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Investigation of Heavy Metals Content in *Artemisia Herba-Alba* Grown in Libya

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فحص مستوى المعادن الثقيلة في نبات الشيح (Artemisia Herba-Alba) المزروع بريا في ليبيا

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Abstract:

The use of herbal and traditional remedies has become more popular in recent years, and there is growing worry that these treatments may be contaminated with heavy metals. This study measured the heavy metal concentrations in Artemisia herba-alba that is grown in natural sites in Gharyan and Qasar Ben Ghesheer Libya. Using inductively coupled plasma mass spectrometry, the concentrations of eleven heavy metals (As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sr, Zn) were measured. The concentrations of all heavy metals, except Ba, Pb, and Sr, were within the permissible limits. The Pb is concentrated in high level in stem than the leaves. Whereas the Ba and Sr are concentrated more in the leaves than in the stems. The plants from Gasser Ben Ghesheer had toxic level from Ba, Ni, and Sr, while plants collected from Gharyan had toxic level of Ba, Pb, and Sr. The plant's parts and the growing site have an effect on the level of heavy metals. In order to ensure safety of Artemisia, an ongoing monitoring plan of heavy metal residues should be applied, and strict measures to prevent pollution should be imposed.

Keywords: Heavy metals, Medicinal plants, Artemisia, Libya.

الملخص :
ازداد استخدام العلاجات العشبية والتقليدية شيوعًا في السنوات الأخيرة، وهناك قلق متزايد من أن هذه العلاجات قد تكون ملوثة بالمعادن الثقيلة. قامت هذه الدراسة بقياس تراكيز المعادن الثقيلة في نبات الشيح (Artemisia herba-alba) الذي ينمو في مواقع طبيعية في مدينتي غريان وقصر بن غشير بليبيا. تم قياس تراكيز أحد عشر معدنًا ثقيلًا (الزرنيخ (As)، الباريوم (Ba)، الكادميوم (Cd)، الكروم (Cr)، النحاس (Cu)، الحديد (Fe)، المنجنيز (Mn)، النيكل (Ni)، الرصاص (Pb)، السترونتيوم (Sr)، الزنك (Zn)) باستخدام مطياف الكتلة بالبلازما المقترنة حثيًا (ICP-MS). كانت تراكيز جميع المعادن الثقيلة، باستثناء الباريوم والرصاص و السترونتيوم، ضمن الحدود المسموح بها.تَرَكَّزَ الرصاص(Pb) بمستوى عالٍ في الساق أكثر من الأوراق. بينما تَرَكَّزَ الباريوم (Ba) والسترونتيوم (Sr) بشكل أكبر في الأوراق مقارنةً بالسيقان. احتوت النباتات التي تم جمعها من مدينة قصر بن غشير على مستويات سامة من (Ba) و(Ni) و(Sr)، في حين أن النباتات التي تم جمعها من مدينة غريان احتوت على مستويات سامة من (Ba) و(Pb) و(Sr). يؤثر كل من أجزاء النبات وموقع النمو على مستوى المعادن الثقيلة. لضمان سلامة نبات الشيح، يجب تطبيق خطة مراقبة مستمرة لتراكيز المعادن الثقيلة، ويجب فرض إجراءات صارمة لمنع التلوث.

الكلمات المفتاحية: المعادن الثقيلة، النباتات الطبية، نبات الشيح، ليبيا.

Introduction

Since the beginning of human history, humans have relied on the plant kingdom for food, fuel, fodder, and medical needs.(Koul et al., 2017) These days, there is a growing demand for herbal remedy over synthetic medication. Herbal medicine use has returned to the forefront due to the expanding list of contraindications to taking synthetic pharmaceuticals and their diminishing efficacy. Also, the medicinal plants are considered safe, effective, affordable, and environmentally friendly,(Koul et al., 2017; Petrovska, 2012) if it is used wisely.(Vinogradova et al., 2023)

