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Trace elements in Libyan Cereals: Estimation of Daily Intakes of Cobalt, Chromium, Molybdenum and Selenium

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Abstract: *Elements such as cobalt (Co), chromium (Cr), molybdenum (Mo) and selenium (Se) are essential elements for human being, these elements occur in cereals which are important food in Libyan population diet. The present study was carried out to determine concentrations of trace metals and evaluate the potential health risk of metal to humans via consumption of cereals. Cereal samples from Libya were digested using nitric acid and by microwave digester then trace elements concentrations in cereal samples were determined by using ICP-MS instrument. Daily intakes of Co, Cr, Mo and Se from all cereals consumption were 19.4, 93, 261 and 34.7 µg/day, respectively. The RDA was used to estimate daily intakes of these elements. Daily intake of Mo exceeded of RDA by 2 fold. More investigations should be done for daily intake of trace elements in Libyan population for cereals and other food consumption.*
Keywords: *Libya, cereals, trace elements, ICP-MS, daily intakes*

I. Introduction

Cobalt, chromium, molybdenum and selenium are essential elements for human being. These days determination of trace elements in food becomes very important to estimate human intake of these elements which illustrates both deficiencies and toxicity for humans.

Cobalt is an integral component of the vitamin B-12 molecule. It is required in the creation of red blood cells and in preventing anaemia. However, an excessive intake of cobalt may cause the overproduction of red blood cells [1]. Chromium (III) occurs naturally in environment and it is essential nutrient required by the human body functions such as sugar and fat metabolism [2]. It is effective to the management of diabetes and it is a cofactor with insulin, Cr(III) and its compounds are not considered a health hazard [3]. While the toxicity and carcinogenic properties of Cr(VI) have been reported for long time exposure.

Molybdenum participated as a cofactor for a limited number of enzymes in humans and in all mammalian molybdoenzymes, functional Mo is present as an organic component called molybdopterin [4]. It is found in many different in food including cereals, however, little is known about the bioavailability of Mo from different food sources, but one study among men and another among women demonstrated that it is less efficiently absorbed from soy, which contains relatively high amounts [5]. Information on dietary intake of Mo is limited because of lack of a simple, reliable analytical method for determining Mo. One U.S. study reported intakes ranging from 120 to 240 µg/day, with an average intake of 180 µg/day [6]. Data from the Total Diet Study indicate an average molybdenum intake of 76 µg/day for women and 109 µg/day for men [7]. Furthermore, the minimum requirement of Mo was estimated to be 25 µg/day, approximately [8].

Selenium is an essential element that has many functions in the human body. It has been reported that Se has preventive potency against Keshan disease and has important antioxidant activities [8-10]. It has been suggested that Se protects the body against As toxicity [11,12] and can have a positive role in the immune system functions [13]. The Recommended Dietary Allowance (RDA) for Se has been estimated to be 55 and 70 µg/day for women and men respectively (dependent upon average body weight) [14]. It is known that selenium levels range from low to high levels in different foods, such as Brazil nuts, cucumber, grain, mushroom, shellfish and wheat [15]**.** In addition, it has been recognised that selenium plays a role in the decrease of arsenic toxicity owing to the two elements behaving as metabolic antipodes [16]. In Chine, deficiency of selenium was initially established, with the disease believed to be instigated through low Se levels in soil in Keshan (China). Accordingly, there was a low intake of Se, sometimes lower than10 µgSe/day [17]. Moreover, toxicity of Se is also linked with thyroid hormones syntheses. A Libya study has estimated daily intake of Se in food [18].

Many techniques are used to measure trace elements, however, these days ICP-MS is widely used to determine trace elements in environmental samples because it has high precision compared with many other techniques [19]. The objectives of the present work are to determine Co, Cr, Mo, and Se in Libyan cereal using microwave digestion method and ICP-MS technique for measurement. The daily intakes of these elements are estimated in the current study.

