



Estimation and comparison of heavy metal concentrations of rosemary plants in the cities of Qasr Bin Ghasheer and Gharyan in Libya

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Abstract

Heavy metal pollution is considered one of the most important types of chemical pollution in addition to being one of the major problems of the age due to the accumulation of these elements in different natural environmental systems, which leads to many health problems.

The aim of the present study is to investigate the heavy metals (As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sr, Zn) accumulated in both the stems and leaves of the rosemary plant in two different geographical areas (Qasr Bin Ghasheer and Gharyan), where (leaves and stems) are considered a vital monitor through which the rate of metal pollution is detected. This is done by determining the ability of these heavy metals to accumulate in the rosemary plant and comparing them with the internationally permitted limits.

Through this study, the results showed that most of the concentrations of heavy elements in (Gharyan sample) whether in the leaves or stems fall within the internationally permitted limit except for element (Ba, Cu, Sr) which was found higher than the permitted range.

As for the results obtained for the rosemary sample in the (Qasr Bin Ghasheer) area, they were within the permissible limit only with the exception of the two elements (Sr, Ba) which was higher than the internationally permissible limit whether in the leaves or stems of rosemary. Based on that, we therefore believe that rosemary plant is one of the most significant methods to determine the amount of the pollution which is related to the heavy metals.

Keywords: pollution, Heavy metals, Rosemary, plants, Libya, leaves, stems

Introduction

Metal pollution problems are becoming progressively common in different areas in the world, with a various known cases of metal toxicity in mining industries, smelters, foundries, agriculture and coal-burning power plants. Heavy metals, such as chromium, copper cadmium, mercury, and lead, are the most significant environmental pollutants, especially in densely populated areas.

Soil is a major source of heavy metal accumulation, causing adverse effects on agricultural production in terms of food safety and marketability, as well as crop growth due to phytotoxicity, and the environmental health of soil organisms[1]. Plants are one of the most important constituents in ecosystems as they transfer elements from the abiotic environment to the biotic one[2]. Because the correlation ship between atmospheric heavy metal deposition and heavy metal concentrations which is has been identified, various plants types are able to absorb and accumulate significant quantities of potentially toxic substances[1,2].

These substances negatively affect growth, metabolism, and biomass production in plants living in metal-polluted environments. These metals also affect a number of physiological and biochemical processes in plants. In industrial and urban areas, where lichen and mosses are frequently absent, urban trees and shrubs—which are crucial in filtering ambient air by eliminating heavy metals and adsorbing particulate matter—are frequently used for bio monitoring in order to examine environmental quality and possible health effects on humans[3,4]. When it comes to their detrimental effects on plant physiological metabolisms, heavy metals alter protein structures, disrupt membrane integrity, and inactivate and denaturant intracellular enzymes. These effects then have an impact on regular plant metabolic functions like respiration, transpiration, and photosynthesis[5].

Furthermore, the introduction of toxic heavy metals into plant tissues causes reactive oxygen species (ROS) to rise, which upsets the redox equilibrium. Accordingly, a subsequent high concentration of hydrogen peroxide (H_2O_2) and superoxide anion (O^{2-}) leads to the death of oxidative cells, the induction of unsaturated fatty acids in significant quantities, the breakdown of biological macromolecules, and further lipid peroxidation of membranes[3].

The amount of cadmium in living things rises with age and food, and it has a significant cumulative effect on people. The length of uptake, the metal's chemical form, the food, the age, sex, and health status of those exposed are some of the variables that affect how much of this xenobiotic is absorbed and accumulated[5]. The International Agency for Research on Cancer (IARC) declared cadmium to be carcinogenic when breathed, although there is insufficient data to declare this xenobiotic carcinogenic when consumed orally[6].

Cadmium is one of the most toxic elements that human beings can be exposed to at work or in the environment and has no known physiological role in mammals[7,8]. Human exposure to Cd can occur through food, water, and the inhalation of cigarettes. Once absorbed, Cd is efficiently retained in the human body, where it accumulates throughout life with a half-life of 25–30 years. Recent studies indicate that cadmium is capable of inducing epigenetic changes in mammalian cells[9].

