



## Levels of Toxic and Essential Elements in Medicinal Herbs Commercialized in Argentina

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### ABSTRACT

The consumption of medicinal herbs, in the form of infusions, such as chamomile (*Matricaria chamomilla*), rosemary (*Rosmarinus officinalis*), wormwood (*Artemisia absinthium*), mint (*Mentha piperita*) and muña-muña (*Clinopodium gilliesii*) is widespread in the region. The determination of toxic and essential elements is relevant to evaluate their incorporation into the human organism. Although the study of elemental levels in different herbs and their infusions is quite widespread, information on plants from Argentina is scarce. In the present work, Cd, Pb, As, Fe, Cu, Ca, Mg, Na and K were quantified in the five commercially available medicinal herbs and in their infusions by atomic absorption and emission spectrometry. In general, the nutrient levels obtained in the herbs studied followed the sequence: K > Ca > Mg > Fe > Na > Cu while in the infusions the order was: K > Mg > Na > Ca > Fe > Cu. Pb was found in the chamomile and wormwood infusions at levels below 10 µg.L<sup>-1</sup>, whereas Cd and As were not detected (LOD= 0.07 µg.L<sup>-1</sup> and 7 µg.L<sup>-1</sup> respectively). The estimated daily intake (EDI) values calculated for the essential elements in the infusions were lower than the recommended daily intake (RDI) levels suggested by the World Health Organization (WHO) and did not provide the diet with significant nutritional values. As for the toxic elements Pb, Cd and As, the EDI values obtained in the infusions were below the provisional maximum tolerable daily intake (PMTDI), indicating that they do not entail a health risk.

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## Introduction

A medicinal plant is a plant in whose composition is found substances that can be used for therapeutic purposes (Akgül et al., 2022; Unal et al., 2022). They are widely consumed throughout the world for the treatment of various diseases. Although often promoted as natural and therefore harmless, herbal remedies are by no means free from adverse effects (Başgel and Erdemoğlu, 2006; Kına et al., 2021; Uysal et al., 2021). Little is known about the relative safety of medicinal herbs compared to synthetic drug treatments. In certain cases, the risk may be lower by using conventional drugs rather than herbal medicines (Fuh et al., 2003; Mohammed et al., 2022). Many medicinal herbs and their mixtures can present a health risk due to the presence of toxic elements such as Pb, Cd, Al and Hg, which are hazardous to humans, depending on their oxidation states and on their concentrations (Karak and Bhagat, 2010; Pehlivan et al., 2021). Over-the-counter herbal products may be contaminated with heavy metals related to growth in a contaminated environment or incorporation during harvest (Chan, 2003).

Metals play a fundamental role as structural and functional components of proteins and enzymes in cells. Each mineral performs a number of different functions in the body (Kirmani et al., 2011). Medicinal plants are either source of minerals in human diet and regular consumption of tea can contribute to the dietary requirements of these elements (Saletovic et al., 2011; Sevindik et al., 2017). The determination of essential elements in medicinal plants and their infusions is important to complement the studies of evaluation of nutritional quality. Ingesting them in excessive amounts can accumulate trace metals and toxic to the human body causing severe health problems (Shaltout and Abd-Elkader, 2016).

Different spectrometric analytical techniques have been carried out for the quantitative analysis of essential and toxic metals such as ETAAS- Electrothermal Atomic Absorption Spectrometry (Wróbel et al., 2000), HR-CS-GF-AAS- High Resolution Continuum Source Electrothermal Atomic Absorption Spectrometry (Shaltout

et al., 2013), ICP-MS- Inductively Coupled Plasma- Mass Spectrometry (Tokalioglu, 2012), ICP-AES-USN- Inductively Coupled Plasma Atomic Emission Spectrometry with Ultrasonic Nebulizer (Vassileva and Hoening, 2001), ICP-OES- Inductively Coupled Plasma Optical Emission Spectrometry plus preconcentration (Marchisio et al., 2005 a, b) and TXRF- Total Reflection X-Ray Fluorescence (Sun et al., 2004).

Chamomile (*Matricaria chamomilla* L.), rosemary (*Rosmarinus officinalis* L.), wormwood (*Artemisia absinthium* L.), peppermint (*Mentha piperita* L.) and muña-muña (*Clinopodium gilliesii* (Benth.) Kuntze) are the medicinal herbs studied in this work. These herbs are widely consumed in the city of Tucumán, generally as an infusion for medical purposes.

Chamomile (*M. chamomilla*) is an annual herbaceous flowering plant native to Europe. It has been used traditionally as a medicinal and pharmaceutical preparation, due to its anti-inflammatory and antispasmodic properties. Recent research supports this use and shows these properties are partly due to its phenolic content (McKay and Blumberg, 2006).

Rosemary (*R. officinalis*) is widely accepted as one of the medicinal herbs with the highest antioxidant activity. It has been reported to possess a number of therapeutic applications in folk medicines in curing or managing of a wide range of diseases such as Diabetes Mellitus, respiratory disorders, stomach problems and inflammatory diseases (Bakirel et al., 2008). The concentration of heavy metals including Pb, Cu, Zn, Cd, Ni and Fe in *R. officinalis* grown in Jordan were evaluated (El-Rjoob et al., 2008).

Wormwood (*A. absinthium*) has been traditionally used as a cytotoxic, antihepatotoxic, antibacterial, antifungal, antioxidant, antimalarial, anthelmintic, antiseptic, antispasmodic, febrifuge, stomachic, cardiac stimulant, for the restoration of declining mental function and inflammation of the liver, and to improve memory (Bora and Sharma, 2010).

