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Assessment of the Concentrations of some Heavy Metals in some Vegetables Traded in the Local Market in Sebha City - Libya

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ABSTRACT

Consuming vegetables as food offers rapid and least means of providing adequate vitamins, minerals, and fibers. Vegetables used as food include those used in making soups or as integral parts of the primary sources of a meal. Leafy vegetables occupy a significant place in the human diet. Environmental exposure to heavy metals is a well-known risk factor for human health. The concentration of the heavy metals (Cu, Pb, Cd, and Cr) in vegetables from the Sebha market was determined using Atomic Absorption Spectroscopy AAS). In the Sebha local market, different vegetable types from different locations are marketed. Therefore this investigation was conducted to study the state of the accumulation of some heavy metals such as Cu, Cd, Pb and Cr. in some selected vegetables which include Solanum tuberosum (Potatoes), Allium cepa L. (Onion), Daucus Corota L. (Carrot), Cucurbita Pepo (Courgette), Solanum melongena L. (Eggplant), Lactuca sativa L. (Lettuce), Petroselinum crispum (mill.) Nym. (Parsley) and Spinacea oleracea (Spinach). The mean levels of these heavy metals ranged from 0.0-0.03, 0.0-2.36 and 0.0.0-8.13. ppm for Pb, Cd, and Cr. respectively. Among the vegetables studied, Cd and Cr exceeded the allowable limits recommended by WHO/FAO in some vegetables, whereas Cu and Pb concentrations are under the detectable limit. Statistical analysis shows a positive correlation between Cd and Cr at 0.01 and between Cd and Cr, Cd and Pb at 0.05.

INTRODUCTION

The Libyan state is making great efforts to achieve sustainable development leading to sustainability and carbon neutrality in the Libyan economy by 2050 (Moumani, 2023; Ahmed et al., 2023; Fathi et al., 2017; Fathi et al., 2018; Awad et al., 2023; Iessa et al., 2022), and decentralization of the energy and water system (Nassar, et al., 2006, 2007, 2016-a, 2016-b, 2023, 2024; Ali et al., 2021). This can be achieved through wise and rational exploitation of available resources, including renewable energy in electricity generation (Alsharifet al., 2023), water desalination, and for industrial and agricultural purposes (Hala et al., 2024; Alatrash et al., 2024). Agricultural waste can also be used to produce organic fertilizers and methane gas, which is used for cooking and heating animal shelters in the winter (Yasser et al., 2023) and Applying the energy saving strategy in all production and service sectors (Abdunnabi et al., 2023; Khaleel et al., 2023;).

Vegetables are essential in human diets, providing key nutrients such as minerals, trace elements, vitamins, carbohydrates, and proteins. Their consumption, particularly in urban areas, has increased (Girmaye, 2014). However, growing vegetables in contaminated soil can accumulate heavy metals in both edible and non-edible parts (Vousta et al., 1996). Soil pollution can result from irrigation, polluted water, fertilisers and pesticides, or industrial emissions (Aydinalp & Marinova, 2012; Iessa, 2024-a; Iessa, 2024-b; Firdous et al., 2024). Vegetables absorb heavy metals through roots or from polluted air, integrating them into the food chain (Solukola & Dairo, 2007; Hipkin, et al., 1999; Salem, et al., 1995). High concentrations of these metals are toxic, competing with essential nutrients and disrupting plant metabolism (Thurman & Colins, 1983; Salem and Alwalayed. (2019; Al-Ethawi. and Salem. 2019; Turner, 1997; Van Assche & Clijsters, 1990). Heavy metals can interfere with mineral uptake, protein metabolism, and overall plant health (Al-Helal, 1995; Tamas. L., et al.,1997; Kim et al., 2003; Azevedo et al., 2005), reducing growth and poor development (Ryser & Sauder, 2006). Plants' absorption of heavy metals depends on metal and soil characteristics, plant species, and soil conditions such as pH and fertiliser use (Solukola, et al., 2010; Yasser et al., 2021; Mansour et al., 2020; Ismail et al., 2005; Sharma et al., 2006). Some plants are more prone to accumulating specific heavy metals (Wenzel & Jackwer, 1999; Scott et al., 1996; Xiong, 1998). The accumulation rate depends on soil properties and the plant's metal removal efficiency (Qishlaqi et al., 2008; Arora et al., 2008). Heavy metals in soil can originate from

