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Estimation of concentrations of some heavy metals in the fruits of Sidr plant(*Ziziphus spina – Christi*) grown in Nasiriyah, Iraq

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Abstract. Different samples of Sidr fruit were collected from different locations in Nasiriyah city, Iraq, and a control sample from the countryside. Location was considered the primary factor and fruit parts the second factor in a randomized complete block design with three replicates. The results showed that all three studied sites—the first site, located near a power plant, the second near gas stations, and the third, located in the city center—contained high concentrations of heavy elements (lead, cadmium, and nickel) above the international standards permitted in fruit (WHO or FAO). The fourth site, located outside the city in a village and used as a reference site for comparison with the other sites, contained concentrations of heavy elements within the internationally permitted ranges. Furthermore, higher concentrations of heavy elements were found in the fruit peels than in the pulp.

Keywords: Heavy Elements, Sidr, Nasiriyah, Environment and Pollution, Lead, Cadmium, Nickel.

INTRODUCTION

Pollution is defined as any damage or disturbance to the ecosystem caused by human intervention [1], or a sudden or gradual change in the physical, chemical, geological, or biological properties of the environment [2]. Environmental pollution is an important topic due to the population expansion and industrial progress the world is witnessing. Maintaining an unpolluted environment or reducing environmental pollution is achieved by identifying the sources of pollution, the type and quantity of pollutants, the extent of their spread, and their negative effects on the environment, as well as working to treat them [3, 4] indicated that pollutants are remnants of materials that are primarily made by humans, which they use and throw away. It has been noted that types of pollution are interconnected, such as air and water pollution, as it can be said that pollution is an integrated system that supports each other [5, 6]. Pollution also occurs in space when radioactive materials, factory gases, and dust mix with clouds and rain, and these pollutants fall on water bodies with the rain. The land on which rain falls may be contaminated with other materials, causing the pollution to seep into groundwater or reach seas, rivers, and lakes, increasing their pollution [7]. Heavy elements are among the most important types of pollutants that contaminate the terrestrial, aquatic, and even air environment. The US Environmental Protection Agency indicates that the term "heavy elements" refers to transitional elements and elements located between groups 2 and 6 in the periodic table [8]. The term "heavy metal" refers to any metallic chemical element that has a relatively high density and is non-toxic or toxic at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), lead (Pb), zinc (Zn), nickel (Ni), and copper (Cu). Heavy elements differ from organic materials in that they do not dissolve or decompose into simpler substances. They are thus transmitted through the food chain through multiple pathways and have the ability to accumulate in the tissues of various living organisms, thus having a broader and more dangerous impact. Furthermore, they disrupt the ecological balance and reduce biodiversity [9]. Heavy elements accumulated in the soil may be transferred to the bodies of living organisms through the organism's contact with it or feeding on the organic materials deposited in it or on the organisms that contain it, such as microbes, worms, and other invertebrates, or they enter plants through the absorption process and from there to humans and animals [10]. Heavy elements are found in the aquatic and terrestrial environment in nature, but in low concentrations. In addition, particulate air pollutants and acid rain can be a significant source of pollution of the terrestrial and aquatic environment with these elements [11]. Heavy metals, even at low concentrations, can cause toxicity to humans and other organisms. The toxicity of metal ions stems from their ability to bind to protein molecules and prevent DNA replication and, consequently, cell division [12]. Heavy metals enter plants through the leaves. It has been found that 20-60% of the cadmium present in plants is due to its absorption through the leaves. Likewise, lead compounds present in the air can enter the leaves through the stomata, in addition to being absorbed through the roots. Many plants are characterized by their ability to absorb pollutants from the soil, water, and air and accumulate them in their tissues in a way that does not cause any harm to them. Thus, they play a role in treating environmental pollution in the locations where they grow [13]. The concentration of these elements in plant tissues varies according to the sources of pollution, the nature of the soil components, and the extent of these elements' readiness for absorption, in addition to their ability to absorb and accumulate pollutants within their tissues, which depends on the plant's genetic ability to remove pollutants. The difference in this ability is due to the difference in the presence of active groups present in the cell walls, as well as phosphate groups. Hydroxyls and amines, which represent ion exchange and binding sites, play a role in binding with these pollutants [14]. Trees are used as effective biomarkers to detect pollutant concentrations, whether in cities or in the atmosphere, due to their widespread abundance in many countries as basic and main plants in polluted urban areas, the ease of their classification, and the low cost of taking samples from them. Also, the process of analyzing heavy elements in their parts is not complicated [15]. Within the strategy of using plant biomarkers to detect environmental pollution (air, soil and water), the aim of the current study is to evaluate environmental pollution with heavy metals in the city of Nasiriyah by estimating the concentrations of some heavy elements (lead, cadmium and nickel) and determining their distribution locations using samples of the fruits of the jujube plant grown in the city and knowing their ability to accumulate heavy elements.