Peppermint (*M. piperita*) presents significant antimicrobial and antiviral activities, strong antioxidant and antitumor actions, and some antiallergic potential (McKay and Blumberg, 2006).

Muña-muña (*C. gilliesii*) is an aromatic species from the Andean region, from southern Peru to northern-central Argentina. It is mainly known as muña-muña and its leaves and tender stems are used as a stimulant, against mountain sickness, aphrodisiac, digestive, antispasmodic, among others traditional uses (Hurrell, 2018).

Current studies on medicinal plants are mainly oriented to investigate the therapeutic properties of their active ingredients and the adverse reactions caused by their consumption. Little information was found regarding trace metal and nutrient content in medicinal plants marketed in the north-west of Argentina.

The present study focused on determining the levels of some toxic elements (Cd, Pb and As) and essential elements (Fe, Cu, Ca, Mg, Na and K) in medicinal plants commercialized in Tucumán city, Argentina and their infusions. Also, on evaluating the daily incorporation of each of the elements to the organism through the consumption of the infusions.

## Materials and Methods

### Instrumentation

To carry out the acid digestion treatment of 5 analyzed medicinal herbs, a Multiwave PRO Anton Paar microwave digester (Austria, Europe) was used.

For determination of Cd, Pb and As, a Perkin-Elmer atomic absorption spectrometer (Norwalk, CT, USA) AAAnalyst 100 was used equipped with deuterium background corrector, graphite furnace HGA 800 (pyrolytic graphite furnace with integrated platform, part N° B3000407) and autosampler AS-72. 99.9% high purity argon was used as purge gas. All measurements were made with hollow cathode lamps of each element, 0.7 nm bandwidth and 10 mA lamp current. The analytical readings of toxic elements were made at 228.8 nm, 283.3 nm and 193.7 nm for Cd, Pb and As respectively. The default temperature program provided by the manufacturer was used in all cases. The drying temperature (120°C), cooling prior to atomization (20°C) and cleaning (2600°C) were the same for the three elements. While the temperatures of pyrolysis and atomization varied: 850°C and 1650°C for Cd, 700°C and 1800°C for Pb and 800°C and 2300°C for As.

To measure concentrations of nutrient elements such as Fe, Cu, Ca and Mg also the atomic absorption spectrometer was used but equipped with a fuel lean air-C<sub>2</sub>H<sub>2</sub> flame. The flame was sustained in an all-titanium, 10cm, single-slot burner head (N040-0102) mounted on an inert, plastic-coated burner-mixing chamber ended with a nebulizer holder and a drainage assemblage. The temperature of the air-acetylene flame is about 2300°C. The readings of nutrient elements were made at 372.0 nm, 327.4 nm, 422.7 nm and 285.2 nm for Fe, Cu, Ca and Mg respectively. Spectral bandwidth of the monochromator was set at 0.2 nm for Fe and 0.7 nm for Cu, Ca and Mg.

On the other hand, the levels of Na and K were measured with a flame photometer Metrolab 315 that presents a nebulizer-lighter system. A mixture of air-propane / butane gases was used. The flame temperature reached 1800°C.

### Reagents, standard solutions and samples

65% Nitric acid, analytical grade (Merck, Darmstadt, Germany) bi-distilled in quartz sub-boiling distiller and 30% hydrogen peroxide was used for the digestion of the samples. A NANOpure water purification system (Barnstead, IA, USA) was used to obtain ultrapure water (18 MΩ.cm resistivity).

For ETAAS, magnesium nitrate and palladium solution (Perkin-Elmer, Singapore) were used as matrix modifier for As, and ammonium dihydrogen phosphate for Cd and Pb. Intermediate standards of each element were prepared with 5%(v/v) nitric acid. The intermediate standard for Cd was 1 mg.L<sup>-1</sup> and those for Pb and As were 10 mg.L<sup>-1</sup>. All of them were prepared from a NIST SRM-traceable standard (Merck, Darmstadt, Germany) of the corresponding element.

For the determination of essential elements by FAAS, intermediate standards of 10 mg.L<sup>-1</sup> were prepared for Fe, Cu and Mg. For Ca it was 100 mg.L<sup>-1</sup>. Standard solutions of each element of 1000 mg.L<sup>-1</sup> traceable to NIST SRM (Merck, Darmstadt, Germany) were used.

For the determination of Na and K by flame photometry, solutions of 1000 mg.L<sup>-1</sup> were prepared using NaCl and KCl p.a. (Cicarelli, Santa Fe, Argentina).

Five medicinal herbs marketed in Tucumán, Argentina: chamomile, rosemary, wormwood, peppermint and muña-muña were analyzed. Ten samples of each species were combined to obtain the test sample.

### Samples preparation

The herbs were ground in glass mortar. The difference between the initial weight of the ground herbs and the weight after drying in a convection air oven for 30 minutes at 110 °C was used to calculate the moisture content.

The five medicinal herb samples were subjected to microwave-assisted acid digestion, for which exactly about 0.5 g of each dried herb was weighed in triplicate on an analytical balance. The weighing was done directly in Teflon digestion vessels. 3 mL of concentrated double-distilled nitric acid and 1 mL of 100 vol hydrogen peroxide were added to each. Vessels were closed and inserted into the rotor. Then, the digestion program with a 400 W ramp for 10 minutes, a 400 W hold for 20 minutes and a 70°C cooling was executed. After cooling and opening vessels, sample digests were transferred to 50 mL volumetric flasks and brought to volume with ultrapure water.