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bedrock, agricultural inputs, waste deposits, or industrial emissions (Huda et al., 2024). While metals like Co, Mn, Ni, Zn, Cu, Fe, and Cr are essential at low levels, they become problematic at higher concentrations. Non-essential metals like Cd, Pb, As, and Hg are toxic (Ahmed et al., 2023). Leafy vegetables accumulate more heavy metals than grain or fruit crops (Ahmed et al., 2023; Salem et al., 2022; Mapenda et al., 2005). Contaminated food can deplete vital nutrients, impairing immune function, growth, and psychosocial abilities, and increasing the risk of gastrointestinal cancers (Arora et al., 2008; Jarup, 2003; Iyengar & Nair 2000; Turkdogan et al., 2003; Al-danasuri, 1967). This study aims to assess the concentrations of heavy metals such as Cd, Pb, and Cr in vegetables marketed in the local market in Sebha City, underscoring the need for further research and action to ensure food safety and public health.

METHOD

Collection of Vegetable Samples

Vegetable samples were collected from Sebha local market in 2023. The collected vegetables, representing leafy, root, and fruit categories, included Petroselinum crispum (Parsley), Spinacia oleracea (Spinach), Lactuca sativa (Lettuce), Solanum tuberosum (Potatoes), Allium cepa (Onion), Daucus carota (Carrot), Solanum melongena (Eggplant), and Cucurbita pepo (Courgette). The vegetable samples were brought to the laboratory, where the edible parts were thoroughly washed with clean tap water and then with distilled water to remove any suspended particles. The samples were dried in an oven for 24 hours at 70°C, ground to a fine powder using a manual grinder, and stored in clean, dry, stoppered plastic containers at room temperature.

Extraction of Heavy Metals

The procedure used for the extraction is based on the method described by (Miyazawa, et al., 2009). One gram of dry powdered vegetable was taken in a digestion flask, to which 5 ml of HNO3 was added and heated until the brownish fumes disappeared. Then, 5 ml of HClO4 and 10 ml of HCl were added, and the mixture was heated until it became transparent. The resulting solution was cooled and filtered using Whatman No. 42 filter paper. Finally, the digest extract was transferred to a 50 ml volumetric flask and made up to volume with deionised water. Heavy metals were measured using an atomic absorption spectrophotometer (NOVA A400). Calibration curves for each element were prepared individually using linear correlation using the least squares method. A blank reading was also taken, and necessary corrections were made when calculating the concentrations of various components.

RESULTS

Heavy Metals in Vegetables Samples

The results of the concentration of the vegetables, whether leafy (lettuce, spinach, and parsley), root (carrot, onion, and potatoes), or fruit (Courgette and eggplant), show variations in their accumulation of heavy metals. Table 1 and Fig. 1 indicate that leafy vegetables such as parsley, spinach, and lettuce accumulate higher levels of heavy metals than grain or fruit crops. Heavy metal concentrations vary among the collected vegetables, as shown in Table 2. The trend of heavy metal concentration in vegetables is Cr > Cd > Pb>Cu. It is clear from the table 1. That Cu was not detected in any vegetable samples. Cd was detected in all samples except eggplant. The results show that the highest concentration of Cd was found in onion and parsley, both at 2.36 ppm. Its concentration in potatoes, spinach, lettuce, Courgette, and carrot were 0.85, 1.05, 1.14, 1.39, and 1.69 ppm, respectively. Variations in Cd concentration among different vegetables may be due to their differential capacity for accumulation .