Materials and methods

study area

This study covered two different geographical regions in Libya (Qasr Bin Ghasheer and Gharyan). Qasr Bin Ghasheer is located approximately 26 km south of the Libyan capital, Tripoli, while Gharyan is located in the north western part of Libya, on top of the Western Mountains. Samples were collected from two different parts of the rosemary plant (leaves and stems), a common medicinal plant, in July 2024.

Extraction for heavy metals analysis

Two sections of the rosemary plant were used for the experiment. The section consists of leaves and stems. The material used (rosemary plant) was collected from two different geographical areas in Libya (Qasr Bin Ghasheer and Gharyan). It was dried using an oven at 90°C for 4-5 hours to remove moisture from the leaves and stems.

The dried materials were grinded to obtain a powder material and were measured the particle size (140µm) using a vibrator sieve shaker to obtain a suitable surface area for the extraction process. For the determination of heavy metals, leaves and stems of rosemary plant of each weighed approximately 5.0 grams into a Teflon digestion vessel, to which was added exactly 0.5 ml high purity concentrated 95% of sulphuric acid (H₂SO₄), and the mixture was lifted for couple of

hours for cold digestion process. the temperature was slowly raised over a period of 4-5 hours until the substance turned into white ash. After that was added 2 ml high purity concentrated 65% of nitric acid (HNO₃) and 1 ml (30%) of hydrogen peroxide (H₂O₂) to the ash. The mixture was heated to 90% using an electric heater until it dried completely, an additional 2 ml of 65% nitric acid was added while gently heating. The digested material was filtered using whatman grade 1.1 µm medium flow filter paper, with the volumetric flask repeatedly rinsed using a small amount of distilled water. The collected filtrate was diluted to a final volume of 50 ml. The resulting solution was then stored in plastic bottles at 4 C⁰ for heavy metals detection. Inductively coupled plasma-optical emission spectroscopy (ICP) was used in order to determine the heavy metals (As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn) content of samples.

Result and discussion

Table 1. Total concentration of heavy metals normal range in plants

Heavy metals	Normal range in plants (mg/kg)	Ref
Arsenic (As)	0.2-5	[10]
Barium (Ba)	0.7	[11]
Cadmium (Cd)	0.3 -4	[12]
Chromium (Cr)	0.006 – 18	[13,14]
Copper (Cu)	0.4 – 150	[13]
Iron (Fe)	640 – 2486	[13]
Manganese (Mn)	2-100	[13]
Nickel (Ni)	0.1 – 5	[15,16]
Plumbum (Pb)	3-10	[12]
strontium (Sr)	1.6	[11]
Zinc (Zn)	1 – 160	[11]

Table 2. The concentration of heavy metals of rosemary plants in leaves and stems

Heavy metal	Leaves		Stems	
	Qasr Bin Ghasheer	Gharyan	Qasr Bin Ghasheer	Gharyan
Arsenic (As)	0.3	0.2	0.2	0.14
Barium (Ba)	17.1	9	19.2	10.9
Cadmium (Cd)	0.2	0.02	0.2	0.02
Chromium (Cr)	1.7	2.1	1.2	2
Copper (Cu)	10	7.1	74.2	141.9
Iron (Fe)	474.8	488.2	388.8	432.7
Magnesium (Mn)	30.7	13.9	25.6	14.3

Nickle(Ni)	0.9	0.9	1.1	1.5
Plumbum (Pb)	0.6	2	2.3	3.7
strontium (Sr)	59..6	113.6	58.6	107.6
Zinc (Zn)	19..5	33.8	45.7	77.7

Arsenic (As)

Arsenic may pose a risk to both humans and animals when inhaled as dust particles or ingested through contaminated water. Due to the association of plant absorption with a change in species, which leads to a change in its toxicity. Nonetheless some researches believe that plants accumulate Arsenic at concentration that are harmful[11].

