10 (FS)				0.094 (U) 0.077 (W)	0.10
	Max.			1.94 (HC) 1.51 (FS)				0.844 (U) 0.856 (W)	1.61
	Mean ± SD		0.13 ± 0.03 (C) 0.12 ± 0.02 (I) 0.14 ± 0.01 (QI) 0.12 ± 0.02 (BC)	0.43 ± 0.47 (HC) 0.46 ± 0.45 (FS)	0.25 (C1, -P) 0.15 (C1, +P) 0.20 (C2, -P) 0.15 (C2, +P)	0.14 ± 0.04	0.19 ± 0.12 (NL, ER) 0.13 ± 0.15 (NL, IL) 0.21 ± 0.21 (OL, ER) 0.12 ± 0.09 (OL, IL)	0.288 (U) 0.272 (W)	0.29 ± 0.30
Sticks	Instrument						ICP-OES		
	Min.								
	Max.								
	Mean ± SD						0.50 ± 0.24 (ER) 0.31 ± 0.12 (IL)		

1- PR: Paraná; SC: Santa Catarina; RS: Rio Grande do Sul (Brazilian states); VS: virgin soil; OF: organic fertilization; CF: chemical fertilization.
2- C: Cascavel; I: Ivaí; QI: Quedas do Iguaçu (municipalities of Paraná, Brazil); BC: Barão de Cotegipe (municipality of Rio Grande do Sul, Brazil).
3- HC: homogeneous crops; FS: forest systems.
4- C1: clone 1; C2: clone 2; -P: without phosphorus; +P: with phosphorus.
5- ER: Erechim; IL: Ilópolis (municipalities of Rio Grande do Sul, Brazil); NL: new leaves; OL: old leaves.
6- U: unwashed; W: washed.
7- FAAS: Flame Atomic Absorption Spectrometry.
8- ICP-MS: Inductively Coupled Plasma-Mass Spectrometry.
9- ICP-OES: Inductively Coupled Plasma-Optical Emission Spectrometry.
10- GFAAS: Graphite Furnace Atomic Absorption Spectrometry.
11- PR: Paraná; SC: Santa Catarina; RS: Rio Grande do Sul (Brazilian states); VS: virgin soil; OF: organic fertilization; CF: chemical fertilization.
12- C: Cascavel; I: Ivaí; QI: Quedas do Iguaçu (municipalities of Paraná, Brazil); BC: Barão de Cotegipe (municipality of Rio Grande do Sul, Brazil).-
13- HC: homogeneous crops; FS: forest systems.
14- C1: clone 1; C2: clone 2; -P: without phosphorus; +P: with phosphorus.
15- ER: Erechim; IL: Ilópolis (municipalities of Rio Grande do Sul, Brazil); NL: new leaves; OL: old leaves.
16- U: unwashed; W: washed.
17- FAAS: Flame Atomic Absorption Spectrometry.
18- ICP-MS: Inductively Coupled Plasma-Mass Spectrometry.
19- ICP-OES: Inductively Coupled Plasma-Optical Emission Spectrometry.
20- GFAAS: Graphite Furnace Atomic Absorption Spectrometry.

Table 6: As content in soils, leaves and sticks of *Ilex paraguariensis* plantations.

As (mg kg-1)				
Sample	Parameter	Barbosa et al.[21] 2015 [48]	Frigo et al.[22] 2020 [64]	Vargas M. et al.[23] 2020 [65]
Soils	Instrument		ICP-OES	
	Min.		4.75 (ER) 4.90 (IL)	
	Max.		6.75 (ER) 7.20 (IL)	
	Mean ± SD			
Leaves	Instrument	ICP-OES[24]	ICP-OES	ICP-MS[25]
	Min.			0.014 (U) 0.009 (W)
	Max.			0.056 (U) 0.042 (W)
	Mean ± SD	0.22 ± 0.12 (C) 0.48 ± 0.18 (I) 0.39 ± 0.16 (QI) 0.34 ± 0.16 (BC)	0.18 ± 0.05 (NL, ER) 0.14 ± 0.08 (NL, IL) 0.16 ± 0.08 (OL, ER) 0.14 ± 0.10 (OL, IL)	0.032 (U) 0.022 (W)
Sticks	Instrument		ICP-OES	
	Min.			
	Max.			
	Mean ± SD		0.26 ± 0.15 (ER) 0.26 ± 0.15 (IL)	

