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THE RELATIONSHIP OF HEAVY METALS CONTENTS IN SOILS TO THEIR CONTENT IN LEGUME SEEDS USED IN FAMOUS TRADITIONAL FOOD IN KURDISTAN REGION-IRAQ

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ABSTRACT

In this work the level of risk heavy metals contents in Cowpea seeds comparison with heavy metal content in soil was studied. For the experiment three cowpea cultivars (brown, red, white) were used. Cowpeas were harvested at full ripeness in Kalak location in Erbil city. The flame AAS (AAS Varian AA Spectr. DUO 240 FS/240Z/UltrAA) was used for the determination of heavy metal contents in soil and plant materials. The soil which cultivated Cowpea, characterized neutral to slit alkali, with a typical content of cations K, Mg and P. Beans and the seeds of faba bean, cowpea and chickpeas boiled with salt eaten in the form of Lablabe, traditionly used heavy sweets such as knafa. Ful, which is fava beans cooked with chickpeas (garbanzo beans) or make soup from fresh cowpea, fresh faba bean, fresh fasoulia, as well as lentil soup (shorbat adas) and different kinds of salad after boiled. Cowpea grain legumes occupy an important place in human nutrition, especially in the dietary pattern of low income groups of people in developing countries. The level risk heavy metal contents in the soil determined was only Cd content was on the level of limit value given for the soil extract by aqua regia as well as Co content was higher than the limit value given for the relationship between soil and plant. All of determined values were lower than critical value extracted by NH₄NO₃ only the maximal available soil content of mobile Pb forms was exceeded but cowpea accumulated seeds in amounts the risky elements contents, with the exception of Ni, did not exceed limit for the maximum levels of chosen risk elements in studied legume. The content of the metals studied with the exception of cadmium, not exceed the maximum permissible value in legumes, as defined in the Codex Alimentarius. The aim of this research, to study or determine the content of risky heavy metals (Cu, Ni, Cr, Pb, and Cd) in the soil and their relationship in selected varieties cowpea seeds cultivar. Faba bean and Fresh bean with tomatoes uses for preparing soup, or a popular snack eaten on boiled and roasted in oil with egg or onion, other legume seeds broad bean, fababean, lentil, pea, chickpea used for different traditional foods in Iraq.

Keywords: cowpea; heavy metals; soil; traditional food

INTRODUCTION

Legume grains have been playing a key role in the traditional diets of human beings throughout the world. They are excellent source of protein, dietary fiber, starch, micronutrients and bioactive compounds with low level of fat (Chang et al., 2000). Grain legumes occupy an important place in human nutrition, especially in the dietary pattern of low income groups of people in developing countries. Legume Grains are normally consumed after processing, which not only improves palatability of foods but also increases the bioavailability of nutrients (Tharanathan and Mahadevamma, 2003). Plant proteins are cheaper than the animal proteins; therefore, the people consume legume seeds worldwide as major source of protein (Petchiammal et al., 2014). Legume grains are a rich source of polyphenols, which have high antioxidant activities (Cardador Martinez et al., 2002; Troszynska et al., 2002). Antioxidant activity has been reported for extracts of legumes such as pea; white, green, red and navy beans; beach pea; lentils; everlasting pea; Jack bean; adzuki bean; and cowpea

(Lopez-Amoros et al., 2006). Phenolic compounds, such as phenolic acids, flavonols, flavones, isoflavones, anthocyannins, and condensed tannins, have been identified and characterized in food legumes (Beninger and Hosfield, 2003; Xu et al., 2007a, b). Important biological activities have now been suggested for these bioactive compounds like enhancement of the antioxidant, antimutagenic, anticarcinogenic and anti-hyperglycemic effects, which makes pulses an important crop for human health (Singh and Basu, 2012). Dry beans are widely known for their fiber, mineral and protein contents; however, its nutraceutical value is yet to gain as much attention in the prevention of chronic diseases (Dinelli et al., 2006). Heavy metals are potential environmental contaminants with the capability of causing human health problems if present to excess in the food. They are given special attention throughout the world due to their toxic effects even at very low concentrations (Das, 1990). Several cases of human disease, disorders, malfunction and malformation of organs due to metal toxicity have been reported (Jarup, 2003). Plants have a natural