II. Materials and methods

2.1. Sample collection

Five types of cereals which are widely consumed in Libya were analysed. Cereals including wheat, Barley, rice and corn, were purchased from Libya during the months of August 2009 and June 2010. The products analysed in this study were mainly of Libyan origin except rice. Cereals samples were treated before digestion, ground using a coffee grinder and then kept for analysis.

2.2. Sample digestion

Cereals samples were digested using a microwave digester. A dry ground weight (0.3 - 0.5 g) of sample was mixed with 4 ml of 70% nitric acid (HNO_3) (Romil-UpA™, Romil Ltd., Cambridge, UK) and 2 ml of hydrogen peroxide (H_2O_2) and then microwave digested for 40 minutes at a total pressure of 20 bars and a maximum temperature of 170°C (CEM, Microwave digestion MAR *X*press, Matthews, NC, USA). The digested solutions were evaporated to dryness and then diluted to 25 ml in volumetric flasks with ultra-pure water (Romil-UpS™, Romil Ltd., Cambridge, UK) prior to analysis.

2.3. Determination of toxic elements concentrations

Concentrations of trace elements (Co, Cr, Mo and Se) in the digested samples were determined by inductively coupled plasma mass spectrometry (ICP-MS). A Thermo-Fisher Scientific X-SeriesII instrument equipped with CCTED (collision cell technology with energy discrimination).

2.4. Quality control and standard reference material

In this study, all the sample masses were measured to an accuracy of ± 0.1 mg. Elemental concentrations obtained by the ICP-MS technique were evaluated using certified reference materials and were found to be in good agreement with the certified values. The analytical procedure and the reliability of the digestion process of the samples were validated by analysis of different types of standard reference materials (see Table 1). The average recoveries of references material ranged from 84 to 103% for all measurement runs.

Table 1: Rice flour (NIES No. 10-b) SRM, concentrations of elements (µg/kg)

Element	Certified value	Found value	Recovery %
Co	20	19.2	96
Cr	220	184.5	84
Mo	420 ± 50	435 ± 38	103
Se	20	18	90

III. Results and Discussion

Results of measurement of Cr, Co, Mo and Se elements in different Libyan cereals are presented as a mean ± SD (µg/kg) in figures (1-4). Cereal species covered in this investigation are wheat, rice, barley and corn. The highest concentrations of Cr and Mo were found in wheat (601 and 2309 µg/kg), respectively. However, the mean concentrations of Cr and Mo in cereals (µg/kg) were wheat (174, 366) barley (254, 913) and rice (50, 955), respectively. For wheat grain, the mean concentrations (±SD) were 38 ± 17 µg/kg of Co, 174 ± 144 µg/kg of Cr, 366 ± 91 µg/kg of Mo and 62 ± 41 mg/kg of Se (figures 1-4).

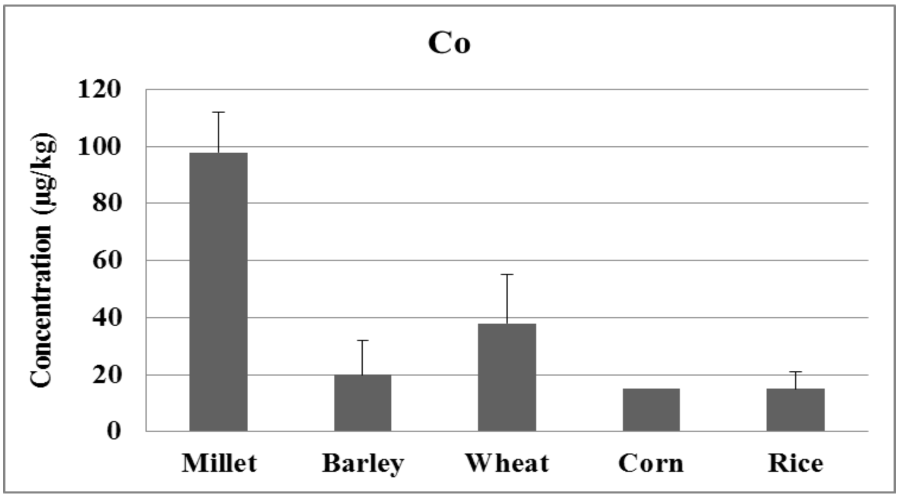

Figure 1: Concentrations (µg/kg) of cobalt in Libyan Cereals (as mean and SD).