21- C: Cascavel; I: Ivaí; QI: Quedas do Iguaçu (municipalities of Paraná, Brazil); BC: Barão de Cotegipe (municipality of Rio Grande do Sul, Brazil).
22- ER: Erechim; IL: Ilópolis (municipalities of Rio Grande do Sul, Brazil); NL: new leaves; OL: old leaves.
23- U: unwashed; W: washed.
24- ICP-OES: Inductively Coupled Plasma-Optical Emission Spectrometry.
25- ICP-MS: Inductively Coupled Plasma-Mass Spectrometry.

Barbosa et al. (2015) [48] studied the Pb, Cd and As content in mature leaves of yerba mate trees (progeny) from different origins (Cascavel, Ivaí and Quedas do Iguaçu from the state of PR and Barão de Cotegipe from the state of RS), grown in Pinhais (PR), Brazil.

Mean values between 0.45 and 0.61 mg kg-1 for Pb, between 0.12 and 0.14 mg kg-1 for Cd and between 0.22 and 0.48 mg kg-1 for As were reported. Mean Pb content in samples from *Quedas do Iguaçu* reached the maximum allowed level.

Magri *et al*. (2017) [62] determined Pb and Cd content in soils and yerba mate leaf samples, coming from homogeneous crops and agroforestry systems of RS, Brazil. In soils, concentrations between 6.50 and 20.63 mg kg-1 for Pb and between 0.62 and 3.61 mg kg-1 for Cd were obtained. In leaves, concentrations between 0.07 and 0.58 mg kg-1 for Pb and between 0.08 and 1.94 mg kg-1 for Cd were obtained. Both soils and yerba mate leaves had similar Pb and Cd content, independently of the cultivation system adopted. Leaf samples did not exceed the maximum allowed limit for Pb. However, some of these samples greatly exceeded the limit value for Cd.

Barbosa et al. (2018) [9] grew 2 clones of yerba mate in pots on 4 types of acid soils, with and without phosphorus addition, and evaluated Pb and Cd content in leaves.

Mean values between 0.38 and 0.54 mg kg-1 for Pb and between 0.15 and 0.25 mg kg-1 for Cd were found. The authors concluded that phosphorus fertilization exerted different effects on Pb content (increase/decrease/null) and Cd content (decrease/null) in leaves. Furthermore, genotypic variation influenced Pb content in leaves. Average Pb and Cd concentrations did not exceed the maximum permitted limits.

Barbosa et al. (2020) [63] analysed Pb and Cd content in yerba mate leaves of native plants from an araucaria forest in the municipality of Cruz Machado (PR), Brazil. Mean contents of 0.21 mg kg-1 for Pb and 0.14 mg kg-1 for Cd were found, both below limit values.

Frigo et al. (2020) [64] studied the Pb, Cd and As content in soils, new and old yerba mate leaves and yerba mate sticks in the municipalities of Erechim (ER) and Ilópolis (IL), Brazil.

In soils, contents between 13.50 and 21.20 mg kg-1 for Pb, between 0.11 and 0.85 mg kg-1 for Cd and between 4.75 and 7.20 mg kg-1 for As were reported. In both new and old leaves, average values between 0.16 and 0.40 mg kg-1 for Pb, between 0.12 and 0.21 mg kg-1 for Cd, and between 0.14 and 0.18 mg kg-1 for As were found. In sticks, average concentrations of 0.17 mg kg-1 for Pb, between 0.31 and 0.50 mg kg-1 for Cd and 0.26 mg kg-1 for As were reported. In each municipality, average Pb concentrations were higher in old leaves, while those of Cd and As were similar in new and old leaves. In addition, mean Pb concentrations in sticks were lower than in old leaves and mean Cd and As concentrations in sticks were higher than in leaves. This may indicate that Pb was deposited on the leaves surface over time. Only average Cd content in ER stick samples exceeded the maximum allowable limit. Vargas Motta *et al*. (2020) [65] determined Pb and Cd content in soils and Pb, Cd and As content in yerba mate mature leaves, in 30 native sites in southern Brazil, with and without leaves washing.