propensity to take up metals. Some of them like Cu^{2+} , Co^{2+} , Fe^{2+} , Mo^{2+} , Mn^{2+} , and Zn^{2+} are essential plant micronutrients (Baker et al., 1991), while few others like Hg²⁺, Cd²⁺, Ni²⁺ and Pb²⁺ are toxic to plants. However, such toxic effects are even varying from genotype to genotype of the same crop (Liu et al., 2001). The toxic dose depends on the type of ion, ion concentration, plant species, and stage of plant differences by the leafy vegetables are attributed to plant differences in tolerance to heavy metals (Itanna, 2002). Zinc is one of the most important trace elements essential to human, and zinc deficiency is common in most of the legume growing areas of the world. Lead and cadmium are non-essential metals as they are toxic, even in trace (Gençcelep et al., 2009). Food contains many different nutrients that help the body function well. The body cannot produce these nutrients, so they must be obtained from the food we eat. Along with essential nutrients, lentils are good sources of many nonnutrient functional phytochemicals such as phytic acid and tannins (Vidal-Valverde et al., 1994), which are considered among the functional antioxidant ingredients (Scalbert et al., 2005; Vucenik and Shamsuddin, 2006). Soil is a dynamic system which is influenced by various factors, whether natural or anthropic, causing the contamination. Legumes: beans, lentils, soybean Cooking competition. Cowpea, Faba beans, Broad beans are can be eaten while still young, enabling harvesting to begin as early as the middle of spring. Cowpea has found utilization in various ways in traditional and modern food processing in the world. Traditionally in Iraq, cowpeas are consumed as boiled vegetables using fresh Cow pea, bean, faba bean as a snack or soup with tomato, roasted in oil with egg or onion, or processed to make other food products. The nutritional and functional properties of Cow pea flours are comparable to chickpea flour (Sreerama et al., 2012). Due to their favourable flour functionality and their phytochemical-associated health benefits, these flours offer an enormous potential for the production of legume composite flours. Pulses have shown numerous health benefits, e.g. lower glycemic index for people with diabetes, increased satiation and cancer prevention as well as protection against cardiovascular diseases due to their dietary fiber content (Chillo et al., 2008). Legumes in generally can be considered as a therapeutic functional foods due to their significant content of functional proteins and carbohydrates and their extraordinary reserve of secondary metabolites and bioactive constituents that are beneficial for managing and preventing several chronic illnesses in humans (Fratianni et al., 2014). The antioxidant activity of plant polyphenols can retard the development of most major age-related degenerative diseases such as cancers, diabetes, cardiovascular disease, and neurodegenerative diseases (Lee, 2013; Seo et al., 2012). A number of epidemiological studies have correlated the consumption of legumes with high phenolic content to the reduced incidence of diseases such as cancer, ageing, diabetes, and cardiovascular disease (Kris-Etherton et al., 2002). Cholesterol-free legumes in combination with their low sodium content form a good food stuff not only for people living in developing

countries but also for those living in industrialized nations (Sebastiá et al., 2001).

The aim of this study was to evaluate the influence of the grown locality on risky metal intake from the soil to the variety Cowpea seeds.

MATERIAL AND METHODOLOGY

Material

Cowpea samples (Three Varity) at full ripeness were provided from Erbil locality Khabat or (Kalak) in Erbil City

Soil

Soil samples were taken by auger tool, depths 20 cm (A horizon). The soil from the same sites, from which the legume samples were taken with the aim to find out the relations between soil traits in grain. Then the pH of soil was determined, the nutrients contents and the risk elements contents in soil. The contents of available nutrients in the solution were determined by Mehlich II method. Contents of risky heavy metals were determined in different soil extracts (aquaregia; $c = 1 \text{ mol.dm}^{-3}$ NH_4NO_3 ; c = 2 mol.dm⁻³ HNO₃). Atomic absorption spectrometry analysis was finally used. In this work soils were evaluated according to recent legislative norm valid in Slovakia (Law No. 220/2004 as ammended). By this norm, the limit values of risky elements are considered to be critical values of agricultural soil in relationship to the plant and are also harmonized with EU limits. In the soil the exchangeable reaction (pH/KCl), the contents of available nutrients (K, Mg, P) and mobile forms of Ca according Mehlich II., content of humus by Tjurin method and content of N were determined. Pseudototal content of risk metals including all of the forms besides residual metal fraction was assessed in solution of aqua regia and content of mobile forms of selected heavy metals in soil extract by NH_4NO_3 (c = 1 mol.dm⁻³). Gained results were evaluated according Law 220/2004.

For the experiment three cowpea variants were realized. Risky element contents in dry seeds were determined using the atomic absorption spectrometry. The flame AAS (AAS Varian AA Spectra DUO 240 FS/240Z/UltrAA) was used for the determination of heavy metal contents in soil and plant materials. The content of risky elements (Cd, Pb, Cu, Cr, Ni) in Cowpea seeds were evaluated according to Food codex of the Slovak Republic.

RESULTS AND DISCUSSION

The soil is characterized by low supply of humus. The soil reaction was alkaline. Soil reaction has a major effect on the uptake of many risky elements, the most of them become more available to plants as pH decreases. The neutral soil reaction suitable for the legume cultivation.

