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RESEARCH ARTICLE

The Assessment of metals accumulation in *Celtis tournefortii* Lam and *Prosopis farcta* from Mazne sub-district, Kurdistan region of Iraq

Samiaa J Abdulwahid-Kurdi[1*], Mohammad Saadatian[1] & Karzan Mohammad Khalid[2]

[1]General Science Department, Faculty of Education, Soran University, Delyzian, Soran, Erbil Kurdistan Region 44008, Iraq
[2]Laboratory of Medical Microbiology, Department of Biology, Faculty of Science, Soran University, Delyzian, Soran, Erbil Kurdistan Region 44008, Iraq

*Correspondence email - samiaa.abdulwahid@gmail.com

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Abstract

A significant portion of the global population relies on medicinal plants as their primary source of healthcare. Therefore, it is crucial to ascertain the amount of heavy metal accumulated in these plants. In this study, 25 elements (Calcium (Ca), Phosphorus (P), Magnesium (Mg), Sodium (Na), Potassium (K), Sulfur (S), Iron (Fe), Copper (Cu), Zinc (Zn), Selenium (Se), Cadmium (Cd), Vanadium (V), Chromium (Cr), Nickel (Ni), Silver (Ag), Beryllium (Be), Strontium (Sr), Barium (Ba), Aluminum (Al), Lead (Pb), Bismuth (Bi), Rubidium (Rb), Boron (B), Arsenic (As) and Antimony (Sb)) were found in the leaves and fruit of *C. tournefortii* Lam and in the pods and seeds of *P. farcta*, collected from the Mazne sub-district of Kurdistan in Iraq. The analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). An exploratory study of samples was conducted using principal component analysis (PCA) and hierarchical cluster analysis (HCA). The concentration of elements, quantified in parts per million (ppm) was as follows: Ca (3403-81948), Mg (1573-7578), Na (108-291), K (6481-23212), Fe (184-623), Cu (8-16), Zn (3-48), Se (0.5-33), Cd (0.11 -0.40 ppm), V (1-3), Cr (2-25), Ni (2-4), Ag (0.5-1.7), Be (0.20-0.40), Sr (79.3-454), B (3-86), Al (100-738), Bi (0.7-2.30), Rb (1-7), B (0.7-2.3), As (0.1 -3.9), Sb (6.60-12). All samples under investigation contained similar levels of K and Pb (218 and 1, respectively). The samples were divided into three major categories, as demonstrated by PCA and HCA. According to the findings, the fruit of *C. tournefortii Lam* is a source of Mg, K, Cu, Cd, Cr, Be, Sr, Ba and Rb. The seeds of *P. farcta* had accumulated a significant level of S, Zn, Se and Ni. Overall, the data suggest that use of these plants may pose potential health risks to humans due to the presence of certain heavy metals.

Keywords: heavy metals; hierarchical cluster; mazne sub-district; medicinal plants; principal component analysis

Introduction

A growing proportion of the global population relies on medicinal herbs and products as their primary source of healthcare. According to estimates by the World Health Organization (WHO), approximately 70% of the world's population utilizes medicinal herbs and related products for basic medical care (1). Natural resources play a crucial role in the development of novel pharmaceuticals, as they provide an extra sources of essential vitamins and minerals (2). The hypoglycemic effects of the leaves of *Murraya koenigii* (L.) Spreng., *Mentha × piperita* L., *Ocimum tenuiflorum* L. and *Aegle marmelos* (L.) may be attributed to the presence of trace elements such as K, V, Zn, Cr, Cu, Ni and Na (3). The efficacy of therapeutic plants depends largely on their secondary metabolites and essential oils; however, excessive heavy metal concentrations may lead to adverse health effects when these bioactive chemicals are consumed over extended periods (4).

Heavy metals can enter the human body through various pathways, including skin contact, dust inhalation and soil ingestion (2). Here, it is easy to introduce pollutants into medicinal herbs through human activities such as industrialization and agricultural processing (5). Plant absorbs several heavy metals, such as Ba, Co, Cu, Fe, Mn, Mo, Se, Si, Sr, V and Zn, which are essential for a variety of physiological and biological activities, primarily from soils and through exposure to industrial processes like chemical manufacturing , engineering and mining) (6). Medicinal plants collected from both developed and developing countries were found to contain significant concentrations of heavy metals that may be harmful (7).

The devastating environmental consequences of the Iran-Iraq war (1980-1988) persist more than three decades later. The Kurdistan Region Government's (KRG) Mine Action Agency reports approximately 13400 victims of mine explosions during the 1990s. Due to continued soil contamination, residents of border towns remain at risk, frequently sustaining injuries or fatalities from landmines scattered throughout the region (8). Moreover, the U.S. military disclosed the use of over 944000 rounds of depleted uranium ammunition during the 1991 Gulf War in Iraq and Kuwait.

Consequently, individuals have likely experienced both acute and chronic exposure to various hazardous substances, heavy metals and particulate matter-factors that can adversely affect the safety and health of wild edible plants (9).

Balanced levels of macro- and micronutrients are crucial for the healthy operation of the major organs. In Hangzhou, China, heavy metal contamination in food has been associated with the spatial distribution and incidence of stomach cancer (10). In Nigeria, multiple studies have investigated the presence of lead (Pb) in three commonly used cosmetics-lipstick, eyeliner and eye pencil-with levels ranging between 78 and 123 ppm (11). It is estimated that women use about 1.8 kg of lipstick throughout their lifetimes (11). The use of such cosmetics has been directly linked to various health risks, including breast cancer, skin allergies, respiratory disorders, reproductive complications, recurrent miscarriages and genetic abnormalities (12). Therefore, toxic elements such as Cd, Ni and Pb must be closely monitored in both biological samples and herbal medicines. Notably, approximately 90% of the herbs and medicinal plants used in India's pharmaceutical industry are harvested from wild sources (13).

The Kurdish population traditionally uses two wild plants, namely *Celtis tournefortii* Lam and *Prosopis farcta*, to treat a variety of conditions. *Celtis Tournefortii* Lam, is a deciduous tree that grows up to 6 m tall in hot climatic plains and dry forests. *Prosopis farcta*, is a perennial shrub that grows to a height of 30 to 100 cm and is a common plant in the Middle East, especially across the alluvial soils typical of Mediterranean agricultural zones. In Iraq, it thrives in diverse habitats from the north to the south (1). The Mazne region, characterised by a Mediterranean climate with cold winters and mild summers, served as the collection site for this study.