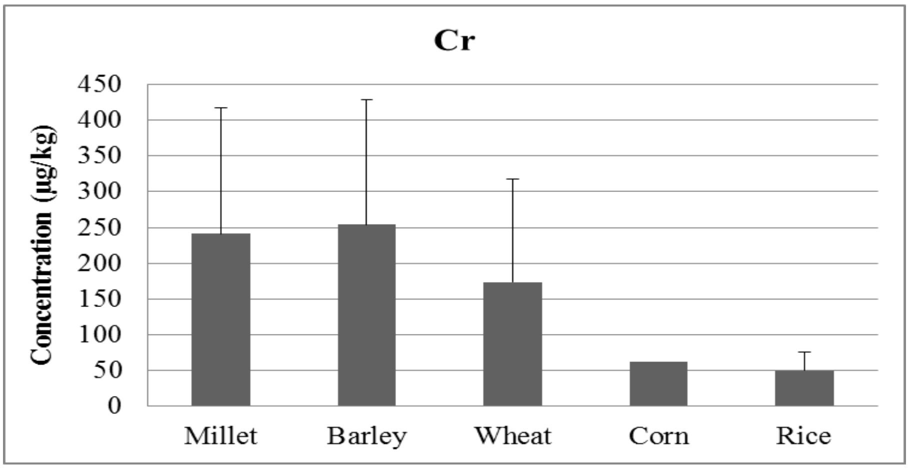

Figure 2: Concentrations (µg/kg) of chromium in Libyan Cereals (as mean and SD).

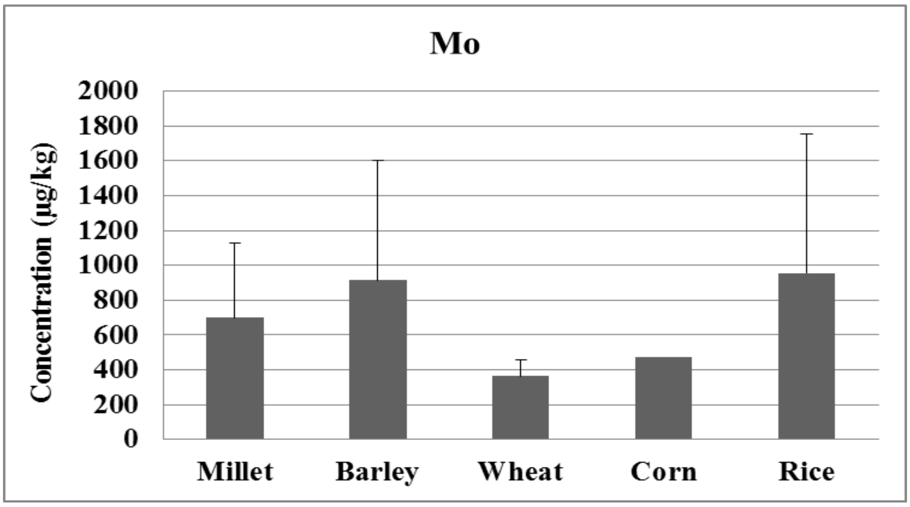

Figure 3: Concentrations (µg/kg) of Molybdenum in Libyan Cereals (as mean and SD).