In addition, infusions of the medicinal herbs were prepared. We worked in triplicate by weighing in erlenmeyers 2 tablespoons of each herb, the amount commonly used to prepare an infusion. 200mL of ultrapure water were added and boiled in a burner for 10 minutes. It was allowed to cool, filtered and stored in decontaminated and labeled bottles for subsequent measurement.

In both, digests and infusions, reagent blanks and recoveries were prepared in triplicate for each of the elements analyzed.

### Elemental analysis

In each case, appropriate sensitivities were worked with the 5 medicinal herbs and their respective infusions.

#### Cadmium, Lead and Arsenic determination

The determination of toxic elements such as cadmium, lead and arsenic was carried out by atomic absorption spectrometry with electrothermal vaporization (ETAAS). Calibration lines were constructed directly using the autosampler of the equipment. The ranges of the lines were from 1 to 5 µg.L<sup>-1</sup> for Cd, from 10 to 100 µg.L<sup>-1</sup> for Pb and from 30 to 150 µg.L<sup>-1</sup> for As. Correlation coefficients (r) equal to 0.9984, 0.9998 and 0.9921 were obtained for Cd, Pb and As, respectively. The limits of detection (LOD) were calculated considering three times the blank signal, obtaining values of 0.07 µg.L<sup>-1</sup> for Cd, 0.7 µg.L<sup>-1</sup> for Pb and 7 µg.L<sup>-1</sup> for As. The limits of quantification (LOQ) were 0.2 µg.L<sup>-1</sup>, 2.4 µg.L<sup>-1</sup> and 25 µg.L<sup>-1</sup> for Cd, Pb and As respectively and were calculated considering ten times the blank signal.

#### Iron, Copper, Calcium and Magnesium determination

The measurements of the levels of the nutrient elements Fe, Cu, Ca and Mg were made by flame atomic absorption spectrometry (FAAS). Calibration curves were prepared with concentration ranges from 0.1 to 5 mg.L<sup>-1</sup> for Fe and Cu, from 0.4 to 5 mg.L<sup>-1</sup> for Ca and from 0.1 to 0.5 mg.L<sup>-1</sup> for Mg. For Ca and Mg, KCl 10% was added as ionization

suppressor and SrCl<sub>2</sub> 10% as releasing agent. Linear regression analysis was performed for each nutrient and correlation coefficient (r) values between 0.9992 and 0.9999 were obtained, indicating excellent linearity. The limit of detection (LOD) gave values of 0.094, 0.151, 0.107 and 0.014 mg.L<sup>-1</sup> for Fe, Cu, Ca and Mg respectively, while the limit of quantification (LOQ) gave values of 0.313, 0.502, 0.358 and 0.047 mg.L<sup>-1</sup> for these elements.

#### Sodium and Potassium determination

The determination of Na and K was carried out by flame photometry. Calibration lines were prepared from 2 to 10 mg.L<sup>-1</sup> for Na and from 0.5 to 2.5 mg.L<sup>-1</sup> for K. Values of r equal to 0.9992 for Na and 0.9928 for K were obtained by linear regression analysis. The limits of detection (LOD) were 0.403 and 0.065 mg.L<sup>-1</sup> and the limits of quantification (LOQ) were 1.34 and 0.217 mg.L<sup>-1</sup> respectively.

#### Estimated Daily Intake Calculation

The incorporation of metals into the body as a result of the consumption of these herbs can be assessed by the estimated daily intake (EDI). The EDI depends on both the amount of tea consumed and the concentration of the metal. The EDI was calculated using equation (1).

$$EDI = \frac{C \cdot E_F \cdot E_D \cdot F_{IR}}{WB \cdot T_A \cdot 1000} \quad (1)$$

where *C* is the metal content (mg.kg<sup>-1</sup>), *E<sub>F</sub>* is the exposure frequency (365 days.year<sup>-1</sup>), *E<sub>D</sub>* is the exposure duration (70 years), *F<sub>IR</sub>* is the tea ingestion rate (g.person<sup>-1</sup>.day<sup>-1</sup>), *WB* is the mean body weight (70 kg for adults) and *T<sub>A</sub>* is the mean exposure time (*E<sub>F</sub>* × *E<sub>D</sub>*).

## Results and Discussion

### Medicinal Herbs

The results reported in Table 1 verify the presence of varied amounts of the analyzed elements in each of the herbal samples. These results show that, in the studied medicinal herbs, Cd content was < 0.200 mg.kg<sup>-1</sup> and Pb content was < 2 mg.kg<sup>-1</sup>. The As and Cu contents were found to be below the detection limits of the implemented techniques corresponding to 0.7 and 15.1 mg.kg<sup>-1</sup> respectively. The highest Fe concentrations were found in the *A. absinthium* and *M. piperita* samples with values around 700 mg.kg<sup>-1</sup>. The highest Ca concentration was 18715 mg.kg<sup>-1</sup> in the *M. piperita* sample and Mg was 3490 mg.kg<sup>-1</sup> in the *M. chamomilla* sample. *M. chamomilla* has a much higher Na content than the rest of the studied medicinal herbs and is 2814 mg.kg<sup>-1</sup>, while K is higher in *A. absinthium*, with 49204 mg.kg<sup>-1</sup>.