The results indicated the presence of heavy metals in these Kurdish wild plants, which also contained specific elements at significant levels, suggesting potential environmental contamination. Accordingly, this study aimed to quantify 25 elements-including macroelements (Ca, P, Mg, Na, K, S) and microelements (Fe, Al, Zn, Sr, Cu, Ni, B, Se, Cr, Pb, V, Be, Ba, Bi, Cd, Sb and As)-in the fruit and leaves of *Celtis tournefortii* Lam., as well as the pods and seeds of *Prosopis farcta* collected from the Mazne sub-district in the Kurdistan region. Elemental analysis was conducted using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). .

Materials and Methods

Description of the study area

Located at the intersection of Iraq, Iran and Turkey, the district of Mergasor lies in the governorate of Erbils' extreme north. Mesrgasor consists of five sub-districts: Barzan, Goratu, Piran, Shirwan Mezn and Mazne (Fig. 1). Mazne sub-district is about 135 km away from the central Erbil province, 25 km from Mergasor district and 15 km from the center of Soran district. It lies along the main road connecting Zargali and Mergasor. The Mazne sub-district has 31 villages and is located 25 km from the Mergasor district. Using the global positioning system (GPS), these sites were identified at 36°47'28.5"N latitude and 44° 25'24.5"E longitude (1).

Celtis tournefortii Lam and *Prosopis farcta* were collected in November 2021 from the Mazne sub-district. The plant specimens were identified by an expert from the National Herbarium of Kurdistan and were coded and kept at the Salahaddin University Herbarium Education College's Herbarium (ESUH) (Table1 and Fig. 2).

Sample preparation and analysis

Plant samples were chosen at random and each tree specimen was replicated three times. Ripe wild plant fruits, leaves, pods and seeds were mashed, cleaned and shade-dried until crisp. After sieving twice, the dry material was ground into powder using a mechanical mixer. The dried samples (0.5 g) was weighed and placed into borosilicate glass digestion tubes.

To each tube, 10 mL of a digestion mixture consisting of HNO_3-HCl-H_2O_2 (8:1:1, v/v/v) was added. The tubes were placed on a heating block set to 120 °C and maintained for approximately 3 h, or until complete digestion was achieved, resulting in clear solutions. These digested solutions were then transferred to 50 mL volumetric flasks and diluted to volume with ultrapure water. The diluted samples were stored in high-density polyethylene bottles until they were analyzed.

The samples were analysed in duplicate. A blank solution, prepared using the same acid mixture (10 mL of HNO3 -HCl-H2O2 (8:1:1, v/v/v)), was included as a control (14). It was then examined using an inductively coupled plasma-optical emission spectrophotometric (ICP-OES) instrument (Optima 5300 DV ICP-OES, Perkin Elmer Instruments, USA) and an inductively coupled plasma mass spectrometry (ICP-MS) instrument (4500 Elan DRC, Perkin Elmer, ION 300X, USA model), both offering wide analytical ranges (15) (Fig. 3)

Statistical analysis

For each mineral, the sample data was analysed using one-way analysis of variance (ANOVA) and means comparisons were performed using the Tukey test, as described by the graph Pad Prism software (version 9.5.1). Statistical significance was established at $P<0.05$ level. Mineral concentrations results are presented as the mean ± standard error of the mean (SEM). Additionally, the data analyzed with XLSTAT were further subjected to principal component analysis (PCA) and hierarchical cluster analysis (HCA) to differentiate and classify the various elements according to plant parts (16)

Results and Discussion

Different components, categorized as macro and micro elements, are necessary for plant growth and development. Macronutrients such as calcium (Ca), phosphorus (P), magnesium (Mg), sodium (Na), potassium (K) and sulfur (S), along with soft and light metals, are required in relatively large quantities. In contrast, microelements are found in trace levels and are primarily heavy metals (Fe, Al, Zn, Cu, Ni, Se, Cr, Pb, Be, Ba, Bi, Cd, Sb and As),

Dietary intake plays a crucial role in determining individual exposure to heavy metals. These metals and metalloids, characterized by relatively high densities, can be toxic even at parts per billion (ppb) quantities. Therefore, it is essential to track and evaluate the levels of these metals in our diet. Understanding the mineral content of foods is critical when