Artemisia is a widely distributed genus that has over 400 species (around 474) and is known as "Worm wood." This genus belongs to the Asteraceae family. Artemisia is an ancient Greek word origin. The Worm wood name comes due to its ancient usage as an intestinal worm remedy. The majority of Artemisia species are

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herbaceous decorative, medicinal, fragrant, and perennial or biennial shrubs. Because they contain terpenoids and sesquiterpene lactones, they have a strong fragrance and a harsh flavor. They might be silver, black, or blue-green in color. It is grown as a crop and used to make tea, tonic, alcoholic drinks, and medications.(Koul et al., 2017)

The species that grows in the Mediterranean region is Artemisia herba-alba. This plant is also referred to as desert wormwood. In Arabic, it is named as "shih." Since ancient times, people from various cultures have utilized this plant to prepare traditional medications that cure hypertension and diabetes. The plant's aerial portions can be used to make aqueous extracts that have antibacterial and antioxidant qualities. This species produces herbal tea with antibacterial, analgesic, and antispasmodic properties. Additionally, this plant is used as animal feed.(Koul et al., 2017)

Heavy metals are metals found in nature and have an atomic density more than 6 g/cm3. Some of them - such as Zn, Cu, Fe, Mn, and Cr- are essential for human physiology at tiny levels, but at larger quantity, they become toxic. The others are nonessential and toxic.(Kohzadi et al., 2019) Heavy metals' toxicity and impacts on the environment are a global problem since they are carried via the air, soil, and water. The human body can absorb heavy metals via food, beverages, or the air, depending on a variety of factors, such as concentration and primary sources. Human cellular, metabolic, and hormonal functions require trace quantities of some of these metals, but excessive levels can have detrimental health effects.(Jyothi, 2020)

Heavy metal exposure may occur in a variety of ways for people. For instance, contamination of the environment from any source can contaminate plants that humans utilize. Medicinal plants are plants with therapeutic properties. These plants have the ability to take up pollutants from the soil through their roots or by allowing the pollutants to deposit onto their leaves.(Kohzadi et al., 2019) Because various organs of the same plant are known to react differently to toxicants, it is convenient to compare the metal concentration of each kind of HM in different organs.(Vinogradova et al., 2023) Given that heavy metals are hazardous and carcinogenic, it is crucial to identify them in the plants air, water, and soil, among other environmental components.(Jyothi, 2020)

Libya is located in the north of Africa. Its climate is hot arid Sahara, but it is moderated along the coastal line by the Mediterranean Sea. Both Qasar Ben Gasheer and Gharyan are cities located in the western south region of the capital city (Tripoli). Both are dependent on the agricultural activities. The Qasar Ben Gasheer is famous for crop and vegetables cultivations. The mountain geographic properties of Gharyan are the feature that allow growing of various wild indigenous medicinal plants. There are a number of indigenous medicinal plants one of them is Artemisia. People are extensively depending on medicinal plants for treatment.

The presence of heavy metals in plants and herbal product like spices has been reported in Libya. Some seeds of the studied plants in Misrata contains higher levels of Cd, and Pb. (المبروك et al., 2024) The levels of Cd, Mn, Ni, and Cr in the studied local cultivated vegetables in Brak city were within the permissible limits.(النكاع et al., 2023) The spices powder obtained from dried plants has amount of Pb and Cu higher than the acceptable limit. Despite the fact that there is rising interest in the analysis of heavy metals in plants and environment and that it is obvious that its status has to be monitored to prevent health risks. Data is still extremely limited to few cities. This study is aimed to determine the concentration of ten heavy metals in samples of the Artemisia herba-alba plant parts (leaves and stems) that are collected from Qasar Ben Ghasher and Gharyan in Libya.

Method

Study Area

The sample of fresh whole arial part of Artemisia herba-alba were collected on July 2024 from two cities Qasar Ben Ghesheer and Gharyan city. Both are located in the western side of Libya. The plant type and species were verified by an expert.