MATERIALS AND METHODS

1- Study Area

The study was conducted in the city of Nasiriyah, which is geographically located in the southeastern part of Iraq, specifically on the Euphrates River. Astronomically, it lies at 46.266667 degrees east of the Greenwich meridian and 31.053888 degrees north of the equator. Its land area is 1,766 km². It has a desert climate characterized by low rainfall and high temperatures in the summer, reaching 50°C, and a warm climate in the winter. Four different sites were selected as follows:

1- Site 1: Located near the power station.
2- Site 2: Located near a gas station.
3- Site 3: Located in the city center and characterized by heavy traffic and congestion throughout the day.
4- Site 4: Located outside the city and used as a reference site for comparison with other sites, as it is characterized by the presence of agricultural villages. Samples were taken from an orchard located in one of the villages. Note that the four locations were determined using the Google Maps GPS system, as shown in (Table 1).

TABLE 1. Description of the study stations for the sites in the city of Nasiriyah

The description	Site	Station symbol
Located near the power station	31°02'12.6"N 46°11'39.3"E	S1
Located near a gas station	31°02'00.2"N 46°13'59.4"E	S2
Located in the city center	31°02'54.3"N 46°14'46.9"E	S3
Located outside the city	30°58'30.7"N 46°19'06.1"E	S4

2- Plants studied:
The sidr plant, which is widespread in the city of Nasiriyah, was selected. It belongs to the Rhamanaceae family and the genus Zizyphus, which includes approximately 100 species of deciduous and evergreen trees and shrubs. There are many sidr varieties found in Iraq, including the olive and apple trees, both belonging to the mauritiana species, and the pombe and malassi, both belonging to spina – christi species [16 ,17].
3- Sample Collection
Plant samples were collected by hand from four sites in the study area during the 2024 ripening season, with three random replicates from each site. They were stored in plastic bags and assigned numbers until they reached the laboratory.
4- Sample Cleaning and Preparation
The sidr fruits were washed with plain water and then distilled water several times. The outer peel was then separated from the fruit to study both the outer peel and the pulp of the sidr fruits.
5- Extraction of Heavy Elements from Samples
Trace elements in plants were extracted according to Method [18]. 0.25 g of each dry, ground sample was sieved through a plastic sieve with a diameter of (40) microns. (5) ml of an acidic mixture consisting of concentrated nitric acid and perchloric acid in a ratio of 4:1, respectively, was added to the sample. The sample was left for 30 minutes, then the mixture was placed on a hot plate at 60°C until the solution became clear. The filtered contents of the flask were then transferred to clean, tightly capped 25 ml plastic bottles, and the volume was completed with deionized distilled water. The resulting sample was then ready for measurement using an atomic absorption spectrometer.
6- Estimation of Heavy Elements
Heavy element concentrations were estimated in parts per million (ppm) dry weight using the flame atomic emission technique according to the method described by [19].

TABLE 2. Standard values of heavy metals in ppm

Heavy metals	Standard values (ppm)	Organizations
Pb	0.1 - 0.3	WHO/FAO (20)
Cd	0.05 - 0.1	
Ni	0.5 - 1	

RESULTS

1 - Lead Content: (Table 3). shows that lead concentrations varied significantly across sites. Site third had the highest average lead concentration of 3.09 ppm, followed by Site second with an average concentration of 2.44 ppm. However, Site first had the lowest average concentration of 1.78 ppm, compared to Site fourth, which had a concentration of 0.16 ppm. The results in (Table 3) also indicate a non-significant difference in the lead content of the plant parts. The peels contained the highest average concentration of 2.85ppm, while the pulp contained the lowest average concentration of 2.50 ppm. (Table 3) also shows that the highest lead value was 3.74 ppm at Site third in the peels, and the lowest value was 0.13 ppm at Site fourth in the fruit pulp.