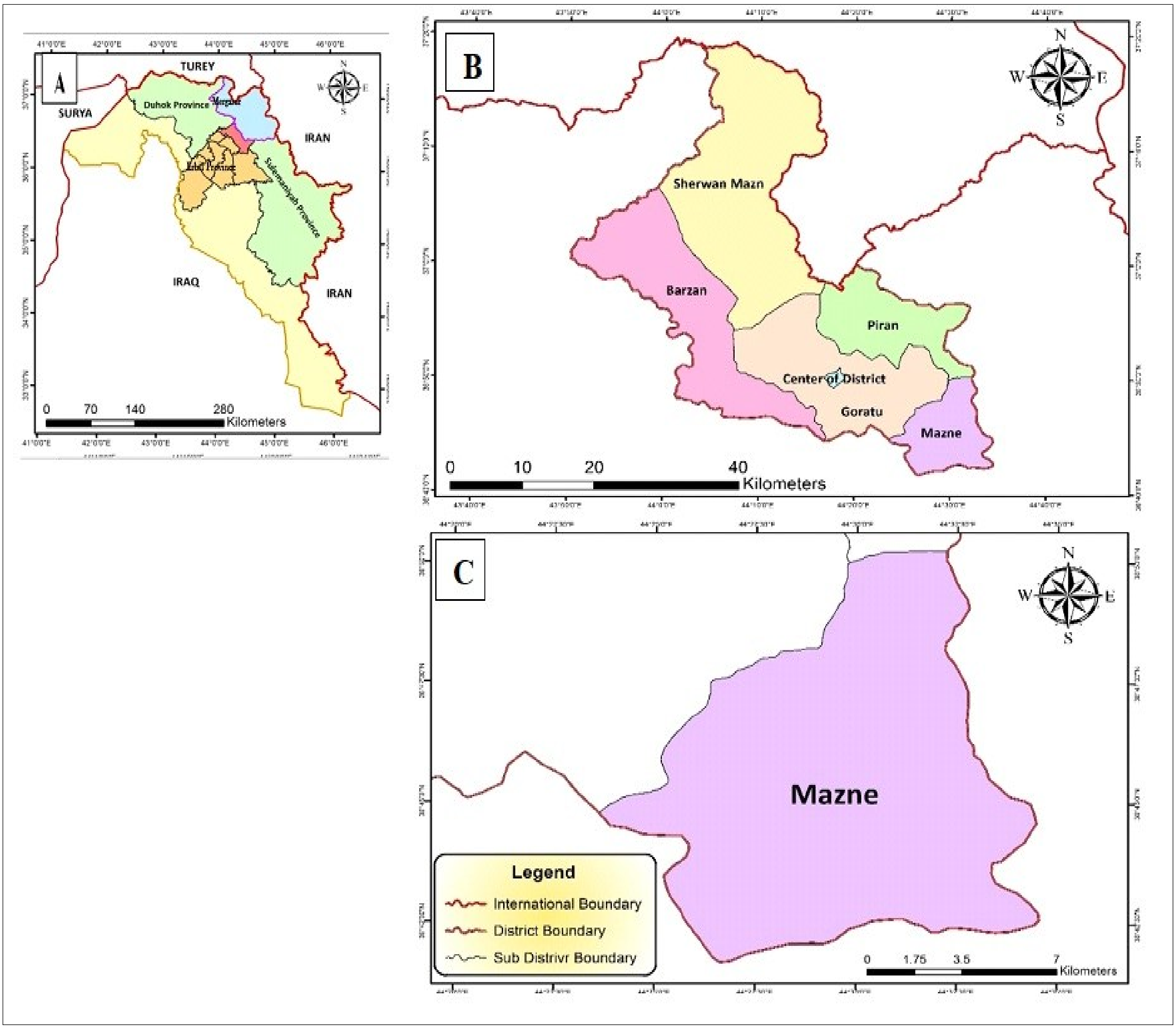

Fig. 1. Maps showing the location of the research area. A. Iraqi map, B. Mergasur district, C. Mazne sub-district.

Table 1. The scientific names and a list of the therapeutic uses for the plants in Mazne Sub-district that were under investigation

Scientific name and voucher species	English and Kurdish Local names	Family	Uses/ailments treated
Celtis tournefortii **Lam (ESUH7901)**	Hackberry (Tawk)	Cannabaceae	Diarrhea, diuretic (14)
Prosopis farcta **(ESUH7913)**	Syrian mesquite (Khrnuk)	Fabaceae (Leguminosa)	Stomach aches, diabetes and diarrhea (15)

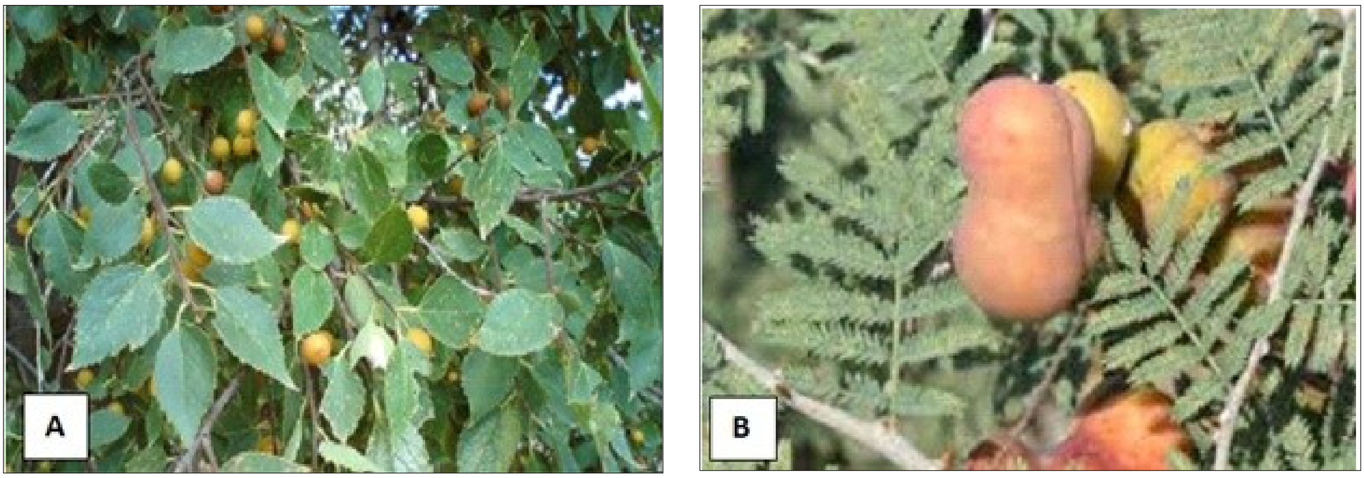

Fig. 2. Two wild plants were collected in Mazne sub-district *A. Celtis tournefortii* Lam, B. *Prosopis farcta.*