On other hands the lowest concentrations of Co and Se elements among cereals were detected in rice grain (figures 1 and 4). Barley is another cereal that consume from Libyan population, with the mean concentrations of Co, Cr, Mo and Se (±SD) were 20 ± 12 µg/kg, 254 ± 174 µg/kg, 913 ± 688 µg\kg and 87 ± 36 µg/kg, respectively (figures 1-4).

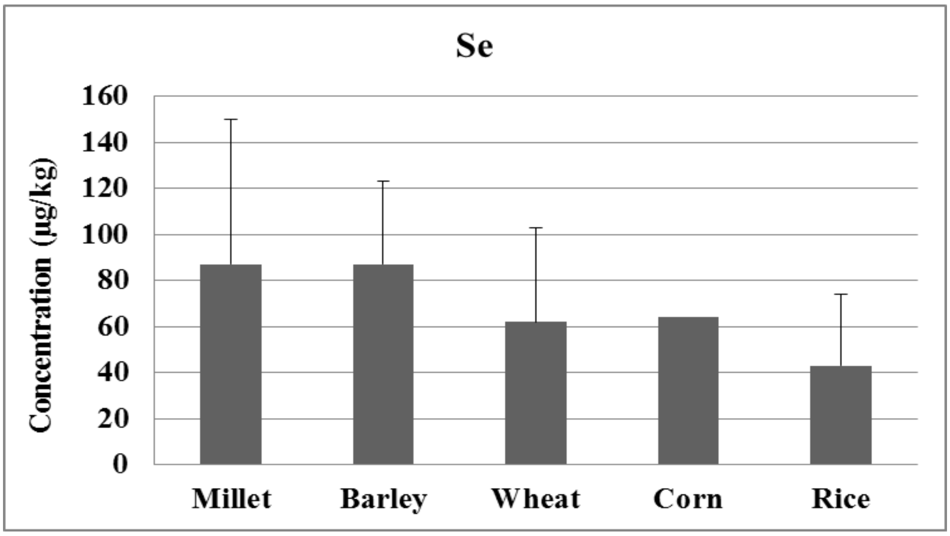

Figure 4: Concentrations (µg/kg) of selenium in Libyan Cereals (as mean and SD).

Table 2 shows that daily intake (DIs) of Cr, Co, Mo, and Se elements (mean concentrations of elements were used). Generally, consumption of wheat can result in high daily intakes of these elements compared to consumption for someone consuming 486 g of wheat (the weight quantity was adapted from FAOSTAT) [20]. The daily intakes of wheat were (Cr 81.45 µg/day), (Co 17 .79 µg/day), (Mo 171.32 µg/day) and (Se 29.02 µg/day), however, intakes of these elements in Libya population consumption of 60.3g of rice per day can reach the daily intakes of Mo to be (57.59 µg/day) and Cr (3.02 µg/day). Otherwise, daily intakes of Se and Co were 2.59 and 0.9 µg/day, respectively (table 2).

Table 2: Daily intake [a] (µg/day) in cereals for Libyan population.

Elements	Wheat (n=4) (468g/capita/day)[b]	Barley (n=6) (33.6g/capita/day)	Rice (n=4) (60.3g/capita/day)	Corn (n=1) (2.8g/capita/day)	All cereals
Co	17.79	0.67	0.90	0.04	19.41
Cr	81.45	8.53	3.02	0.18	93.18
Mo	171.32	30.68	57.59	1.33	260.9
Se	29.02	2.92	2.59	0.18	34.72

[a] the total mean concentrations were used to calculate daily intake. [b]Food supply quantity (g/capita/day) was adapted from FAOSTAT [20].

In barley grain, daily intakes of Mo was (30.68 µg/day) and Cr (8.53 µg/day), however daily intakes of Co and Se were 0.67 and 2.92 µg/day, respectively (Table 2). Corn grain has the lowest daily intakes of trace elements because it has low consumption by Libyan population (2.8 g/day). Wheat can be the major source of daily intakes of Cr, Co, Mo, Se and other; however, rice can be the second cereal source of these elements.