Sampling and Analysis of Metals

Two samples of indigenous Artemisia herba-alba were taken one from Qasar Ben Ghesheer and the other sample from Gharyan. After being appropriately labelled, the plant was transported to the lab and kept in plastic bags. In the lab, the plants were washed twice with distilled water, separated according to leaves and stem based on the plant parts, then dried by the oven for twenty-four hours at 65 °C, and finally grinded into a fine powder.

Reagents

For samples preparation, we used analytical grade reagents. These reagents were distilled water, nitric acid 65%, hydrogen peroxide 30%, and sulfuric acid 95%. The lab glassware was washed with deionized water, immersed in a 10% nitric acid solution for the whole night, and then allowed to air dry before use.

Digestion of Medicinal Plant Samples

A 500g weight of the dried separated plant parts (leaves and stem) was grinded and sieved. The 5 g was taken in a porcelain crucible, and 0.5ml of sulfuric acid (95%) where allowed to stand for a few hours for cold digestion. The porcelain curable was put in the oven for hot digestion. The temperature was increased gradually for 4 to 5 hours until the content became a white ash, then 2ml nitric acid 65% and 1ml of hydrogen peroxide 30% were added to the ash.

The content was heated by an electric heater to 90ºC until it becomes dry, another 2ml of nitric acid 65% was added with gentle heating. The digested material was filtered through a Whatman Grade 1: 11-µm medium flow filter paper by repeatedly washing the conical flask with a small volume of distilled water. The filtrate collected was made up to 50 ml. Finally, the obtained solution was stored in plastic bottles at 4°C for heavy metal detection.

The detection of heavy metals of As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sr, and Zn was performed on inductively coupled plasma-optical emission spectroscopy under an optimized measurement condition. All analyses were performed in once. The data was analysed by Excel® 2024. Mean and standard deviation was calculated for concentration of heavy metals across the plant parts and two geographical sites.

Results and Discussion

Table 1 lists the acceptable limits for the concentration of heavy metals in plants. Tables 2, 3, and 4 provide a summary of the heavy metal analysis results for the chosen medicinal plant as overall, according to the studied plant’s part, and to the collection site, respectively.

Table 1. The acceptable limits of heavy metals in the literature.

Heavy metal	Permissible limit (mg kg^{-1})	Reference
As	0.2-5	(Vinogradova et al., 2023)(Abdulwahid-Kurdi et al., 2023; Vuong, 2020)
Ba	0.7	(Hajar et al., 2014)
Cd	0.3-4	(Abdulwahid-Kurdi et al., 2023; Gasser et al., 2009; Vinogradova et al., 2023; Vuong, 2020)
Cr	0.006-18	(Abdulwahid-Kurdi et al., 2023)
Cu	0.4-150	(Abdulwahid-Kurdi et al., 2023; Karahan et al., 2023)
Fe	20-2486	(Abdulwahid-Kurdi et al., 2023; Karahan et al., 2023)
Mn	2-100	(Abdulwahid-Kurdi et al., 2023; Karahan et al., 2023)
Ni	0.1-5	(Abdulwahid-Kurdi et al., 2023)
Pb	3-10	(Abdulwahid-Kurdi et al., 2023; Gasser et al., 2009; Vinogradova et al., 2023; Vuong, 2020)
Sr	1.6	(Hajar et al., 2014)
Zn	1-160	(Abdulwahid-Kurdi et al., 2023)

The overall concentration of each heavy metals in all samples regardless to plant part or the location from where the plant was collected are presented in Table 1. All the heavy metals were detected in the plant at varied amount. The detected concentrations of As, Cd, Cr, Cu, Fe, Mn, Ni, and Zn were below the acceptable limit. The concentration of the following heavy metals Ba, Pb, Sr were higher than the acceptable levels.