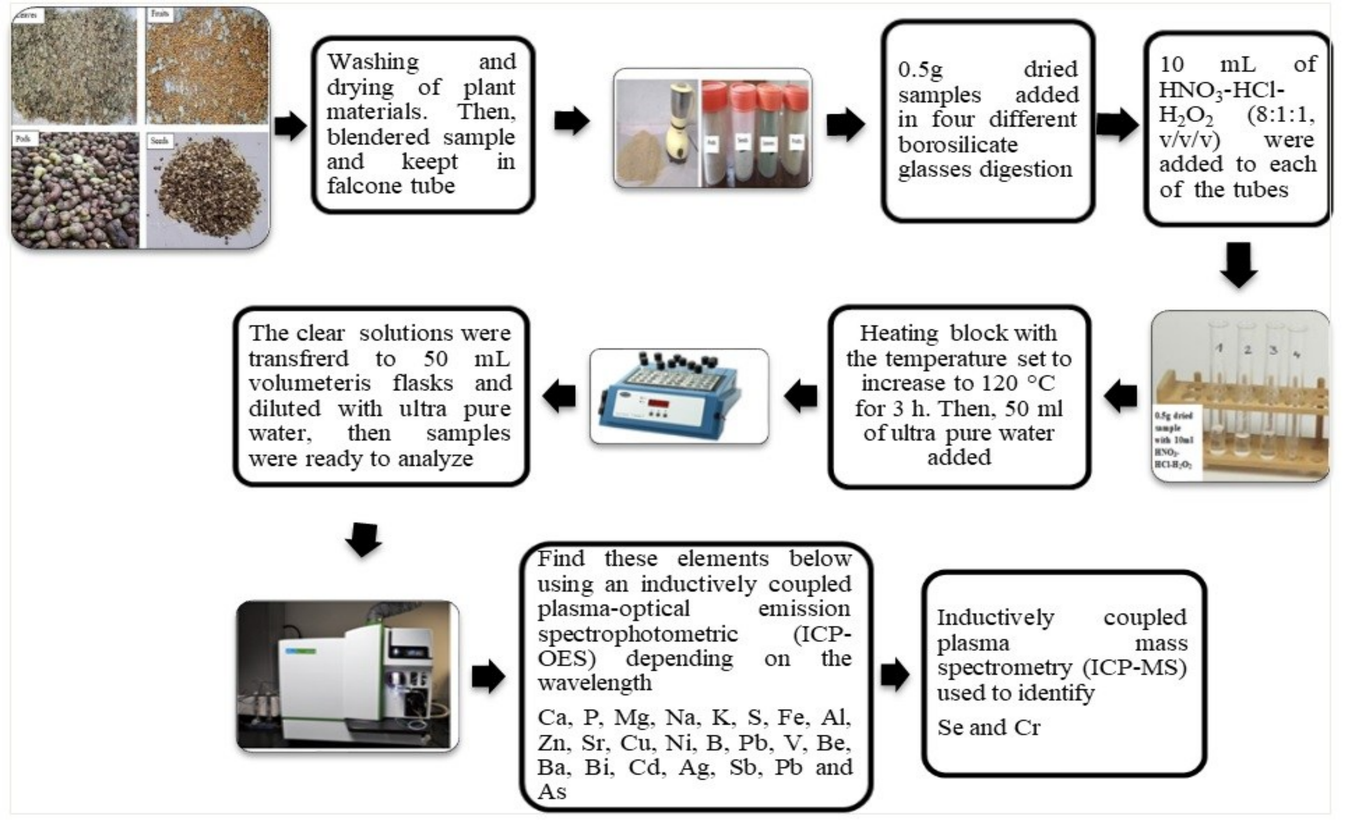

Fig. 3. Sample preparation flow chart.

evaluating daily mineral intake requirements. Researchers continue to investigate the minimal required levels and the potentially toxic thresholds of minerals in the human diet.

Various factors influence mineral concentrations in plant, like crop species, climatic conditions, soil properties and the stage of plant maturity. For elemental analysis, ICP-OES is a powerful tool capable of determining metals in diverse sample matrices (15). More recently, the combination of inductively coupled plasma with mass spectrometry has given rise to inductively coupled plasma-optical mass spectrometry (ICP-MS), which allows for the highly sensitive detection of trace elements with exceptionally low detection limits. Additionally, ICP-MS offers the advantage of distinguishing and quantifying isotopes of the same element.

In the current study, the accumulation of calcium (Ca) was observed in the following order: leaf>fruit of *C. tournefortii* Lam>pod>seed of *P. farcta*, with concentrations of 81948, 77584, 4370 and 3403 ppm, respectively. The leaf and fruit of *C. tournefortii* Lam exhibited significantly higher Ca content compared to the pod and seed of *P. farcta* (Table 2). On the other hand, raw mint leaves have been reported to contain a relatively low Ca content of 15.331 ppm (17). The recommendation daily intake of calcium ranges from 800 and 1300 mg per day (18), excessive intake beyond this limit may lead to adverse health effects, such as hypercalcemia (19).

The accumulation of magnesium (Mg) concentration in the fruit >leaf of *C. tournefortii* Lam >seed >pod of *P. farcta* is 7578, 4569, 2646 and 1573 ppm, respectively (Table 2). Comparatively, researchers found that fruits and vegetables had a magnesium content of 55 to 1900 ppm (fresh weight), while raw mint leaves had a magnesium content of 5778 ppm (17). The recommendation daily intake for magnesium from fruits and vegetables is 200-400 mg daily (20). Common side effects of excessive magnesium intake include headache, nausea, hypotension and widespread discomfort in the stomach and bones (21).

The present investigation found that there was an accumulation of sodium (Na) in the leaf > pod >fruit ≥ seed at 291, 137, 108 and 108 ppm, respectively (Table 2). Among all plant parts, the leaves of *C. tournefortii* Lam showed the highest concentration of Na. The range of Na level found in fruit juices and raw vegetables was between 0.4 - 2770 ppm and 22.8 - 940 ppm, respectively (22). The recommendation daily intake of Na is less than 1500 mg/day (23).

According to the results of the current investigation, the potassium (K) concentrations in the fruit>pod>seed>leaf was 23212, 18011, 12335 and 6481 ppm, respectively (Table 2). The fruit of *C.tournefortii* Lam has a much higher K concentration (23212 ppm) compared to the pod, seed and leaves. Fresh plants typically have 200-7300 ppm of K; while nuts and seeds may contain levels as high as 22400 ppm (20). The recommendation daily intake for K ranges from 550-5625 mg per day (24). However, in case of hyperkalemia, especially under catabolic conditions accompanied by oliguria resulting from renal failure, the body might not be able to metabolize more K (25).

Prosopis farcta has more sulfur (S) stored in it than *Celtis tournefortii* Lam. According to Table 2, the detected values were arranged as follows: seed>pod of *Prosopis farcta*>fruit>leaves of *Celtis tournefortii* Lam. The concentrations of these compounds were 4494, 2599, 2060 and 1701 ppm, respectively. The results showed that the S absorption was considerably different in each portion of the plants. The World Health Organization recommends a daily intake of 13 mg of sulfur in the form of amino acids (26). Reduced forms of sulfur, such as glutathione in rice grains, Smethylmethionine in wheat, or sulfate in legume pods, are known to be transported to seeds through the phloem (27). Owing to their elevated S concentration, these two natural plants can serve as additives and are an excellent alternative.