The results of the study, presented in Table (2), showed that the concentration of arsenic in the studied samples (leaves and stems) in Qasr Bin Ghasheer and Gharyan regions was within the limits permitted by the World Health Organization and the Food and Agriculture Organization.

The concentration of arsenic in Qasr Bin Ghasheer and Gharyan regions in leaves sample was ranged between 0.2 mg/kg and 0.3 mg/kg, respectively, while the concentrations of arsenic in the studied sample (stems) of both regions ranged between 0.14 mg/kg and 0.2 mg/kg, respectively.

Barium (Ba)

Barium (Ba), a nonessential element, can exert harmful effects on a wide range of organism. In plants, high concentrations of Ba may lead to toxicity, potentially impairing growth and disrupting physiological homeostasis[17].

The results in leaves samples of (Qasr Bin Ghasheer and Gharyan) indicated high concentrations of barium, exceeding the permissible limits set by the World Health Organization and the Food and Agriculture Organization (FAO) (0.7 mg/kg). The highest concentration of barium in the Gharyan sample was founded in the leaves and stems samples, at 10.9 mg/kg and 19.2 mg/kg, compared to the leaves and stems samples of Qasr Bin Ghasheer regions, at 9 mg/kg and 17.1 mg/kg, respectively.

Cadmium (Cd)

Cadmium is recognized as one of the most hazardous toxic elements to which humans may be exposed to at work or in the environment and has not any known physiological role in mammals. Exposure to Cadmium can occur through food, water, as well as inhalation of

cigarettes[9]. Although Cadmium does not contribute to plant development, it is readily absorbed and accumulates in various plant tissues, including the edible parts of crops by exploiting metabolic pathway utilized by essential nutrients for the plants, such as zinc and iron. respectively, its entry into the food chains of both human and animals poses significant risks, potentially leading to numerous acute and chronic toxicological effects[18].

The results obtained of leaves and stems samples studied in Qasr Bin Ghasheer and Gharyan regions were below the permissible detection limits. Cadmium concentrations were equal for both parts of the rosemary plant for Qasr Bin Ghasheer region, reaching 0.2 mg/kg, while 0.02 mg/kg was recorded for both leaves and stems for Gharyan region.

Chromium (Cr)

Chromium is considered a non-essential and toxic metal for plant growth. it suggested that plants do not have a specific mechanism of transport of Chromium. Chromium compounds exhibit highly toxicity to plants, adversely affecting to their growth and development. while certain crops may tolerate low levels of Cr ($3.8 \times 10^{-4} \mu\text{M}$) concentration without significant[19].

The results of this study in Table (2) showed that the concentration of chromium in the rosemary plant for Qasr Bin Ghasheer and Gharyan regions, whether in the leaves or stems sample, was within the limits permitted by the World Health Organization and the Food and Agriculture Organization, where was recorded for the leaves and stems sample for Qasr Bin Ghasheer region at 1.7 mg/kg and 2.1 mg/kg, while it was 1.2 mg and 2 mg/kg for both parts of the rosemary plant in the Gharyan region..

Copper (Cu)

Copper (Cu) is an essential necessary micronutrient required for plant growth in trace concentrations, functioning as a structural component of various enzymes. it is primally absorbed in the form of divalent cation (Cu^{2+}) or as Copper chalets. however, excessive accumulation of Cu in the environment can result in concentrations that are toxic to biological organism, including plants and other components of the biota[11].

If viewed concentration of copper in leaves and stems of the rosemary plant as shown in Table 2, these were still in normal range(0.4-150

mg/kg) in both regions (Qasr Bin Ghasheer and Gharyan), which reached (10 mg/kg) for leaves and (7.1 mg/kg) for Qasr Bin Ghasheer and Gharyan, respectively, while the concentration of copper for the Gharyan sample (stems) reached 142 mg/kg, which is much higher than its concentration for Qasr Bin Ghasheer sample (stems), although both concentrations were within the permissible limits.