Table2. Overall mean concentration of each heavy metal in the Artemisia

Heavy metal	Mean	SD
As	0.16	0.1
Ba	8.23	5.6
Cd	0.23	0.3
Cr	1.08	0.3
Cu	14.23	14.7
Fe	320.93	137.9
Mn	25.23	15.6
Ni	2.15	2.3
Pb	11.88	18.7
Sr	45.03	15.7
Zn	22.68	3.9

Based on the plant part, all heavy metals were detected in the both studied plant's parts at varied amount. The following heavy metals were concentrated in the leaves in higher amount than their corresponding concentration in the stem: Ba, Cd, Cr. Mn, Ni, and Sr, whereas the concentrations of As, Cu, Fe, Pb, and Zn were higher in stems than the leaves. The levels of Ba, and Sr in both parts exceeded the permissible limits. The level of Pb was higher than the acceptable limit only in the stems.

Table 3. Comparison between mean heavy metals concentration across the studied plant part of Artemisia

Heavy metal	Leaves		Stem	
	Mean	SD	Mean	SD
As	0.10	0.00	0.22	0.03
Ba	10.45	7.57	6.00	4.24
Cd	0.40	0.42	0.06	0.06
Cr	1.20	0.42	0.95	0.21
Cu	6.55	0.64	21.90	20.36
Fe	318.80	6.65	323.05	238.79
Mn	32.05	23.26	18.40	2.26
Ni	3.30	3.25	1.00	0.57
Pb	3.70	4.38	20.05	27.65
Sr	47.55	2.90	42.50	26.59
Zn	19.85	3.75	25.50	0.28

According to the collection site, all heavy metals were existed in the plant that are collected from both sites at varied amount. The samples that are collected from Gharyan contains higher level of Cd, Cu, Fe, Mn, Ni, and Pb than the samples that are from Qasar Ben Ghesheer. whereas, the levels of As, Ba, Cr, and Sr were higher in the samples that are collected from Qasar Ben Ghesheer. In comparison to the acceptable levels, Ba and Sr levels in both cities were higher than the acceptable values. The level of Ni in Qasar Ben Ghesheer exceeded the acceptable level, and level of Pb in Gharyan samples was higher than the acceptable level.

Table4. Comparison between mean heavy metals concentration in Artemisia among the cities

Heavy metal	Gharyan		Qasar Ben Ghesheer	
	Mean	SD	Mean	SD
As	0.15	0.07	0.17	0.10
Ba	4.05	1.48	12.40	4.81
Cd	0.06	0.06	0.40	0.42
Cr	0.85	0.07	1.30	0.28
Cu	21.65	20.72	6.80	0.99
Fe	238.85	119.71	403.00	125.72
Mn	32.65	22.42	17.80	3.11
Ni	0.80	0.28	3.50	2.97
Pb	20.10	27.58	3.65	4.45
Sr	36.65	18.31	53.40	11.17
Zn	24.10	2.26	21.25	5.73

Arsenic (As) is a very toxic non-essential metalloid that has a major negative impact on human health, including hypotension, polyneuropathy, gastrointestinal and hepatic diseases, blindness, and cancer. The primary human-caused sources of As exposure for plants include mining, smelting, the application of herbicides containing As in agriculture, and the use of As-contaminated groundwater for irrigation. In our study, the overall level of As was 0.16 mg/kg. Its concentration was higher in stems sample (0,22 mg/kg) and in samples collected in Qasar Ben Ghesheer (0.17 mg/kg), but all were below the acceptable limit. Suggesting that the plant picks up As from the soil through the plant roots. Since both cities depends largely on agriculture, the source of contamination is possibly due to improper and uncontrolled use of pesticides. Our finding was lower than that reported in Romania (0.78 mg/kg) (Marinescu et al., 2020).

Barium (Ba) is nonessential heavy metal. The toxicity that is resulted from Ba is reported as cardiac arrhythmias, respiratory cessation, gastrointestinal issue, muscle jerking movement, and hypertension (Mishra et al., 2019). The overall of Ba was 11.88 mg/kg with higher concentration in leaves 10.45 mg/kg, and in samples that were collected from Qasar Ben Ghesheer 12.40. all of the detected levels exceeded the permissible limit. Our findings are lower than those reported in Brazil (47–136 mg/kg).