In the present study, the iron (Fe) level of *Celtis tournefortii* leaf was significantly higher (P 0.05) than in the pod and seed of *Prosopis farcta*. The Iron (Fe) concentrations followed a descending order: leaf>fruit of *Celtis tournefortii* > pod>seed of *Prosopis farcta*, with respective concentrations of 623, 424, 196 and 84 ppm, respectively (Table 2). The aerial parts of *Grammosciadium platycarpum a*nd *Leonurus cardiana*, exhibited Fe concentrations ranging from 184 to 623 ppm, along with significant amounts of phenolic and flavonoid compounds (28). In a different investigation, *Withania somnifera* samples were taken from the PCSIR Lab complex's field in Karachi (Pakistan), revealed Fe concentrations of 9,417.7 ppm in the shoot and 3,750.3 ppm in the leaves, which exceeded permissible limits (29). Therefore, *Celtis tournefortii* Lam and *Prosopis farcta* may be beneficial for individuals with iron deficiency. The recommended daily intake (RDI) for iron is 10-18 mg/day (24).

In the current study, accumulation levels of zinc (Zn) was observed in the following order: seed>pod of *Prosopis farcta*>fruit>leaf of *Celtis tournefortii* Lam, with concentrations of 48, 17, 8 and 3 ppm, respectively (Table 2). Plants typically contain Zn in the range of 0.5 and 118 ppm (22). In a different investigation, samples of *Withania somnifera* from the PCSIR Lab complex field in Karachi (Pakistan), showed Zn concentrations of 422.2 ppm in shoots and 375 ppm in leaves (29). It is important to note that high levels of other metals, such as Fe and Cu, can reduce the bioavailability of Zn (30). The RDI for zinc is considered to be between 10 and 20 mg/day (31).

Selenium (Se) accumulation in this study was found to be highest in the seeds of *Prosopis farcta* (33.48ppm),followed by the pod (2.76ppm), fruit (0.5ppm) and leaf (0.5 ppm) of *Celtis tournefortii* Lam (Table 2). Notably, *Prosopis farcta* seeds accumulated substantially more Se than those of *Celtis tournefortii* Lam. S and Se had shared metabolic and root absorption mechanisms, which were present and distributed similarly in many plants (32). High concentrations of Se accumulated are reported in the genera *Astragalus, Stanleya, Morinda, Neptunia, Oonopsis and Xylorhiza.* They can accumulate from hundreds to thousands of mg Se/kg dry mass in their tissues (33). The RDI of selenium in the USA is 0.055 mg /day (34).

Chromium (Cr) concentrations were recorded in the following descending order: fruit>leaf of *Celtis tournefortii* Lam>seed> pods of *Prosopis farcta*, with values of 25, 6, 4 and 2 ppm, respectively (Table 2). The primary food sources of Cr

Table 2. Profile metals concentration of wild plants from Mazne sub-district Kurdistan region of Iraq

Element (ppm)			*Celtis tournefortii* Lam		*Prosopis farcta*		P-Value
		Physical properties	Leaf	Fruit	Pod	Seed	
Macro-elements							
1	Calcium (Ca)	Soft	81948±0.57^{a}	77584±2.30^{b}	4370±3.51^{c}	3403±0.57^{d}	<0.0001
2	Phosphorus (P)	Soft	218± 1.1^{a}	218±1.15^{a}	218±1.15^{a}	218±1.2^{a}	1
3	Magnesium (Mg)	Light	4569±0.58^{b}	7578±1^{a}	1573±0.57^{d}	2646±0.58^{c}	<0.0001
4	Sodium (Na)	Light	291±0.33^{a}	108±0.33^{c}	137±0.57^{b}	108±0.33^{c}	0.001
5	Potassium (K)	Light	6481± 0.03^{d}	23212±0.02^{a}	18011±0.03^{b}	12335±0.02^{c}	0.0001
6	Sulphur (S)	Soft	1701±0.54^{d}	2060±0.56^{c}	2599±0.57^{b}	4494±0.57^{a}	<0.0001
Micro-elements							
7	Iron (Fe)	Heavy	623±0.57^{a}	424±0.57^{b}	196±0.57^{c}	184±0.58^{d}	<0.001
8	Aluminium (Al)	Heavy	738±1.15^{a}	100±0.57^{b}	100±1.154^{b}	100±0.57^{b}	0.0001
9	Zinc (Zn)	Heavy	3 ± 0.28^{d}	8± 0.15^{c}	17 ± 0.57^{b}	48 ± 1^{a}	<.000
10	Strontium (Sr)	Soft	430±1^{b}	454±0.57^{a}	133±0.57^{c}	79.3±0.40^{d}	<0.0001
11	Copper (Cu)	Heavy	8±0.15^{c}	16±0.87^{a}	12± 0.36^{b}	16± 0.87^{a}	<.0001
12	Nickel (Ni)	Heavy	4±0.29^{b}	2±0.28^{c}	2±0.29^{c}	5±0.28^{a}	0.0002
13	Boron (B)	Lightest	0.8±0.03c	0.7± 0.01^{d}	2.3± 0.05^{a}	1.6±0.08^{b}	0.0001
Trace-elements							
14	Selenium (Se)	Heavy	0.5±0.02^{c}	0.5±0.03^{c}	2.76±0.08^{b}	33.48±0.57^{a}	<0.001
15	Chromium (Cr)	Heavy	6±0.06^{b}	25±0.58^{a}	2.01±0.04^{d}	4±0.05^{c}	<0.0001
16	Lead (Pb)	Heavy	1±0.10^{a}	1±0.04^{a}	1±0.05^{a}	1±0.05^{a}	0.9
17	Vanadium (V)	Light transition	3±0.01^{a}	1± 0.00^{b}	1±0.02^{b}	1±0.01^{b}	<0.0001
18	Beryllium (Be)	Heavy	0.30±0.01^{ab}	0.40± 0.05^{a}	0.20±0.57^{b}	0.20± 0.67^{b}	0.025
19	Barium (Ba)	Heavy	77±1.15^{b}	86±0.57^{a}	3±0.05^{c}	3±0.11^{c}	<0.0001
20	Bismuth (Bi)	Heavy	0.80±0.03^{c}	0.70±0.01^{c}	2.3±0.05^{a}	1.60±0.89^{b}	<.0001
21	Cadmium (Cd)	Heavy	0.30 ±0.02^{b}	0.40 ±0.01^{a}	0.11 ±0.1^{d}	0.20± 0.05^{c}	0.001
22	Silver (Ag)	Heavy	1±0.17^{bc}	1.4±0.20^{ab}	1.7±0.11^{a}	0.50± 0.15^{c}	0.004
23	Antimony (Sb)	Heavy	7±0.05^{bc}	6.60±0.09^{c}	12±0.57^{a}	9.5±0.28^{b}	<.0001
24	Rubidium (Rb)	Soft	1±0.28^{c}	7±0.3^{a}	5±0.28^{b}	2±0.27^{c}	0.0001
25	Arsenic (As)	Heavy	1.8±0.05^{b}	0.1±0.01^{c}	3.9±0.05^{a}	1.8±0.5^{b}	<0.001