Pb content in the vegetables from the present study sites was within permissible limits (Ahmed et al., 2023). Its concentration in vegetables is generally deficient due to its low bioavailability. Pb concentrations in most vegetable samples studied were below the instrument's detection limit. However, 0.014 and 0.03 ppm concentrations were recorded in potatoes and lettuce, respectively. Despite being recorded in soil samples at 6.45 ppm in Table 2, Pb is known to be toxic and harmful to plants. Our findings on the Cr content in selected vegetables are particularly significant, as they exceeded the maximum permissible value of 0.05 ppm determined by (Ahmed et al., 2023), except for eggplant. Significantly high concentrations of Cr were recorded in parsley and onion, with 8.13 and 6.16 ppm, respectively. This result is compatible with the findings of [Yasser et al., 2023]. The other examined vegetables had different values of Cr, as shown in Table 1, underscoring the need for further research in this area.

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Table 1. Concentration of heavy metals in vegetables (mg/kg/dwt)

Vegetables	**Heavy metals**			
	Cu	Pb	Cd	Cr
Eggplant	N. D	N. D	N. D	N. D
Courgette	N. D	N. D	20.8	11.4
Onion	N. D	N. D	12.1	04.9
Potatoes	N. D	0.02	20.6	.032
Carrot	N. D	N. D	2.14	4.62
Lettuce	N. D	0.03	0.73	41.5
Parsley	N. D	N. D	1.80	6.20
Spinach	N. D	N. D	0.83	62.1
(FAO/WHO,2011) *	73	0.3	0.2	2.5

N.D = not detected; *Permissible limit of HMs

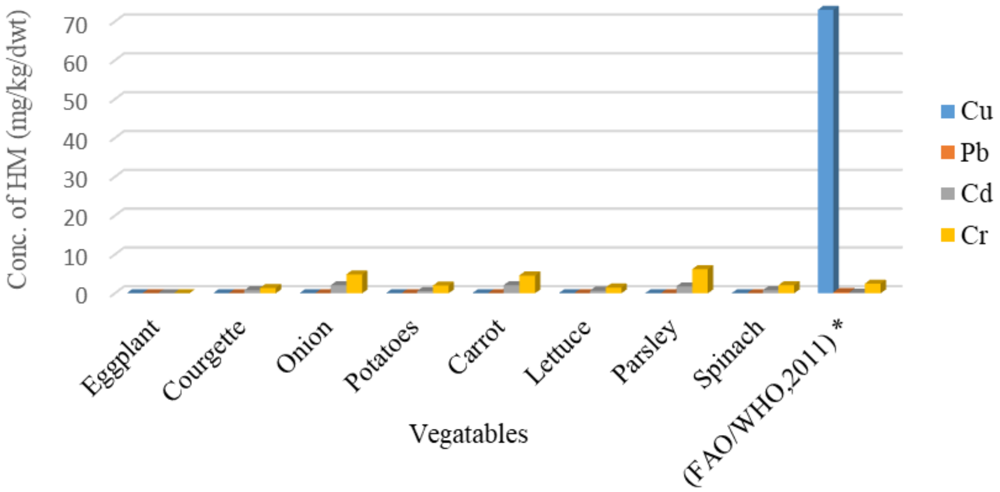

Figure 1. Conc. of Heavy metals (mg/kg/dwt) in studied vegetables

Pearson's correlation coefficient between measured metals

Statistically significant correlation coefficients at 0.01 and 0.05 probability level were measured between metal concentrations, the results show no correlation between Cu and any of the other metals, whereas, a good correlation at 0.01 between Cr and Cd. While at 0.05 there is good correlations between Cr and Cd, and Cd and Pb. these results were compatible with the results reported (Shakya & Khwaounjoo, 2013; Salem & Al-Ethawi, 2013).