Figures 1 and 2 show graphically and comparatively only those essential and toxic elements that could be quantified in the medicinal herbs. Figure 1 shows that the major nutrient in all herbs is K, followed by Ca, while Fe and Na are the minority essential elements. In the case of *R. officinalis*, Ca and K levels were found to be similar. Figure 2 highlights that Pb is the major toxic element in all herbs. However, the levels of toxicants do not exceed what is reported in the literature for the same herbs, as seen in Table 2. This table summarizes the results of toxic and essential element levels in previously published medicinal plants from other parts of the world.

It is observed that in *M. chamomilla*, our Fe, Pb, Cd, Mg and K levels were of the same order as the data reported in literature, while Ca values were found to be well below those reported by Ražić et al. (2005). In the analysis of *R. officinalis*, we obtained much lower Pb values than those reported by El-Rjoob et al. (2008). On the other hand, our Ca values were higher than those reported in the bibliography. Fe, Mg and K concentrations were in the same order as previously reported. In *A. absinthium*, Fe and Ca contents were found to be higher than those reported by

Ražić et al. (2005), while Mg and K were in the same order. No bibliography references were found with Pb and Cd data in such herb. In the case of *M. piperita*, the data obtained for Fe, Pb, Ca, Mg and K turned out to be in the same order as those reported in the bibliography. Neither elemental analysis of *C. gilliesii*, nor Na and As for any of the herbs studied were found in the bibliography. Although no Cd, As and Cu levels were detected in the samples, values for these have been reported in the bibliography.

Table 1. Concentration of toxic and essential elements in mg.kg<sup>-1</sup> dry weight of herbs ± standard deviation (mean ± s)

Samples	Cd	Pb	As	Fe	Cu
<i>Matricaria chamomilla</i>	0.156 ± 0.006	0.896 ± 0.103	< LOD <sup>b</sup>	267 ± 22	< LOD <sup>c</sup>
<i>Rosmarinus officinalis</i>	< LOD <sup>a</sup>	0.542 ± 0.003	< LOD <sup>b</sup>	392 ± 110	< LOD <sup>c</sup>
<i>Artemisia absinthium</i>	0.0665 ± 0.054	1.72 ± 0.11	< LOD <sup>b</sup>	737 ± 48	< LOD <sup>c</sup>
<i>Mentha piperita</i>	< LOD <sup>a</sup>	0.726 ± 0.005	< LOD <sup>b</sup>	777 ± 29	< LOD <sup>c</sup>
<i>Clinopodium gilliesii</i>	< LOD <sup>a</sup>	0.517 ± 0.217	< LOD <sup>b</sup>	213 ± 30	< LOD <sup>c</sup>
Samples	Ca	Mg	Na	K	
<i>Matricaria chamomilla</i>	5630 ± 194	3490 ± 146	2814 ± 181	40565 ± 1977	
<i>Rosmarinus officinalis</i>	15755 ± 177	2103 ± 81	51.0 ± 1.4	16652 ± 268	
<i>Artemisia absinthium</i>	16915 ± 1350	2969 ± 264	228 ± 97	49204 ± 3843	
<i>Mentha piperita</i>	18715 ± 262	2149 ± 49	63.8 ± 3.6	28752 ± 3583	
<i>Clinopodium gilliesii</i>	5462 ± 960	1184 ± 113	106 ± 40	17240 ± 726	

<sup>a</sup>LOD= 0.007 mg.kg<sup>-1</sup>, <sup>b</sup>LOD= 0.7 mg.kg<sup>-1</sup>, <sup>c</sup>LOD= 15.1 mg.kg<sup>-1</sup>

Table 2. Previously published levels of toxic and essential elements in medicinal plants

Herbs	Concentration (mg.kg <sup>-1</sup> )	Technique	Country	R
<i>Matricaria chamomilla</i>	Fe (253); Cu (10.89); Ca (805500); Mg (4100); K (589000)	FAAS/FAES	Serbia	1
<i>Matricaria chamomilla</i>	Fe (567); Pb (1.40); Cd (0.45)	FAAS/ETAAS	B/M	2
<i>Matricaria chamomilla</i>	Fe (130); Cu (14.2)	AAS/ICP-MS	Serbia	3
<i>Rosmarinus officinalis</i>	Fe (546); Cu (5.92); Ca (9500); Mg (2300); K (21100)	FAAS/FAES	Serbia	1
<i>Rosmarinus officinalis</i>	Fe (578); Cu (10.7); Pb (75.3); Cd (4.8)	AAS	Jordán	4
<i>Artemisia absinthium</i>	Fe (182); Cu (12.25); Ca (5500); Mg (2100); K (33200)	FAAS/FAES	Serbia	1
<i>Mentha piperita</i>	Fe (405); Cu (10.94); Ca (14300); Mg (5300); K (18000)	FAAS/FAES	Serbia	1
<i>Mentha piperita</i>	Fe (263); Pb (0.71); Cd (0.16)	FAAS/ETAAS	B/M	2
<i>Mentha piperita</i>	Fe (444); Cu (17.2)	AAS/ICP-MS	Serbia	3

B/M: Bulgaria and Macedonia ; R: Reference; 1: Ražić et al. (2005); 2: Gentscheva et al. (2010); 3: Mihaljev et al. (2014); 4: El-Rjoob et al. (2008)