Classification of metals based on their physical properties: The data are expressed as mean ± SEM. Means with different letters were significantly different at the level of P<0.05. SEM = standard error of the mean. ppm=parts per million. Heavy metals; are relatively high densities, atomic weights, or atomic numbers. Light metals; are relatively low density. Soft metals; are shiny metals with low melting points, making them easily workable. Transition metals; are an incomplete inner orbit in their atomic structure.

consumption are fruits and vegetables (20). Elevated Cr levels in plants often reflect high chromium content in the surrounding soil (35). Using inductively coupled plasma atomic emission spectroscopy, the accumulation of Cr in 22 kinds of medicinal plants was gathered from five distinct local herbalists in Hatay, Turkey (36). The Riesenfenchelm (*Ferula communis*) had the lowest Cr values (0.33ppm), whereas chamomile had the highest quantities (4.21ppm). The recommended daily intake of Cr ranges from 0.02 to 0.25 mg/day (24) and this is not considered to be threatened by the presence of hazardous Cr(VI) species typically found in herbal teas (24). Nickel (Ni) levels were found in the order: seed> leaf>fruit≥ pods, with respective values of 5, 4, 2 and 2 ppm, respectively. The seeds of *Prosopis farcta* exhibited significantly higher Ni levels when compared with the leaf, fruit and pods (Table 2). The shape, number of seeds and germination are all strongly impacted by the amount of Ni present. However, excessive Ni concentrations can change the metabolic activity of plants (37). Among various herbal infusions, senna tea had the lowest nickel amounts (0.90 ppm), whereas fennel had the highest (5.40 ppm). Conversely, the Ni concentrations in the fennel and nettle infusions ranged from 2.90 to 0.04 ppm, respectively (38). Furthermore, samples of *Withania somnifera* collected from the PCSIR Lab complex in Karachi, Pakistan, revealed Ni concentrations in the shoot and leaves of 16.2 and 10.3 ppm, respectively exceeding permissible limits (29). Ni's recommendation daily allowed is 0.32-0.735 mg/day (39).

Overall, the results revealed that alkaline metals were more consistently accumulated in *Celtis tournefortii* Lam than in *Prosopis farcta*. Beryllium (Be) and barium (Ba) were more concentrated in the fruit and leaf tissues of *Celtis tournefortii* Lam, with Be concentrations of 0.4 and 0.3 ppm and Ba concentrations of 86 and 77 ppm, respectively. In contrast, *Prosopis farcta* pods and seeds contained only 0.2 ppm of Be and 3 ppm of Ba, significantly lower than levels found in *Celtis tournefortii* Lam (Table 2). For reference, dried tobacco leaves typically contain 105 ppm of Ba, most of which remains in the ash after combustion (40). Barium is considered to have low mobility and presents minimal risk to livestock at concentrations up to 1260 ppm in crops like beans, alfalfa and soybeans. According to a study, naturally occurring Be concentrations in soils range from 1 to 15 ppm. However, both Ba and Be are classified as human carcinogens based on substantial evidence of carcinogenicity in humans (41). The recommended daily intake levels are 0.75 mg/kg for Ba and 0.00012 mg/day for Be (41, 42).

Bismuth (Bi) concentrations were found in the following order: pod > seed of *Prosopis farcta* > fruit > leaf of *Celtis tournefortii* Lam, with values of 2.3, 1.6, 0.8 and 0.7 ppm, respectively (Table 2). Bismuth is considered a "green" heavy metal and is often used as a safer alternative to lead (Pb) in various industrial applications, thereby reducing environmental contamination. Bi is also employed therapeutically as an anti-*Helicobacter pylori* agent and is considered non-toxic to humans (43). The fruit and leaf of *Celtis tournefortii* Lam contained significantly lower Bi levels compared to the pod and seed of *Prosopis farcta*. According to research by Agirman et al. (44), *Prosopis farcta* fruit extract may have hepatoprotective properties, while the seed extract may induce hepatocyte damage and enzyme leakage. For therapeutic purposes, seeds and pods of *Prosopis farcta* at Bi concentrations of 2.3 and 1.6 ppm/body weight, respectively, have shown potential benefits for treating kidney stones in rats (45). The recommended daily intake of Bi ranges from 0.005 to 0.02 mg/day (46).

In the present study, arsenic (As) concentrations followed the order: pod > seed of *Prosopis farcta* ≥ leaf > fruit of *Celtis tournefortii* Lam, with values of 3.9, 1.8 and 0.1 ppm, respectively (Table 2). The acceptable limit for As in plants has been set at 2 ppm (5). Among vegetable crops, potato roots have the highest As content, reaching up to 2.9 ppm, while lower levels are found in vegetables like tomato, *Lal Shak*, *Datashak*, cabbage and cauliflower (47). To detect As using ICP-MS, rice samples collected from local markets in Australia were found to contain As levels ranging from 0.026 to 0.464 ppm (48). The recommended daily intake for As is 0.015-0.1 mg/kg of body weight (49). However, arsenic toxicity can occur at levels exceeding 1 mg/kg/day, potentially leading to hepatotoxicity and anemia (50).

Multivariate analysis of *Celtis tournefortii* Lam and *Prosops farcta*

According to the 25 key characteristics (Ca, P, Mg, Na, K, S, Fe, Cu, Zn, Se, Cd, V, Cr, Ni, Ag, Be, Sr, Ba, Al, Pb, Bi, Rb, B, As and Sb), HCA and PCA were used to classify elemental accumulation in different parts of two wild plants. The HCA was performed to examine the similarity among different plant parts in terms of heavy metal accumulation. The resulting dendrogram (Figure X) illustrates the clustering patterns based on the measured variables. The x-axis represents the plant parts analyzed (pod, seed, leaf and fruit), while the y-axis indicates the Euclidean distance, which reflects the dissimilarity between clusters (Fig. 4).