In soils, concentrations varied between 7.13 and 33.37 mg kg-1 for Pb and between 0.021 and 0.285 mg kg-1 for Cd. In leaves, concentrations ranged between less than the detection limit and 0.602 mg kg-1 for Pb, between 0.077 and 0.856 mg kg-1 for Cd and between 0.009 and 0.056 mg kg-1 for As. According to the authors, washing decreased Pb and As concentrations, suggesting atmospheric contributions and dust deposition for these elements. Some Pb values were close to the maximum allowable limit, while some Cd values greatly exceeded the limit. Magri et al. (2021) [7] evaluated Pb and Cd content in soils and mature leaves of yerba mate in Brazil, Argentina and Paraguay, both in agroforestry systems and in full sun cultivation. In soils, values between 5.80 and 37.51 mg kg-1 for Pb and between 0.11 and 1.54 mg kg-1 for Cd were reported. Concentrations in leaves ranged between 0.11 and 2.59 mg kg-1 for Pb and between 0.10 and 1.61 mg kg-1 for Cd. According to the authors, the cultivation management adopted did not reflect differences in Cd and Pb concentrations between soils and leaves. In addition, these metal concentrations in leaves were not related to soil type. The 38 % of samples presented Pb levels above the limit, 21 % of samples presented Cd levels above the limit, and in 9 % of samples both elements were present in concentrations higher than permitted limits. Some authors mention that the distinction by country of origin is mainly due to the way yerba mate is grown and processed, which may contribute to the elemental concentration profiles of yerba mate [66]. However, other authors suggest that the differences found in heavy metal concentrations can be explained by the geological formation of each region [61] and that the soil used for the cultivation of Ilex paraguariensis is probably the main factor influencing its elemental composition and not the country of origin [67].

Conclusions

Pb, Cd, and As levels in soils and yerba mate plantations in *Misiones* (Argentina) show great variability. The contents of these elements in the soils are below the guideline levels and the maximum permissible limits, complying with the quality of soils for agricultural use.

None of the 6 leaf samples exceeded the Pb, Cd, and As maximum limits allowed. Considering the 6 stick samples, 2 exceeded the Cd maximum limit (33.3 %). Considering the 6 mixtures of leaf and stick samples, 1 exceeded the As limit (16.7 %).

Determinations made according to soil acidity indicate that there are significant differences between the north area and other areas and also between plant fractions. However, soil acidity does not have a significant effect on Pb and Cd content in plantations. As content in stick samples could not be quantified. Therefore, the statistical analyses for this element were not performed. Determinations made according to the fertilization level applied indicate that there are no significant differences between areas (unlike previous experience) or between fertilization systems.

It is important to highlight that Pb and Cd content in sticks is higher than the content of these elements in leaves. This implies that the package composition of processed yerba mate (leaf and stick percentages) would also contribute with these metals to the commercial product.

When comparing concentrations obtained with those reported by other authors in *Ilex paraguariensis* soils and plantations, lower and higher values are found. Several variables could influence Pb, Cd, and As concentration in yerba mate, such as crop type and its characteristics, plant age, elements toxicity and their availability in soil solution, interaction with other elements, physical and chemical soil properties or agricultural inputs use. Taking into account that Pb, Cd and As are toxic and that the maximum content of this contaminants in yerba mate are regulated for commercialization in MERCOSUR, it is important to consider mitigation measures so that plants do not accumulate them excessively in their tissues.

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