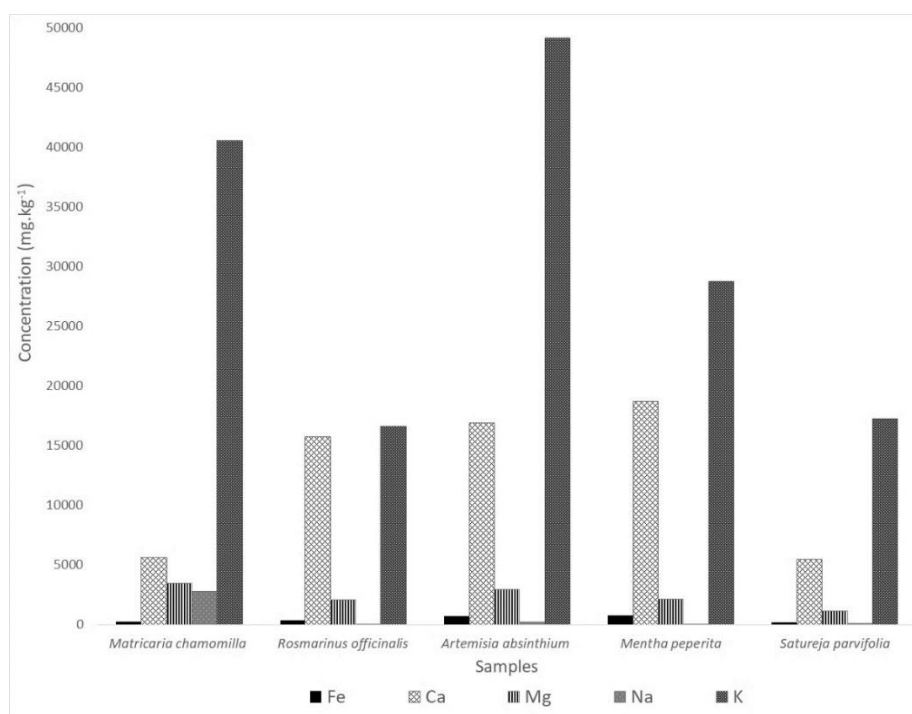


Figure 1. Concentration of essential elements in medicinal herbs

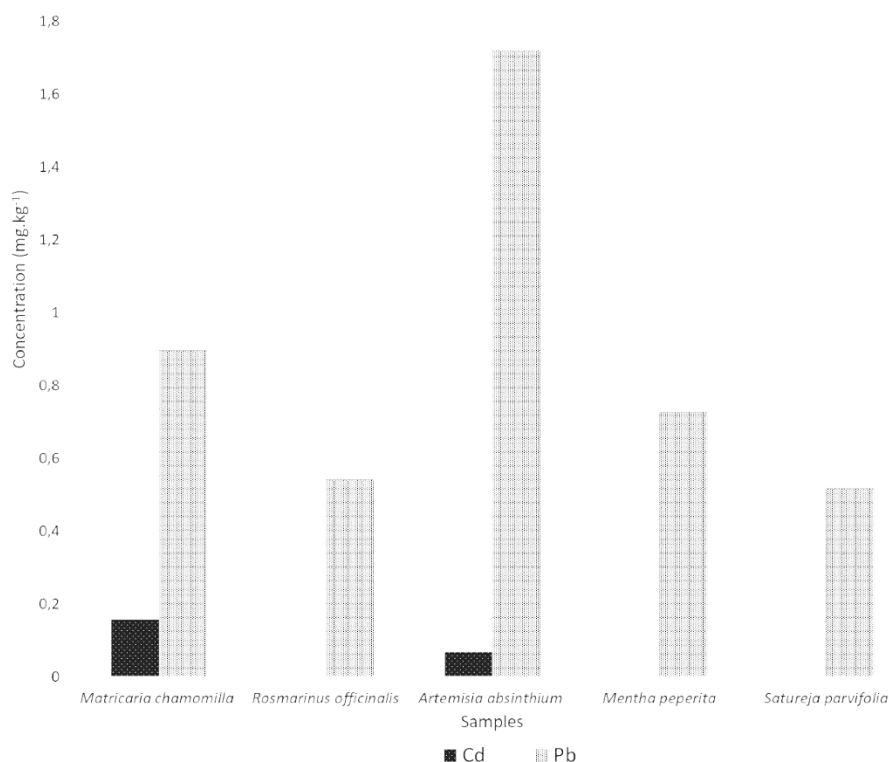


Figure 2. Concentration of toxic elements in medicinal herbs

Table 3. Concentration of toxic elements in  $\mu\text{g.L}^{-1}$  and essential elements in  $\text{mg.L}^{-1}$  in infusions  $\pm$  standard deviation (mean  $\pm$  s)

Samples	Cd	Pb	As	Fe	
<i>Matricaria chamomilla</i>	< LOQ <sup>b</sup>	$9.59 \pm 0.366$	< LOD <sup>e</sup>	< LOQ <sup>f</sup>	
<i>Rosmarinus officinalis</i>	< LOD <sup>a</sup>	< LOQ <sup>d</sup>	< LOD <sup>e</sup>	< LOQ <sup>f</sup>	
<i>Artemisia absinthium</i>	< LOD <sup>a</sup>	$7.32 \pm 0.08$	< LOD <sup>e</sup>	$0.427 \pm 0.004$	
<i>Mentha piperita</i>	< LOD <sup>a</sup>	< LOD <sup>c</sup>	< LOD <sup>e</sup>	< LOQ <sup>f</sup>	
<i>Clinopodium gilliesii</i>	< LOD <sup>a</sup>	< LOD <sup>c</sup>	< LOD <sup>e</sup>	< LOQ <sup>f</sup>	
Samples	Cu	Ca	Mg	Na	K
<i>Matricaria chamomilla</i>	< LOD <sup>g</sup>	$2.80 \pm 0.16$	$44.8 \pm 1.2$	$49.6 \pm 1.6$	$546 \pm 23$
<i>Rosmarinus officinalis</i>	< LOD <sup>g</sup>	$4.73 \pm 0.06$	$49.6 \pm 2.2$	$1.94 \pm 0.11$	$436 \pm 28$
<i>Artemisia absinthium</i>	< LOD <sup>g</sup>	$1.71 \pm 0.02$	$37.1 \pm 4.2$	$7.48 \pm 0.37$	$926 \pm 54$
<i>Mentha piperita</i>	< LOD <sup>g</sup>	$2.91 \pm 0.001$	$23.3 \pm 0.3$	$1.64 \pm 0.11$	$314 \pm 18$
<i>Clinopodium gilliesii</i>	< LOD <sup>g</sup>	$0.844 \pm 0.034$	$17.0 \pm 0.3$	$2.62 \pm 0.43$	$366 \pm 100$