The analysis identified three primary clusters. The leaf formed the first cluster, characterised by the highest concentration of Na, V, Al and Fe. The second cluster corresponded to the fruit of *Celtis tournefortii* Lam, which exhibited maximum accumulation of Be, Mg, Cd, Ba and Sr. The third cluster comprised the seed and pod of *Prosopis farcta*, with elevated levels of Sb, B, Bi, Zn, S, Se, As and Ni. The classification obtained from PCA supported the HCA results (Fig. 5).

To simplify the multidimensional dataset and provide a two-dimensional representation of the variance, PCA was used. The first and second principal components (PC1 and PC2) explained 53.84% and 27.53% of the total variance, respectively, amounting to 81.34%. Elements accumulating in the leaves were strongly correlated with PC1, while those prevalent in the fruit of *Celtis tournefortii* Lam were associated with PC2. Notably, Zn, S, Se, Bi, B, As and Sb were dominant in PC1, while Cr, Cu, K and Rb were more aligned with PC2. Ag and As were associated with PC3. Bi had no significant loading on PC2 or PC3, while K and Rb were not influenced by PC1 or PC3, as shown in Tables 3 and 4.

A data matrix comprising four plant parts and 25 elements (4×25) was used for the principal component analysis and data were auto-scaled as part of the preprocessing (Table 4). The results showed significant correlations among several elements. Cd showed strong associations with V, Cr, Cu, Ni, Ag, Zn, Na, Se, Al, K and Rb. Fe correlated with Cr, Ni, Ag, K and Rb; while Cr was associated with Ag, Zn, Na and Al. Cu showed high

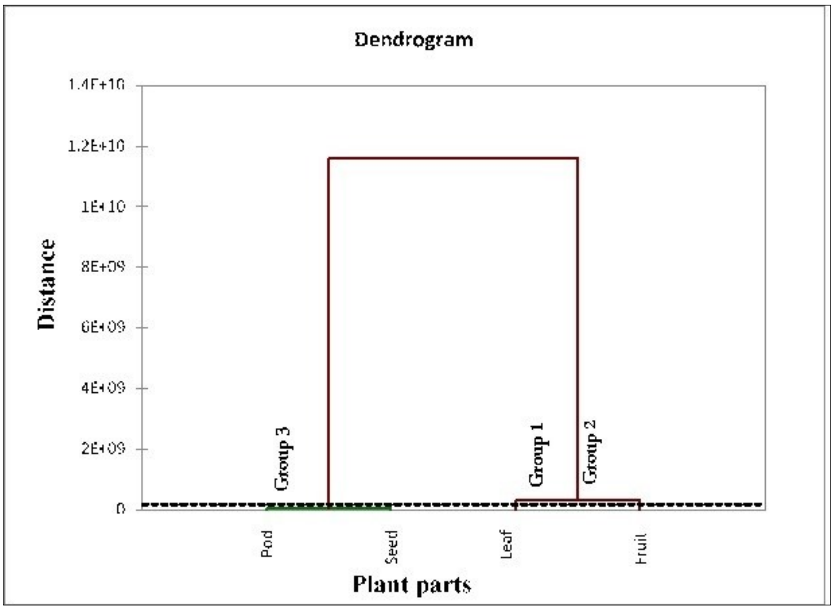

Fig. 4. Hierarchical cluster analysis (HCA) of elements of two wild plant parts.

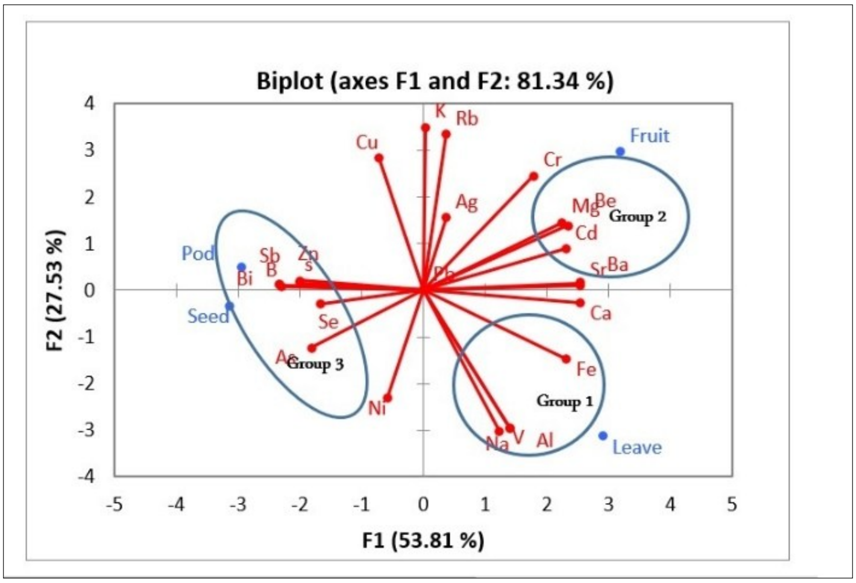

Fig.5. Principal component analysis (PCA) of two wild plants using the 25-primary characteristic.

Table 3. Loading of principle components (PC) of 25 elements for different plant parts of *Celtis tournefortii* Lam *and Prosopis farcta*

Elements	PC1	PC2	PC3
Ca	0.997	-0.075	-0.003
P	0.000	0.000	0.000
Mg	0.880	0.409	-0.243
Na	0.481	-0.843	0.240
K	0.012	0.982	0.190
S	-0.783	0.060	-0.619
Fe	0.908	-0.414	0.059
Cu	-0.283	0.798	-0.533
Zn	-0.783	0.043	-0.621
Se	-0.647	-0.082	-0.758
Cd	0.902	0.251	-0.351
V	0.550	-0.829	0.100
Cr	0.701	0.689	-0.187
Ni	-0.228	-0.642	-0.732
Ag	0.142	0.434	0.889
Be	0.918	0.390	-0.074
Sr	0.996	0.030	0.087
Ba	0.999	0.045	-0.029
Al	0.550	-0.829	0.100
Pb	0.000	0.000	0.000
Bi	-0.916	0.030	0.401
Rb	0.144	0.937	0.318
B	-0.916	0.030	0.401
As	-0.707	-0.342	0.619
Sb	-0.903	0.023	0.429

correlation with Ni, Ag, Be, Ba, Mg, B and Sb. Ag was also associated with Na, Mg, Ca, Ba, Al and Sb. Zn correlated with K, Rb and As. Na was linked with Be, Mg and As, while Be was connected with Al and K. Se showed associations with K, Rb and Ca. Bi was found to be associated with Al alone. Furthermore, a correlation was observed between As and Sb with B. Ba and Mg were related only to K and Ca showed correlations with K and Rb.