Table 2. Person's correlation factor between measured heavy metals

	Cu	Pb	Cd	Cr
Cu	1.0			
Pb	0.245	1.0		
Cd	0.320	0.894*	1.0	
Cr	0.189	0.993**	0.847**	1.0

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

DISCUSSION

The results indicate that significant variations of heavy metal concentrations in vegetables grown at the same site can be attributed to differences in their morphology and physiology of heavy metal uptake, exclusion, accumulation, and retention (Mansour et al., 2022; Kumar et al., 2009). The metal species and plant parts influence the uptake of metal ions (Hipkin et al., 2004; Tani & Barrington 2005). The heavy metals in leafy vegetables may be due to their higher transpiration rate to maintain growth and moisture content (Tani & Barrington, 2005). The accumulation of Cd in vegetables is attributed to farmers' application of large amounts of phosphate fertilisers, as phosphate fertilisers are a significant source of Cd, which is naturally found as an impurity in phosphate rocks; soils accumulate Cd due to the extensive use of phosphate fertilisers (Salem & Chergawi, 2013). Cd is highly mobile and can be easily absorbed by plants through root surfaces, moving to wood tissue and then to the upper parts of plants (Gardiner et al., 1995). High concentrations of Cd have been reported in lettuce and spinach grown in urban areas and in spinach, coriander, parsley, onion, and lettuce (Torabian & Mahjouri, 2002; Salem et al., 2014; Demirzen & Ahmet, 2006; Labhade, 2013).

Many plants can accumulate high concentrations of lead without visible changes in their appearance or yield. Contamination of vegetables by heavy metals can occur due to irrigation with contaminated water, emissions from industries, and using fertilisers and metal-based pesticides (Salem, 2012). High concentrations of Pb have been reported in vegetables and fruits grown near industrial areas or irrigated with sewage or treated wastewater (Demirzen & Ahmet, 2006; Sharma et al., 2008). High Pb concentrations were reported in vegetables irrigated with polluted water in Hamadan City, Iran (Salem & Abuhadara, 2010). The low concentration of Pb in the vegetable samples is attributed to the location of the study area, which is away from industrial complexes and traffic roads, and its irrigation with underground water. High Pb concentrations (17.54-25.00 ppm) have been reported in vegetables grown in industrial areas [21 (Sharma et al., 2006). Our results agree with those reported by (Raphael & Adebayo, 2011). The ability of various crops to accumulate heavy metals influences their concentrations in the edible parts (Salem & Noralldien, 2018). In a survey conducted by (Shakya and Khwaounjoo, 2013) to determine the concentration of some metals in leafy vegetables collected from markets, the concentration of Cr was below the instrument's detection limit. However, high concentrations of Cr (6.9-7.4 ppm), close to our results, were observed in vegetables near industrial areas and roadsides (Salem et al., 2018). The source of Cr in the vegetables was probably the agricultural lands fertilised with inorganic fertilisers and synthetic pesticides for an extended period (Yasser et al., 2023).

The results of Pearson's correlation coefficient between measured metals show a significant correlation between Cd, Pb and Cr. These were compatible with the reported results (Shakya & Khwaounjoo, 2013; Salem & Al-Ethawi, 2013).

CONCLUSIONS AND RECOMMENDATIONS

The Sebha local market in the Aljaded area is the biggest market for vegetables and fruits, and most inhabitants of Sebha buy their needs of vegetables and fruits from it. The people usually claim that the foodstuff in the market is contaminated with heavy metals due to the excessive addition of fertilisers and pesticides to crops by farmers to enhance their production. However, many researchers reported that crops treated with high amounts of chemicals, either fertilisers or pesticides, can cause diseases in human beings. Therefore, this study investigated whether some vegetables are contaminated with heavy metals. The survey results, which include the most consumed vegetables, indicated that these vegetables were not contaminated with the studied heavy metals (Cu, Pb, Cd and Cr). This study is the first to analyse heavy metals in some vegetables grown and consumed in the surrounding area. Concentrations of heavy metals must be monitored regularly to ensure they are within permissible limits. Chemical fertilisers must also be added wisely to avoid any contamination from them.

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