<sup>a</sup>LOD= 0.07  $\mu\text{g.L}^{-1}$ , <sup>b</sup>LOQ= 0.2  $\mu\text{g.L}^{-1}$ , <sup>c</sup>LOD= 0.7  $\mu\text{g.L}^{-1}$ , <sup>d</sup>LOQ= 2.4  $\mu\text{g.L}^{-1}$ , <sup>e</sup>LOD= 7  $\mu\text{g.L}^{-1}$ , <sup>f</sup>LOQ= 0.313  $\text{mg.L}^{-1}$ , <sup>g</sup>LOD= 0.151  $\text{mg.L}^{-1}$

### Infusions

Table 3 presents the concentrations of toxic and essential elements determined in the herbal sample infusions. No toxic elements were detected except for Pb in *M. chamomilla* and *A. absinthium*. Fe was quantified only in *A. absinthium*. The Cu concentration proved to be below the LOD (0.151  $\text{mg.L}^{-1}$ ) of the technique used, as it occurs in herbs. The highest Ca and Mg contents appeared in *R. officinalis*. The highest levels of Na and K in the infusions correspond to *M. chamomilla* and *A. absinthium* respectively, this situation is similar to that observed when analyzing the herbs.

Analyte recovery studies were carried out, obtaining values between 91.5 and 106.7 %.

### EDI evaluation

From the elemental concentrations of the infusions, estimated daily intake (EDI) values were calculated for each sample. EDI could not be calculated for those

elements with concentrations lower than the LOD or LOQ in the infusions. For this reason, Pb was the only toxic element which could have its EDI calculated. Its value in *M. chamomilla* was  $2.74 \times 10^{-5} \text{ mg.Kg}^{-1}\text{BW.day}^{-1}$  and in *A. absinthium* was  $2.09 \times 10^{-5} \text{ mg.Kg}^{-1}\text{BW.day}^{-1}$ . The incorporation of Pb by consuming *M. chamomilla* or *A. absinthium* is lower than the provisional maximum tolerable daily intake (PMTDI) allowed by WHO ( $3.57 \times 10^{-3} \text{ mg.kg}^{-1}\text{BW.day}^{-1}$ ), as reported by Mohamed et al. (2017).

The EDI ( $\text{mg.kg}^{-1}\text{BW.day}^{-1}$ ) values of the essential elements studied are reported in Table 4. The EDI data expressed in  $\text{mg.pers}^{-1}\text{.day}^{-1}$ , calculated for an average adult of 70 kg, are also shown. In addition, the recommended daily intake (RDI) values in  $\text{mg.pers}^{-1}\text{.day}^{-1}$  are presented as a comparison parameter.

As can be seen, the consumption of one or more infusions of these herbs does not contribute significantly to the recommended daily intake for each element.

Table 4. Comparison of EDI in nutrient elements with RDI from previous publications

Element	Infusion	EDI (mg.Kg <sup>-1</sup> BW.día <sup>-1</sup> )	EDI (mg.pers <sup>-1</sup> .día <sup>-1</sup> )	RDI (mg.pers <sup>-1</sup> .día <sup>-1</sup> )
Fe	<i>Artemisia absinthium</i>	1.22×10 <sup>-3</sup>	0.1	8 – 18 <sup>a</sup>
Ca	<i>Matricaria Chamomilla</i>	8×10 <sup>-3</sup>	0.6	1000 – 1300 <sup>b</sup>
	<i>Rosmarinus officinalis</i>	1.35×10 <sup>-2</sup>	0.9	
	<i>Artemisia absinthium</i>	4.88×10 <sup>-3</sup>	0.3	
	<i>Mentha piperita</i>	8.28×10 <sup>-3</sup>	0.6	
	<i>Clinopodium gilliesii</i>	2.41×10 <sup>-3</sup>	0.2	
Mg	<i>Matricaria Chamomilla</i>	0.128	9	300 – 420 <sup>b</sup>
	<i>Rosmarinus officinalis</i>	0.142	10	
	<i>Artemisia absinthium</i>	0.106	7	
	<i>Mentha piperita</i>	6.65×10 <sup>-2</sup>	5	
	<i>Clinopodium gilliesii</i>	4.86×10 <sup>-2</sup>	3	
Na	<i>Matricaria Chamomilla</i>	0.142	10	1500 – 2500 <sup>b</sup>
	<i>Rosmarinus officinalis</i>	5.54×10 <sup>-3</sup>	0.4	
	<i>Artemisia absinthium</i>	2.13×10 <sup>-2</sup>	1.5	
	<i>Mentha piperita</i>	4.69×10 <sup>-3</sup>	0.3	
	<i>Clinopodium gilliesii</i>	7.48×10 <sup>-3</sup>	0.5	
K	<i>Matricaria Chamomilla</i>	1.56	109	4700 <sup>b</sup>
	<i>Rosmarinus officinalis</i>	1.24	87	
	<i>Artemisia absinthium</i>	2.64	185	
	<i>Mentha piperita</i>	0.897	63	
	<i>Clinopodium gilliesii</i>	1.04	73	