TABLE 3. lead concentrations (ppm) in plant samples at study stations

The Site	plant parts		Average for sites
	Pulp	Peel	
S1	1.75	1.84	1.78
S2	2.62	2.98	2.44
S3	3.13	3.74	3.09
S4	0.13	0.19	0.16
Average for the plant part	2.50	2.85	---
LSD	0.79		

2- Cadmium content: It is noted from (Table 4) that the lead concentration differed significantly across sites. Site second gave the highest average lead concentration of 1.62 ppm, followed by site third with an average concentration of 1.09 ppm. However, site first gave the lowest average concentration of 0.73 ppm compared to the comparison site fourth, which gave a concentration of 0.06 ppm. The results in (Table 4) also indicate a non-significant difference in the lead content of the plant part. The peels contained the highest average concentration of 0.98 ppm, while the pulp contained the lowest average concentration of 0.76 ppm. The results in (Table 4) also showed that the highest value of cadmium was 1.68 ppm in site second in the peels and the lowest value was 0.04 ppm in site fourth in the fruit pulp.

TABLE 4 Cadmium concentrations (ppm) in plant samples at study stations

The Site	**plant parts**		
	Pulp	**Peel**	**Average for sites**
S1	**0.54**	**0.93**	**0.73**
S2	**1.56**	**1.68**	**1.62**
S3	**0.92**	**1.26**	**1.09**
S4	**0.04**	**0.08**	**0.06**
Average for the plant part	**0.76**	**0.98**	**---**
LSD	**0.54**		

3 - Nickel Content: (Table 5) shows that nickel concentrations varied significantly across sites. Site third had the highest average lead concentration of 1.98 ppm, followed by Site second with an average concentration of 1.84 ppm. However, Site first had the lowest average concentration of 1.49 ppm, compared to the comparison site fourth, which had a concentration of 0.37 ppm. The results in (Table 5) also indicate a non-significant difference in the lead content of the plant parts. The peels contained the highest average concentration of 1.52 ppm, while the pulp contained the lowest average concentration of 1.33 ppm. The results in (Table 5) also showed that the highest lead value was 2.13 ppm at Site third in the peels, and the lowest value was 0.32 ppm at Site fourth in the fruit pulp.

TABLE 5. Nickel concentrations (ppm) in plant samples at study stations

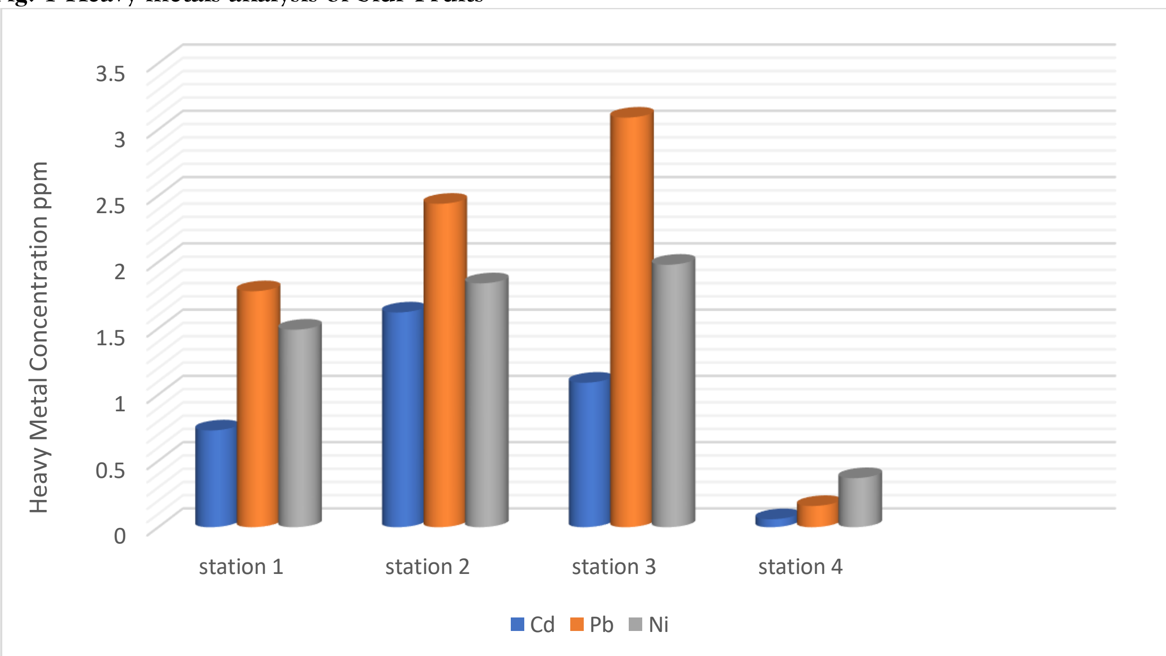
The Site	**plant parts**		**Average for sites**
	Pulp	**Peel**	
S1	**1.45**	**1.54**	**1.49**
S2	**1.71**	**1.97**	**1.84**
S3	**1.84**	**2.13**	**1.98**
S4	**0.32**	**0.42**	**0.37**
Average for the plant part	**1.33**	**1.52**	**---**
LSD 0.05	**0.41**		