Cadmium (Cd) is a dangerous heavy metal that is not necessary to the human. It has detrimental effects on the kidney, liver, arteries, and immune system (Karahan et al., 2023). The prolonged exposure to large amounts of Cd causes osteomalacia, osteoporosis, and severe renal tubular dysfunction. Plant contamination with Cd is mostly caused by burning fossil fuels, applying phosphate fertilizers, non-ferrous smelters, mining, and sewage sludge. The overall mean of Cd in all samples was 0.23 mg/kg. The highest concentration was detected in the plant leaves 0.4 mg/kg, in the plant grown in Qasar Ben Ghesheer (0.4 mg/kg). In comparison to other countries, Our values were higher than those that are reported in Romania (0.01 - 0.05 mg/kg) (Marinescu et al., 2020), and lower than values detected in Turkey (0.61mg/kg) (Karahan et al., 2023), Romania (0.783 mg/kg) (Radulescu et al., 2013), UAE (1.11 mg/kg) (Dghaim et al., 2015), and india (2.7 mg/kg) (Subramanian et al., 2012)

Chromium (Cr) has been deemed not necessary for mammals and has no known biological function. The overall detected level of Cr was 1.08 mg/kg. Its concentration in leaves was higher (1.20 mg/kg) than the stems, and in the samples that were collected from Qasar Ben Ghesheer (1.30 mg/kg). But all of these were within the permissible limit. Our findings was higher than that are reported in Romania (0.970 mg/kg) (Radulescu et al., 2013), and lower than Turkey (47.79 mg/kg) (Karahan et al., 2023).

Copper (Cu) is considered as an essential trace element in both plants and humans. Along with being a cofactor of many enzymes, it plays a significant role in iron metabolism and other physiological processes, including immunological response, neuropeptide synthesis, and antioxidant defence. Furthermore, proper plant growth and development depend heavily on Cu. High levels of Cu can cause liver damage, gastrointestinal discomfort, upper respiratory tract dysfunction, and skin irritation and hypersensitivity (Karahan et al., 2023;

Vinogradova et al., 2023). Plant Cu contamination may be caused by mining and industrial processes. The overall mean of Cu concentration in the studied samples was 14.23 mg/kg. The highest concentration was detected in stems 21.9 mg/kg and in samples collected from Gharyan 21.65, but all of them were below the acceptable level. Our findings were consistent with Romania (4 to 24 mg/kg) (Marinescu et al., 2020) and higher than Pakistan (4.1 mg/Kg) (Hassan et al., 2013), and lower than India 94.05 mg/kg (Subramanian et al., 2012), UAE (156.24mg/kg), and Turkey (43.13 mg/kg) (Karahan et al., 2023).

Iron (Fe) is a trace element that is biologically necessary for all living creatures. Cellular respiration, DNA and protein synthesis, cell division and proliferation, immunity, gene expression control, electron transport and oxygen delivery, and many other cellular functions are all impacted by it. Its higher dose is associated with hepatic and renal failure, metabolic acidosis, cardiomyopathy, and gastrointestinal issues (Karahan et al., 2023). The overall mean concentration of Fe in the studied samples was 320.9 mg/kg. its level in leaves 323.05 mg/kg was higher than that in stems 318.8 mg/kg. Samples from Qasar Ben Ghesheer contained 403 mg/kg higher level than samples from Gharyan 238.85 mg/kg. All these detected values were below the acceptable limit. Our values were higher than those detected in pakistan (28.5mg/kg) (Hassan et al., 2013), and lower than (21020 mg/kg) (Mar inescu et al., 2020) and India (21.98 mg/kg) (Subramanian et al., 2012), and Turkey (1109.39 mg/kg)(Karahan et al., 2023)