The Recommended Daily Allowance (RDA) scale was used in the current study (see Table 3). From RDA estimation, Mo intake from wheat was exceeded the RDA by 2 fold (228.4 %), this may demonstrate that Libyan population consume high content of Mo. Rice also can provided a high quantity of Mo by consume just 60.3 g of rice per day, RDA of rice consumption was estimated to be 76.8% for Mo. Particularly, the total RDA of Mo by cereals consumption in this study was 347.9% (3.5 fold). Concentration of selenium in wheat showed high intake with RDA (83%), however, Cr was providing 67.9% of RDA form wheat consumption. On the other hands, the PMTDI scale was used for estimating daily intakes of Co from cereals consumption, 59.3% was estimated from only wheat consumption, while for all type of cereals the PMTDI was 64.7%. High intake of wheat is clearly a major factor for elevated exposure to Mo and Co in Libyan population. Our results showed that wheat and rice were the mean source of Co, Cr, Mo, and Se elements in Libya compared with other cereals. Cereals are a staple food for Libyan population and it can be the main source of micronutrients for them. The present study focused on concentration of Co, Cr, Mo and Se in Libyan wheat and barley originating mainly from Libyan and the others rice and corn which are imported from outside.

Table 3: The RDA% of Libyan cereals [a]

Cereals	Co[b]	Cr	Mo	Se
Wheat	59.30	67.88	**228.43**	82.91
Barley	2.23	7.11	40.91	8.34
Rice	3.00	2.52	76.79	7.40
Corn	0.13	0.15	1.77	0.51
All cereals	64.66	77.65	**347.89**	99.17

[a] the RDA: The Recommended Daily Allowance [21]. [b] the PMTDI was used: The Provisional Maximum Tolerable Daily Intake, assuming the body weight for adult is 70kg [22].

Very little information is available in the literature about the trace elements content of Libyan cereals. The literature review reveals that these are a gap in knowledge on the essential elements in Libyan cereal. Therefore, this study tried to fill this gap by determination of trace elements. Some studies from other countries have been reported concentration of trace elements including Co, Cr, Mo and Se elements in cereals and some of them have estimated total daily intake of trace elements for foods including cereal [23-25]. Selected cereals including wheat and barley from Ethiopia were investigated [23]. Concentration of Cr, and Co in Ethiopia study were 290 and 140 µg/kg for barley and 430 and 350 µg/kg for wheat, respectively [23]. Compared to our results, the level of elements in Ethiopian study higher than that in the present study (figures 1-4). In Indian study Co levels in both wheat and barley were measured [24]. Concentrations of Co in Indian cereals were (mean ± SD) 20 ± 10 and 18 ± 5 for wheat and barley, respectively. These data were very similar to our results for Co content in both wheat and barley. Latvia study has reported Cr content in wheat and barley [25], Cr content was ranged in wheat 53-295 µg/kg; however, in barley was 21-921 µg/kg. These data was also similar to that obtained from the present study.

El-Ghawi et. al. (2005) has reported that daily intake of Se in Libyan population for all food ranged between 13 to 44 µg/day [18]. However, here in the current study, the data showed daily intake of Se from cereal consumption can be exposed 34 µg/day. El-Ghawi et. al. study [18] appearance that Libyan population has Se deficiency. From our study we can say more investigations should be done to have good view of Se situation in Libyan population.

From our study, Mo content was higher than RDA by 2 fold. However, the daily intake in the present study exposed that consumption of Libyan cereal does not reach to the risk. Daily intakes of trace elements from consuming cereal in Libya were less than the PMTDI of these elements and no risk was detected from the present study. We concluded that Libyan population dose not expose to high levels of trace elements from cereals consumption however more study should be done for total daily intake of trace elements from consumption of different types of foods and to have complete sight of Libyan situation, also and assess the risk of these trace elements among the Libyan population.

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