The findings suggest that macro- and microelements such as Ca, K, Mg, Na, P, Cu, Fe, Mn, Se and Zn are distributed across the leaves, fruits, pods and seeds. PCA and HCA were validated as effective tools for evaluating elemental accumulation in the two wild species, *Celtis tournefortii* Lam and *Prosopis farcta*. These wild plants were found to contain multiple elements across different parts, positioning them as potential sources of element accumulation. Several studies support the pharmacological benefits of these elements for human health. However, due caution should be exercised when consuming these plants due to the potential presence of toxic substances.

Table 4. Correlation matrix for 24 elements in *Celtis tournefortii* Lam and *Prosops farcta* from Mazne sub-district Kurdistan region of Iraq

Variables	Ca	Mg	Na	K	S	Fe	Cu	Zn	Se	Cd	V	Cr	Ni	Ag	Be	Sr	Ba	Al	Bi	Rb	B	As	Sb
Ca	1	0.847	0.542	-0.062	-0.784	0.936	-0.340	-0.781	-0.636	0.882	0.610	0.648	-0.177	0.107	0.886	0.991	0.993	0.610	-0.917	0.072	-0.917	-0.681	-0.904
Mg		1.000	0.021	0.365	-0.514	0.615	0.207	-0.520	-0.418	0.982	0.121	0.943	-0.285	0.086	0.985	0.867	0.904	0.121	-0.891	0.432	-0.891	-0.912	-0.890
Na			1.000	-0.776	-0.576	0.801	-0.936	-0.562	-0.424	0.138	0.988	-0.288	0.256	-0.084	0.095	0.475	0.436	0.988	-0.370	-0.644	-0.370	0.097	-0.351
K				1.000	-0.068	-0.384	0.678	-0.085	-0.233	0.191	-0.788	0.649	-0.772	0.597	0.380	0.058	0.050	-0.788	0.095	0.982	0.095	-0.227	0.093
S					1.000	-0.773	0.599	1.000	0.971	-0.474	-0.543	-0.392	0.593	-0.636	-0.650	-0.832	-0.762	-0.543	0.471	-0.253	0.471	0.150	0.443
Fe						1.000	-0.619	-0.765	-0.598	0.694	0.849	0.340	0.015	0.002	0.667	0.897	0.887	0.849	-0.820	-0.239	-0.820	-0.463	-0.804
Cu							1.000	0.587	0.521	0.132	-0.870	0.451	-0.058	-0.168	0.091	-0.304	-0.232	-0.870	0.070	0.537	0.070	-0.403	0.045
Zn								1.000	0.974	-0.477	-0.529	-0.403	0.606	-0.645	-0.656	-0.832	-0.762	-0.529	0.469	-0.270	0.469	0.154	0.441
Se									1.000	-0.338	-0.364	-0.368	0.755	-0.802	-0.570	-0.712	-0.628	-0.364	0.286	-0.411	0.286	0.016	0.257
Cd										1.000	0.253	0.871	-0.111	-0.074	0.952	0.875	0.922	0.253	-0.959	0.254	-0.959	-0.941	-0.959
V											1.000	-0.204	0.333	-0.192	0.174	0.532	0.509	1.000	-0.489	-0.666	-0.489	-0.043	-0.473
Cr												1.000	-0.466	0.233	0.926	0.702	0.736	-0.204	-0.696	0.687	-0.696	-0.847	-0.697
Ni													1.000	-0.962	-0.406	-0.310	-0.236	0.333	-0.104	-0.867	-0.104	-0.071	-0.122
Ag														1.000	0.235	0.232	0.136	-0.192	0.239	0.711	0.239	0.301	0.263
Be															1.000	0.919	0.936	0.174	-0.858	0.474	-0.858	-0.828	-0.852
Sr																1.000	0.993	0.532	-0.876	0.199	-0.876	-0.660	-0.861
Ba																	1.000	0.509	-0.924	0.176	-0.924	-0.739	-0.913
Al																		1.000	-0.489	-0.666	-0.489	-0.043	-0.473
Bi																			1.000	0.024	1.000	0.885	1.000
Rb																				1.000	0.024	-0.226	0.028
B																					1.000	0.885	1.000
As																						1.000	0.896
Sb																							1.000

Conclusion

According to the current study, *Celtis tournefortii* Lam exhibited a higher concentration of metals than *Prosopis farcta*. A total of 25 elements were found during the screening of both species using ICP MS and ICP OES. *Celtis tournefortii* Lam was found to have accumulated greater amount of Cd, V, Fe, Cr, Na, Be, Mg, Ca, Sr, Ba, Al, K and Rb. In contrast, *Prosopis farcta* contained significantly higher levels of Ni, Ag, Zn, S, Se, Bi, B, As and Sb.. The three elements Cu, P and Pb are present in similar amounts in both wild plants.

In order to efficiently and precisely measure trace elements in plants, both ICP-MS and ICP-OEC were utilized. The results indicate that the studied medicinal plants and dietary supplements contain elements in the ppm range, with notable variability in elemental concentrations. This variation can be explained by environmental and agronomic conditions, differential exposure to pollutions and cultivation in contaminated areas, suboptimal storage conditions and bad purchasing sources. Additionally, geographical region, plant genetics and composition of the soil may significantly influence the levels of toxic metals present.

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Authors' contributions

SJAK Conceived the study, designed the methodology and conducted the data analysis and wrote the manuscript. MS participated in collection of the data, contributed to the methodology development and reviewed and edited the manuscript. KMK participated in the analyses of samples. All authors read and confirmed the final version of the manuscript.

Compliance with ethical standards

Conflict of interest: The authors declare no conflict of interest.

Ethical issues: None

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