<sup>a</sup><https://www.fao.org/3/w0073s/w0073s1a.htm>; <sup>b</sup> Karppanen and Mervaala (2006)

## Conclusion

The present study enriches the knowledge on the contents of toxic and essential elements found in medicinal herbs (*M. chamomilla*, *R. officinalis*, *A. absinthium*, *M. piperita* and *C. gilliesii*) commonly commercialized in Tucumán, Argentina. The levels of toxic elements (Pb, Cd and As) determined in the infusions of the herbs studied were below the maximum tolerable limits established by international organizations; therefore, their consumption does not represent a health risk. The concentrations of essential elements (Fe, Cu, Ca, Mg, Na and K) in these infusions were lower than the recommended daily intake levels. Consequently, it is considered that their consumption does not have a significant nutritional value for the organism.

## Declarations

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**Ethics Approval:** Not applicable.

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## References

Akgül H, Mohammed FS, Kına E, Uysal İ, Sevindik M, Doğan M. 2022. Total Antioxidant and Oxidant Status and DPPH Free radical activity of *Euphorbia eriophora*. Turkish Journal of Agriculture-Food Science and Technology, 10(2): 272-275. <https://doi.org/10.24925/turjaf.v10i2.272-275.4685>

Bakirel T, Bakirel U, Keleş OU, Ülgen SG, Yardibi H. 2008. In vivo assessment of antidiabetic and antioxidant activities of Rosemary (*Rosmarinus officinalis*) in alloxan-diabetic rabbits. J Ethnopharmacol, 116:64-73. <https://doi.org/10.1016/j.jep.2007.10.039>

Başgel S, Erdemoğlu SB. 2006. Determination of mineral and trace elements in some medicinal herbs and their infusions consumed in Turkey. Sci Total Environ, 359:82-89. <https://doi.org/10.1016/j.scitotenv.2005.04.016>

Bora KS, Sharma A. 2010. Phytochemical and pharmacological potential of *Artemisia absinthium* Linn. and *Artemisia asiatica* Nakai: A Review. J Pharm Res, 3(2):325-328.

Chan K. 2003. Some aspects of toxic contaminants in herbal medicines. Chemosphere, 52:1361-1371. [https://doi.org/10.1016/S0045-6535\(03\)00471-5](https://doi.org/10.1016/S0045-6535(03)00471-5)

El-Rjoob AWO, Massadeh AM, Omari MN. 2008. Evaluation of Pb, Cu, Zn, Cd, Ni and Fe levels in *Rosmarinus officinalis labiatae* (Rosemary) medicinal plant and soils in selected zones in Jordan. Environ Monit Assess, 140(1):61-68. <https://doi.org/10.1007/s10661-007-9847-3>

FAO. Recommended nutrient intake. Available from: <https://www.fao.org/3/w0073s/w0073s1a.htm> [Accessed 21 April 2022].

Fuh CB, Lin HI, Tsai H. 2003. Determination of lead, cadmium, chromium, and arsenic in 13 herbs of Tocolysis formulation using atomic absorption spectrometry. J Food Drug Anal, 11(1):39-45. <https://doi.org/10.38212/2224-6614.2732>

Gentscheva GD, Stafilovb T, Ivanova EH. 2010. Determination of some essential and toxic elements in herbs from Bulgaria and Macedonia using atomic spectrometry. Eurasian J Anal Chem, 5(2):104-111.

Hurrell JA. 2018. *Clinopodium gilliesii* (Benth.) Kuntze. In Albuquerque U, Patil U, Máthé A. (editors). Medicinal and Aromatic Plants of South America (pp.163-172). Medicinal and Aromatic Plants of the World, vol 5. Springer, Dordrecht. [https://doi.org/10.1007/978-94-024-1552-0\\_14](https://doi.org/10.1007/978-94-024-1552-0_14)

Karak T, Bhagat RM. 2010. Trace elements in tea leaves, made tea and tea infusion: A review. Food Res Int, 43:2234-2252. <https://doi.org/10.1016/j.foodres.2010.08.010>