Manganese (Mn) is a part of the antioxidant enzyme superoxide dismutase that is essential to combat free radicals. Comparing Mn compounds to those of other common metals like copper and nickel, the former are less toxic. Manganese poisoning in human is associated cognitive problems and decreased motor skills. The overall mean value of Mn in the studied plant is 25.23 mg/kg. Its concentration was higher in leaves (32.05 mg/kg), and in plant samples collected from Gharyan 32.65 mg/kg. but all were within the acceptable limit. Our findings were higher than that reported in Pakistan (4.9 mg/kg) (Hassan et al., 2013), and lower than India 101 mg/kg (Subramanian et al., 2012) and Turkey (715.48 mg/kg) (Karahan et al., 2023)

Nickel (Ni) is an essential heavy metal but its excessive amount can cause cancer of the lungs, allergic disease, affects fertility and hair loss (Mishra et al., 2019). The overall mean concentration of Ni detected in the plant was 2.15 mg/kg. Its level was higher in the leaves 3.30 mg/kg, and in samples collected from the Qasar Ben Ghesheer 3.50 mg/kg. All values were below the acceptable limit. Our findings were higher than that reported in Pakistan (0.2 mg/kg) (Hassan et al., 2013), and lower than Turkey (9.42 mg/kg) (Karahan et al., 2023).

Lead (Pb) is a highly toxic metal that can influence any organ but primarily affects the central nervous, cardiovascular, haematological, and renal systems (Karahan et al., 2023). Plants are exposed to lead (Pb) through mining, smelting, the steel industry, electroplating, inorganic fertilizers and pesticides, fuel combustion, vehicle exhaust, and sewage sludge. The mean content of Pb in all samples was 11.88 mg/kg. The highest levels were found in stems 20.05 mg/kg and in samples that were collected from Gharyan 20.1 mg/kg. The levels of this element were higher than the acceptable limit. Our findings were higher than India 9.89 mg/kg (Subramanian et al., 2012), and Vietnam (0.247 mg/kg) (Vuong, 2020), and lower than Turkey (22.11 mg/kg) (Karahan et al., 2023), and UAE (23.52 mg/kg) (Dghaim et al., 2015).

Strontium (Sr) is a nonessential heavy metal. It can accumulate in human body and damage bones, teeth, and skin (de Aragão Tannus et al., 2021).The overall concentration of Sr was 45.03 mg/kg with higher concentration in the leaves 47.55 mg/kg, and in samples that are collected from Qasar Ben Ghesheer 53.40 mg/kg. All these figures exceeded the acceptable limit. This element was less studied in the literature. The comparison with other studies is not feasible.

Zinc (Zn) is considered as an essential trace metal; however, long-term overconsumption of zinc can lead to neurotoxicity, anaemia, , mitochondrial impairment, haematological, respiratory, and gastrointestinal system issues, as well as vomiting, fever, and fainting (Karahan et al., 2023). The detected overall level of Zn was 22.68 mg/kg. its concentration was higher in stem 25.5 mg/kg, and in sample that are collected from Gharyan (24.10 mg/kg). Our findings were within the acceptable limit, and lower than that reported in other countries like Pakistan (35.3 mg/kg) (Hassan et al., 2013), Romania (48.976 mg/kg) (Radulescu et al., 2013), India (49.776 mg/kg) (Subramanian et al., 2012), and Turkey (260.08 mg/kg) (Karahan et al., 2023)

Conclusion

The current investigation demonstrated that most of heavy metal levels in the Artemisia fell within the ranges that were allowed for the medicinal plants. Although Artemisia had low heavy metals concentrations, because they can build up, their presence may be harmful to health, as shown in situations when long-term usage is undertaken. As previously mentioned, consumers of Artemisia under study may be at risk for health problems due to the Ba, Ni, Pb, and Sr contents. The elderly with cardiovascular problems and renal insufficiency, are more vulnerable to the toxicities. They should be warned before using this plant for extended periods of time. Strategies for monitoring and reducing pollution from heavy metals should be started to protect Libyans from their negative health consequences.

Compliance with ethical standards

Disclosure of conflict of interest

The authors declare that they have no conflict of interest.

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