DISCUSSION

Plants are the most sensitive organisms to environmental diversity due to their high sensitivity to heavy metal toxicity, and their effectiveness as the first stage in the food chain that collects pollutants compared to organisms living at higher trophic levels [21]. As a result of the accumulation of elements within plant tissues, they provide a clearer picture of pollution than in the case of relying on other measurements [22]. The results of the current study showed rates of heavy elements in the fruits of the sidr plant (Pb, Ni, Cd) for samples of the study sites 1.86, 1.42, 0.87 ppm dry weight, respectively. The order of the abundance of the elements was as follows: Pb > Ni > Cd (Figure 1). The results of the current study showed a significant variation in the concentrations of heavy elements in the fruits of the sidr plant between the studied sites, as site three in the city center recorded an increase in the concentrations of lead and nickel, and the concentrations also increased in sites two and number one compared to site fourth (comparison). The study also recorded an increase in the concentrations of cadmium in site two with a significant difference at the probability level of 5% compared to site fourth. It is noted from the results of the study that there was an increase in the rates of concentrations of heavy elements (lead, cadmium and nickel) in all the studied sites except site fourth (comparison), where the results were higher than the standards permitted in fruit (WHO or FAO) (Table 2). The increase in the concentrations of heavy elements (lead, cadmium and nickel) in different locations in the fruits of the Sidr plant may be attributed to soil pollution with heavy elements [23] or the main reason for the increase in the concentration of heavy elements in vegetables and fruits may be due to the pollution of the surrounding densely populated areas, in addition to vehicle exhausts and waste near residential areas, which play a role in increasing the concentrations of pollutants [24]. The main sources of heavy metal pollution include urban industrial aerosols, solid waste, mining activities, industrial and agricultural chemicals, vehicle exhausts, and the battery and paint industries. Vehicle movement and high traffic density have an impact on increasing some concentrations of heavy elements, especially lead, which is abundant in vehicle exhausts [25]. Consequently, the concentration of heavy metals increases in the tissues of plants growing in such environments. The high concentrations of these elements in plant tissues are a result of increased absorption from the external environment in accordance with the physical and chemical properties of these environments. Plants absorb heavy metals by absorbing them from airborne sediments on plant parts exposed to air from polluted environments, as well as from polluted soil through the roots. Fruits and vegetables may also become contaminated with heavy metals as a result of irrigating them with polluted water [26].

The lead, cadmium, and nickel levels in the sidr fruit samples taken from Site fourth were consistent with those reported in apple samples from Wasit, Iraq 0.23, 0.11, and 0.21 ppm [27] but higher than those reported in apple samples from Pakistan 0.045, 0.003, and 0.007 ppm [28]. The lead and cadmium levels in Site fourth samples were also consistent with those reported in sidr fruit samples from China, where lead concentrations were in the range of 0.074–0.154 ppm and cadmium concentrations were in the range of 0.055–0.034 ppm [29]. They were also consistent with another study from China, where cadmium concentrations were 0.013 ppm and nickel concentrations were 0.90 ppm [30] and with Study [31], where nickel concentrations were 0.4 ppm and cadmium concentrations were 0.027 ppm. The lead and cadmium levels for Site fourth were Four inconsistencies of those found in Sidr samples from India lead 2.98 ppm, cadmium 0.11 ppm, μg/g [32].

Fig: 1 Heavy metals analysis of Sidr Fruits



CONCLUSION

The current study revealed varying concentrations of heavy metals across different study sites in laboratory-analyzed samples of Sidr fruit collected from Nasiriyah, Iraq. Some samples exceeded permissible limits according to international standards (WHO or FAO). The sources of this pollution are believed to be due to various environmental factors such as soil, water, or air pollution, and pollution resulting from transportation, generators, solid waste, and others. Concentrations of heavy elements increase depending on the geographical location and the extent of pollution. Plants play a significant role in phytoremediation to limit the spread of polluting elements by extracting them from the soil or atmosphere and accumulating them in their various parts. The results of the current study demonstrated the Sidr plant's ability to accumulate heavy elements in polluted environments, and therefore it can be used in phytoremediation and as a pollution detector.

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