Currently, contamination of soil in cultivated fields with toxic heavy metals such as cadmium, copper, nickel and zinc has emerged as a new threat to agriculture (Singh et al., 2007). Excessive intake of either copper or zinc has been reported to be toxic (Somer, 1974; Graham and Cordano, 1976). Cadmium is an unnecessary element for both plants and animals and has toxic effects when its concentration has exceeded a limit.

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Table 1 Agrochemical characteristics of the soil in (mg.kg⁻¹) and hums content (%) of the soil surse of different color (variety) of Cowpea.

Area sorse/Variety	pH (H2O)	pH (KCl)	Cox (%)	Humus (%)
1 A/brown	8.48	7.39	0.52	0.89
2A/red	8.76	7.43	0.64	1.01
3A/white	8.58	7.32	0.59	0.98

Note: n = 3 (three samples soil).

Area/Variety	Macroelements	Ca	Mg	K	Р	Ν
1 A/brown		9260.40	385.80	360.55	31.92	603.00
2A/red		8927.20	382.70	379.35	35.49	56.00
3A/white		8644.50	409.50	321.50	38.80	550.00

Note: n = 3 (three samples of soil).

Table 3 Heavy metals content (mg.kg⁻¹) in soils from Iraq (soil extract by *aqua regia*). of different color(variety) of Cowpea.

Area/Variety	Zn	Cu	Со	Ni	Cr	Pb	Cd
1 A/brown	76.20	28.80	22.20	43.00	66.40	17.00	0.62
2A/red	69.80	30.00	21.60	44.20	65.80	18.60	0.70
3A/white	68.60	29.20	20.60	45.70	57.90	18.40	0.64
Limit value*	150	60	15	50	70	70	0.70

Note: *Low No.22/2004, **European Commission (2006) n = 3 (three samples of soil).

Table 4 Risk elements content in mg·kg⁻¹ by NH4NO3 extract ($c = 1 \text{ mol·dm}^{-3}$) in the soil of different color(variety) of Cowpea.

			00	111	Cr	PD	Ca
1 A/brown 0).67 (0.078	0.172	0.265 0	0.027	0.030	0.08
2A/red 0).58 (0.066	0.154	0.237 0	0.023	0.185 (0.066
3A/white 0).74 (0.069	0.144	0.267 0	0.053	0.165 (0.072
critical value*	2	1	_	1.50	_	0.10	0.10

Note: *Low No.22/2004, n = 3 (three samples soil).

Table 5 Nutrients contents (Mehlich II) in cowpea seeds (mg.kg ⁻¹ DM) Kalak (Khabat) locatio

Seeds	K	Na	Ca	Mg	Р	Ν	DM
Brown	19400	87	22400	2480	3834.4	30500	90.90
Red	17920	125	1980	1980	4760.8	34100	90.15
White	18790	108	2128	2530	4390	32200	90.70

Note: n = 3 (three samples of soil).

Table 6. Heavy metal contents ($M \pm S.D.$) in cowpea seeds (mg.kg⁻¹ DM) Kalak (Khabat) location.

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Variant	Cu	Ni	Cr	Pb	Cd
Brown	12.00 ± 0.50	3.5 ± 0.13	1.92 ± 0.60	0.20 ± 0.30	0.09 ± 0.04
Red	14.03 ± 0.80	3.8 ± 0.70	2.10 ± 0.40	0.20 ± 0.20	$0.06\pm\!\!0.01$
White	15.40 ± 0.75	2.04 ± 0.40	1.80 ± 0.04	$0.18\pm\!0.10$	0.09 ± 0.18
Limit **	15.0	3.0	4.0	0.2	0.1

Note: **Food Codex of the Slovak Republic.

Generally, it makes negative effect on their metabolisms by influencing the activity of cellular enzymes (Yang et al., 1986). Cadmium and lead are among the most abundant heavy metals and are particularly toxic. The excessive content of these metals in food is associated with etiology of a number of diseases (WHO, 1992, 1995). Cadmium exposure may cause kidney damage or skeletal damage (WHO, 1992). The soil was only determined Cd content was on the level of limit value given for the soil extract by *aqua regia* as well as Co content was higher than the limit value given for the relationship between soil and plant (Table 3). In soil samples the releasable risk elements contents were also determined in the solution of NH_4NO_3 (c = 1 mol.dm⁻³). All of determined values were lower than critical value (Table 4) only the maximal available soil content of mobile Pb forms was exceeded. In soils with alkali soil reaction these forms are less mobile (soil reaction is one of the factors influencing risk elements toxicity to plants: Heavy metals at supra-optimal concentrations affect the agronomic traits of plants (**Sinha and Gupta, 2005**). Lead is accumulated in the skeleton and cause renal tubular damage and may also give rise to kidney damage (**WHO, 1995**). International Agency for



Figure 1 Location Kalak or (Khabat, خبات) on the Erbil map is no 6.