- Karppanen H, Mervaala E. 2006. Sodium intake and hypertension. *Prog Cardiovasc Dis*, 49(2):59-75. <https://doi.org/10.1016/j.pcad.2006.07.001>
- Kına E, Uysal İ, Mohammed FS, Doğan M, Sevindik M. 2021. In-vitro antioxidant and oxidant properties of *Centaurea rigida*. *Turkish Journal of Agriculture-Food Science and Technology*, 9(10): 1905-1907. <https://doi.org/10.24925/turjaf.v9i10.1905-1907.4603>
- Kirmanı MZ, Mohiuddin S, Naz F, Naqvi II, Zahir E. 2011. Determination of some toxic and essential trace metals in some medicinal and edible plants of Karachi city. *J Basic Appl Sci*, 7(2):89-95.
- Marchisio PF, Sales AM. 2005 a. On-Line pre-concentration of cadmium in commercial tea samples using polyurethane foam as filter associated with ultrasonic nebulization-inductively coupled plasma optical emission spectrometric detection. *Instrum Sci Technol*, 33:449-459. <https://doi.org/10.1081/CI-200063721>
- Marchisio PF, Sales AM, Cerutti S, Marchevski E, Martinez LD. 2005 b. On-line pre-concentration/determination of lead in *Ilex paraguariensis* samples (mate tea) using polyurethane foam as filter and USN-ICP-OES. *J Hazard Mater*, 124(1-3):113-118. <https://doi.org/10.1016/j.jhazmat.2005.04.017>
- McKay DL, Blumberg JB. 2006. A review of the bioactivity and potential health benefits of chamomile tea (*Matricaria recutita* L.). *Phytother Res*, 20:519-530. <https://doi.org/10.1002/ptr.1900>
- McKay DL, Blumberg JB. 2006. A review of the bioactivity and potential health benefits of peppermint tea (*Mentha piperita* L.). *Phytother Res*, 20:619-633. <https://doi.org/10.1002/ptr.1936>
- Mihaljev Ž, Živkov-Baloš M, Čupić Ž, Jakšić S. 2014. Levels of some microelements and essential heavy metals in herbal teas in Serbia. *Acta Pol Pharm*, 71(3):385-391.
- Mohamed H, Haris PI, Brima EI. 2017. Estimated dietary intakes of toxic elements from four staple foods in Najran city, Saudi Arabia. *Int J Environ Res Public Health*, 14(12):1575. <https://doi.org/10.3390/ijerph14121575>
- Mohammed FS, Kına E, Uysal İ, Mencik K, Dogan M, Pehlivan M, Sevindik M. 2022. Antioxidant and Antimicrobial Activities of Ethanol Extract of *Lepidium spinosum*. *Turkish Journal of Agriculture-Food Science and Technology*, 10(6): 1116-1119. <https://doi.org/10.24925/turjaf.v10i6.1116-1119.5207>
- Pehlivan M, Mohammed FS, Şabik AE, Kına E, Dogan M, Yumrutaş Ö, Sevindik M. 2021. Some Biological activities of ethanol extract of *Marrubium globosum*. *Turkish Journal of Agriculture-Food Science and Technology*, 9(6): 1129-1132. <https://doi.org/10.24925/turjaf.v9i6.1129-1132.4382>
- Ražić S, Onjia A, Đogo S, Slavković L, Popović A. 2005. Determination of metal content in some herbal drugs—Empirical and chemometric approach. *Talanta*, 67:233-239. <https://doi.org/10.1016/j.talanta.2005.03.023>
- Saletovic M, Zorica H, Banjanin B, Kesic A. 2011. Bioavailability of microelements (Cu, Zn, Mn) in medicinal plants. *HealthMED*, 5(5):1358-1364.
- Sevindik M, Akgul H, Pehlivan M, Selamoglu Z. 2017. Determination of therapeutic potential of *Mentha longifolia* ssp. *longifolia*. *Fresen Environ Bull*, 26(7): 4757-4763.
- Shaltout AA, Abdel-Aal MS, Welz B, Castilho INB. 2013. Determination of Cd, Cu, Ni and Pb in black tea from Saudi Arabia using graphite furnace atomic absorption spectrometry after microwave-assisted acid digestion. *Anal Lett*, 46(13):2089-2100. <https://doi.org/10.1080/00032719.2013.784918>
- Shaltout AA, Abd-Elkader OH. 2016. Levels of trace elements in black teas commercialized in Saudi Arabia using inductively coupled plasma mass spectrometry. *Biol Trace Elem Res*, 174:477-483. <https://doi.org/10.1007/s12011-016-0728-x>
- Sun H, Qiao F, Suo R, Li L, Liang S. 2004. Simultaneous determination of trace arsenic (III), antimony (III), total arsenic and antimony in Chinese medicinal herbs by hydride generation-double channel atomic fluorescence spectrometry. *Anal Chim Acta*, 505:255-261. <https://doi.org/10.1016/j.aca.2003.10.071>
- Tokaloğlu Ş. 2012. Determination of trace elements in commonly consumed medicinal herbs by ICP-MS and multivariate analysis. *Food Chem*, 134:2504-2508. <https://doi.org/10.1016/j.foodchem.2012.04.093>
- Unal O, Eraslan EC, Uysal I, Mohammed FS, Sevindik M, Akgul H. 2022. Biological activities and phenolic contents of *Rumex scutatus* collected from Turkey. *Fresenius Environmental Bulletin*, 31(7): 7341-7346.
- Uysal İ, Mohammed FS, Şabik AE, Kına E, Sevindik M. 2021. Antioxidant and Oxidant status of medicinal plant *Echium italicum* collected from different regions. *Turkish Journal of Agriculture-Food Science and Technology*, 9(10): 1902-1904. <https://doi.org/10.24925/turjaf.v9i10.1902-1904.4588>
- Vassileva E, Hoenig M. 2001. Determination of arsenic in plant samples by inductively coupled plasma atomic emission spectrometry with ultrasonic nebulization: a complex problem. *Spectrochim Acta Part B*, 56:223-232. [https://doi.org/10.1016/S0584-8547\(01\)00156-2](https://doi.org/10.1016/S0584-8547(01)00156-2)
- Wróbel K, Wróbel K, Colunga Urbina EM. 2000. Determination of total aluminum, chromium, copper, iron, manganese and nickel and their fractions leached to the infusions of black tea, green tea, *Hibiscus sabdariffa* and *Ilex paraguariensis* (mate) by ETA-AAS. *Biol Trace Elem Res*, 78:271-280. <https://doi.org/10.1385/BTER:78:1-3:271>