Iron (Fe)

Iron is essential micronutrient for plant growth and development. It plays a central role in energy transformations and crucial for biosynthetic pathways and various physiological processes within plant cells [20]. While iron itself is not toxic, it plays an important environmental role due to its interactions with toxic metals [22]. Iron oxides can adsorb various elements and help reduce the presence of many trace and heavy metals participate in the attenuation of most trace and heavy metals. However, high levels of heavy metals -especially cobalt, nickel, and manganese caused a reduction in absorption and translocation of iron and leading to lower chlorophyll production. On the other hand, high concentrations of iron compounds in the soil are known to significantly reduce the uptake of trace metal. Interactions between iron (Fe) and manganese (Mg) are frequently observed, and the ratio of these two elements in both growth medium and plant tissue appears to play a more critical role in plant metabolism than their individual concentrations [23].

The result shows in Table 33, that by using inductively coupled plasma mass spectrometry (ICP-MS), iron in leaves Rosemary was 474.8 and 488.2 mg/kg-1 in both cities respectively. Meanwhile, the results of iron in stems were 388.8 and 432.7 mg/kg-1. That means the level of iron concentration in leaves or stems was within the limited range.

Manganese (Mn)

Manganese plays a significant role in plant growth; however, high concentrations of manganese in the soil can significantly impede plant growth [24]. According to the data in Table 2, manganese concentrations in the leaves of Rosemary (Qasr Bin Ghasheer and Gharyan) were 30.7 and 13.9 mg/kg-1, while its concentrations in the stems were 25.6 and 14.3 mg/kg-1. Which was within the limits permitted by the World Health Organization and the Food and Agriculture Organization (2-100) mg/kg⁻¹.

Nickel (Ni)

Nickel is an important micronutrient for plant growth and plays a key role as a part of the enzyme urease, which is essential for nitrogen metabolism in higher plants. However, at higher concentrations, nickel becomes highly toxic to plants. Typical signs of nickel toxicity include reduced growth, chlorosis (yellowing of leaves), tissue death and wilting. Nickel affects the plants metabolic process and can lead to the formation of reactive Oxygen Species which may cause oxidative stress. High levels of Nickel can also inhibit cell division at root meristem of sensitive plants, and decreases plant growth[25].

In this study, the results showed that nickel concentrations in Rosemary plants, collected from two different cities - Qasr Bin Ghasheer and Gharyan- varied slightly between samples. In Qasr Bin Ghasheer, the nickel concentration in both the leaves and stems was recorded at 0.9 mg/kg whereas in Gharyan, the concentration measured 0.9 mg/kg in the leaves and 1.5 mg/kg in the stems. In the comparison with the permissible limit (0.1-5 mg/kg) according to the international organization were found all measured values fall within the acceptable range established by international standards. Nevertheless, the concentration in Gharyan stems (1.5 mg/kg) was notably higher than in other parts but still remains within safe limits. However, the relatively higher concentration observed in Gharyan indicates the necessity for regular environmental monitoring to ensure continued compliance with safety standards.

lead (Pb)

The lead (Pb) is one of the most common heavy metal contaminants in soils. Plants are exceedingly harmful to it. Pb has no biological purpose in plants, although it can create morphological, physiological, and biochemical problems[29]. The accumulation of heavy metals contaminates food by interference between the soil and roots. Adsorption of lead in the roots is observed in several species of plants. Absorbed lead is accumulated in the roots, and only a small fraction is transported to aerial plant parts[30]. As a result, root vegetables like carrots and sweet potatoes may contain the highest levels of lead. Then come leafy greens like lettuce and Swiss chard. Tomatoes, for example, are the least likely to have Pb absorbed from the soil[26]. Lead can last up to 2000 years in the soil and is hazardous to plants in a variety of ways. Several hyperaccumulator plant species (e.g., *Brassica pekinensis* and *Pelargonium*) are capable of transporting higher

concentrations of lead to aerial plant parts, without causing damage to their metabolic functions[27].