Research on Cancer (IARC) classified cadmium and lead as human carcinogen (IARC, 1993; Steenland and Boffetta, 2000).

The heavy metals contents in soil did not exceeded the limit values specified by law 531/1994 - 540 (Decision of the Ministry of Agriculture SR). However, from the point of view of risky metal intake by plants, is important content of accessible, respectively potentially mobilizable forms of heavy metal. And from this perspective soil can be described as relatively uncontaminated. Any of the determination of heavy metals content in the soil below the threshold does not guarantee that the plants growing on this soil will always contain their tolerable amounts. It is therefore crucial in terms of hygiene, whether the heavy metals accumulate in parts of plant used for consumption (Zrůst 2003).

The determination of macro- and trace elements in foodstuffs is an important part of nutritional and toxicological analyses. Cadmium and lead are best known for their toxicological properties. Pb and Cd can be accumulated in biological systems becoming potential contaminants along the alimentary chain. Copper, chromium, iron, and zinc in adequate amounts are essential micronutrients for human health. These elements play an important role in human metabolism, and interest in these elements is increasing together with reports of relationships between trace element status and oxidative diseases. On the other hand, e.g. Cu and Zn are essential micronutrients, they can be risk elements when taken in excess. Legumes are known as zinc accumulators (Genccelep et al., 2009). Food Codex of Slovak Republic has set a limit for the maximum levels of chosen risk elements in legumes as shown in Table 6. Limits for contaminants in Slovak food commodities are harmonized with EU limits (Cimboláková and Nováková 2009). The risky elements contents, with the exception of Ni, did not exceed limit for the maximum levels of chosen risk elements in studied Cowpea legume. (Gadd, 1992) and (Giller et al., 1998) postulated that some metals such as

Zn, Cu, Ni and Cr are essential or beneficial micronutrients for plants, animals and microorganisms, whereas others, such as Cd, Hg, and Pb have no known biological and/ or physiological functions. However, all these metals could be toxic at relative low concentrations. Nickel is an essential element for plants, in small quantities, has been reported to improve crop yield and quality (**Brown et al., 1990; Atta-Aly, 1999**). These metals are taken up from soils and bioaccumulated in crops, causing damage to plants when reach high levels and under certain conditions becoming toxic to human and animals fed on these metal enriched plants (**EL-Sokkary and Sharaf, 1996**). Heavy metals at supra-optimal concentrations affect the agronomic traits of plants (**Sinha and Gupta, 2005**).

The determined contents of Cr, Cu and Pb (0.1 mg.kg⁻¹, 0.7 mg.kg⁻¹ and 0.1 mg.kg⁻¹ respectively) by **Hicsonmez et** al., (2012) in fababea seeds lower than those determined in our Cowpea cultivar results only Ni content determined by these authors was similar to that in our samples (3.4 mg.kg⁻¹ DM), On the other hand, Haciseferoğullari et al., (2003) determined higher amounts of Cr, Cu and Pb (11.25 mg.kg⁻¹, 18, mg.kg⁻¹ and 1.5 mg.kg⁻¹ respectively), and a similar Ni content (3.83 mg.kg⁻¹) in comparison to our results. Dalaram et al., (2013) in fresh fababea seeds determined content of Cr, Cu, Pb (1.54 mg.kg⁻¹, 7.5 mg.kg⁻¹ and 5.6 mg.kg⁻¹ respectively) in comparison our results in Cowpea seeds with the result by Dalaram et al., (2013) Cr and Cu content higher but Pb lower. Heavy metal accumulation in plants depends upon plant species, and the efficiency of different plants in absorbing metals is evaluated by either plant uptake or soil-to plant transfer factors of the metals (Rattan et al., 2005).

CONCLUSION

In present study the determined contents of Ni higher than the hygienic limit and content of Cu slightly exceeded the hygienic limit too, the risky elements contents, with the exception of Ni and Cu, did not exceed limit for the

maximum levels of chosen risk elements in studied Cowpea legume. Our results confirmed the low ability to accumulate large amounts of risky metals. The presented results indicate the serious risk heavy metal intake by human organism due the consumption of foodstuffs based on Cowpea. It is permanently necessary to monitor the content of risky heavy metals if it is content a high amount and to apply measures for the minimization of risky metal input into the human food chain. Heavy metal accumulation in plants depends upon plant species, and the efficiency of different plants in absorbing metals is evaluated by either plant uptake or soil to plant transfer factors of the metal. Some metals like Fe, Se, Mn, Co, Zn, Mo and Ni, are essential micronutrient for most of the redox reactions which are fundamental for cellular functions. Some famous and traditional Iraqi foods have some bioactive components related with health benefits, such as polyphenols, lectins, and carbohydrates. Adequate consumption of the foods with high functional content can result in improved health thereby reducing diseases.

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