In this study, the concentration of lead was measured in the leaves and stems of rosemary plants from the cities of Qasr Bin Ghasheer and Gharyan. The results showed that the lead concentration in the leaves of rosemary in Qasr Ben Ghasheer was 0.6 mg/kg, while in Gharyan it was 2 mg/kg. For the stems the lead concentration in Gasr Bin Ghasheer was 2.3 mg/kg. These concentrations are significantly lower than the permissible range set by the world health organisation, which is between 3-10 mg/kg for lead in rosemary plants. The observed differences in lead levels between the two cities may be attributed in local environmental conditions, such as soil contamination or industrial pollution .Nevertheless, the lead concentration in both the leaves and stems of rosemary from both cities fall within the safe limits defined by international health guideline, suggesting that these plants are safe for culinary or medicinal use. However, further research is recommended to better understand the long-term effects of environmental factors on these concentrations.

strontium (Sr)

The concentration of strontium was measured in two different cities, Qasr Bin Ghasheer and Gharyan, by analysing Naturally occurring stable strontium (Sr) is widespread and can be found in a different types of plants. Radio strontium , a by-product of nuclear activates, is released into environment in both volatile and non-volatile components. , where it had remained in the environment for several decades due to its persistence. only the soluble strontium which can be absorbed by plans, primarily through their roots and leaves, from sources such as soil, air, and water. when strontium is absorbed through the leaves, strontium is transported via the phloem(assimilation stream) from the leaves to other parts of the plant[28]. Results showed that the reference concentration for rosemary according to the World Health Organisation is 1.6 mg/kg. in Qasr Bin Ghasheer the strontium concentration in the leaves reached 6.59 mg/kg and in the stems 6.58 mg/kg .In contrast, in Gharyan, the concentration in the leaves was 113.6 mg/kg and 107.6 mg/kg in the stems, indicating a significant excedance of the permissible limits. This notable difference in strontium concentration between the two cities is attributed to varying levels of environmental pollution, with Gharyan likely being more

exposed to industrial or agricultural contamination sources, leading to higher strontium accumulation in plants compared to Qasr Bin Ghasheer

Zinc (Zn)

Zinc (Zn), an essential micronutrient for plants, is integrals to various metabolic and regulatory processes. however, excessive Zn exposure proves toxic to both plants and humans. in humans, high Zn levels manifest as headache, abdominal pain, and nausea[33]. within plants, Zn influence extends beyond its primary accumulation in roots; its effects on stems, leaves and subcellular structures are critical for overall plant health and development. therefore, optimal Zn concentrations are vital for plant growth and survival, while excessive levels lead to toxicity[34]. In this study, the Zinc concentration in the leaves and stems of rosemary plants was analysed in the cities of Qasr Bin Ghasheer and Gharyan . the results showed that the zinc concentration in the leaves of rosemary in Qasr Bin Gasheer 19.5 mg/kg, while in Gharyan it was 33.8 mg/kg . Regarding the stems the zinc concentration in Qasr Bin Ghasheer was 45.7 mg/kg, and in Gharyan ,it was 77.7 mg/kg . These findings indicate a variation in zinc concentration between the two cities, which may be related to the environmental and soil characteristics in each region . It is noteworthy that the zinc concentration in rosemary in both cities fall within the permissible range sit by the world health organization for nutrition , which is between 1-160 mg/kg .however it may be important to further investigate the environmental impact on these concentrations and the potential effect of these levels on human health , especially if used as dietary supplements medicinal purposes.

Conclusion

This study evaluated the concentrations of heavy metals in the leaves and stems of the rosemary plant collected from two regions, Qasr Bin Ghasheer and Gharyan in Libya .The findings showed elevated concentrations of certain elements particularly iron (Fe) and cuper (Cu). Iron levels in stems were measured at 432.7 and 488.2 mg/kg in Gharyan, and 388.8 and 474.8 mg/kg in Qasr Bin Ghasheer exceeding commonly accepted safe levels concentrations of zinc and manganese where generally within or near the acceptable range. Meanwhile, Cadimium, chromioum, nickel and lead concentrations remained within

safe margins across most samples .These results indicate variability in heavy metal accumulation between the two study regions .Further research and continuous monitoring are necessary to better understand the environmental factors influencing these variations and to insure the safe use of local plants.

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