IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)
e-ISSN: 2319-2402,p- ISSN: 2319-2399.Volume 10, Issue 10 Ver. III (Oct. 2016), PP 51-55
www.iosrjournals.org

Determination of Toxic Elements in Libyan Cereals using Inductively Coupled Plasma Mass Spectrometry

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Abstract: *Cereals are staple food for a large number of people in Libya. In the current study, cereals including wheat, rice and barley were digested using microwave digestion method. We report here on total intake of As, Cd, Pb and U in Libyan population, based on inductively coupled plasma mass spectrometric (ICP-MS) analysis of Libyan cereals. In this study, the Provisional Maximum Tolerable Daily Intake (PMTDI) which estimates the maximum daily intake of a toxic element from individual food or more than one types of food was used. Wheat and rice were the main cereal sources of dietary As and Pb for Libyans. Daily intakes of arsenic (19.85 µg/day), cadmium (7.57 µg/day), lead (34.47 µg/day) and uranium (0.84 µg/day) in the Libyan cereals were calculated. The levels of toxic elements determined in the analysed cereal samples were found to be below the PMTDI; hence, the concentration of these toxic elements in the selected cereals analysed, may not presently pose a health hazard in the population and can as well serve as good and reliable sources of essential trace metals to the human population. This requires further investigation and detailed dietary and human biomonitoring studies on the Libyan population should be conducted.*
Keywords: *Libya, cereals, toxic elements, ICP-MS, daily intakes*

I. Introduction

Trace elements are potential environmental contaminations with the capability of causing human health problems if present to excess in the food chain. They are given special attention throughout the world duo to their toxic effects even at very low concentrations. Cereal and cereal production are essential foodstuffs for human diet. Cereals are the major staple food, contributing most of the human daily calorie and minerals intake in many cultures [1]. Cereal grains have been a primary source of nourishment for humans for thousands of years [2]. Many studies have been reported levels of trace elements in cereals [3-7]. However, other studies pointed out cereal contaminated with different levels of trace elements [8-9]. Heavy metals toxicity can affect mental development and central nervous system functions alter the blood compositic and disturb the function of organs like kidneys lungs and liver [10]. Cadmium (Cd) is one of the most toxic elements in world and human exposure can result in the development of various diseases, Cd can accumulate in the body with a half-life 10 to 30 years [11]. Lead (Pb) and Cd are highly toxic elements, which are quickly absorbed from the alimentary trace. Afterwards, they easily pass through biological barriers and accumulation in internal organs. Even small amounts of Pb and Cd may cause metabolic disorders [12]. Arsenic (As) is a naturally occurring element present in water, soils, and rock. Inorganic As species more toxic than organic As species [13]. The toxic effects of As are well documented and our previous study demonstrated that a correlation exists between rice; which is content high quantities of As; consumption and exposure to As [14]. Uranium (U) is a toxic radioactivity element, and its determination is a great importance. Unlike many other radioactive elements, its half-life is commensurate with the age of the earth and, because of this, small amounts of uranium are found almost everywhere in the soil, rocks and water [15]. Uranium exists normally in the environment as aqueous uranyl ion (UO_2^{+2}) [16]. Uranium can exist to food chain from soil and contaminated irrigating water.

Cereals; especially wheat; are major sources in Libyan diet; they eat wheat from different types of food including bread, cakes and wheat derivatives. Measurement of toxic elements in Libyan cereals become more important these days, because there is a lack of studies in this area, and more investigation should be done for collecting more information and data base about Libyan diet. Many techniques are used to determine toxic elements, however, these days ICP-MS is widely used to determine trace elements in environmental samples including soil, water, biological samples, and it has high precision compared with many other techniques [17]. In the current study ICP-MS technique was used to measure the quantities of As, Cd, Pb and U elements in Libyan cereals.

The aim of the current study to investigate As, Cd , Pb and U concentrations in Libyan cereals and to estimate the daily intakes of these elements. Also the PMTDIs of toxic elements in cereals were calculated in this study.

II. Materials and methods

1.1 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, which is exported from different countries. Cereals samples were treated before digestion, ground using a coffee grinder and then kept for analysis.

1.2 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.

1.3 Determination of toxic elements concentrations

Concentrations of toxic elements (As, Cd, Pb and U) 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). The instrument parameters used were as follows: forward power (1,404W); hexa-pole bias (-18.0V); pole bias (-14.0V); reaction cell gas flow rate (4ml/min); nebuliser (carrier gas) flow rate (0.82 L/min); extraction lens (-129.4V); quadru-pole dwell times (20 ms). External calibration standards for elements were prepared in the range 0 – 100 µg/L. Samples were introduced *via* a covered autosampler (CetacASX-520) through a concentric glass venture nebuliser (ThermoFisher Scientific Inc., Waltham, MA, USA).

1.4 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 87 to 105% for all measurement runs.

1.5 Estimation of risk assessments of toxic elements

In this study, the Provisional Maximum Tolerable Daily Intake (PMTDI) which estimates the maximum daily intake of a toxic element from individual cereal or more than one types of cereal and the unit that is used for this scale is µg of element per day. The PMTDIs of toxic elements in cereals defined by Joint FAO/WHO Expert Committee on Food Additives (JECFA) (FSA, 2009) [18], However, for lead PMTDI was taken from EFSA (EFSA, 2010) [19]. The average adult body weight was assumed to be 70 kg for Libyan population.

Table 1: ICP-MS determined As, Cd, Pb and U concentrations (µg/kg±SD) in SRMs.

Reference material	Element	Certified value	Found value
Rice flour (NIES No. 10-b)	As	0.110	0.103
	Cd	0.320 ± 0.02	0.331 ± 0.04
Seaweed (NIES No. 9)	As	115 ± 9	105 ± 12
	Cd	0.150 ± 0.02	0.164 ± 0.05
	Pb	1.35 ± 0.05	1.45 ± 0.07
Typical Japanese diet (NIES No.27)	As	0.60 ± 0.04	0.28 ± 0.07
	Cd	0.069 ± 0.009	0.072 ± 0.01
	Pb	0.62	0.596
	U	0.0029 ± 0.0004	0.0025 ± 0.0007

NIES: National Institute for Environmental Studies

III. Results and Discussion

Very little information is available in the literature about the toxic element contents of Libyan cereals. Results of toxic elements in Libyan cereals (which are the staple food of Libyan population) are presented in Figures (1-4). These results showed a variation in the concentration of toxic elements investigated in all samples. Figures have shown that rice has the highest concentrations of As (155 µg/kg) and Pb (233 µg/kg) over other cereals analysed.

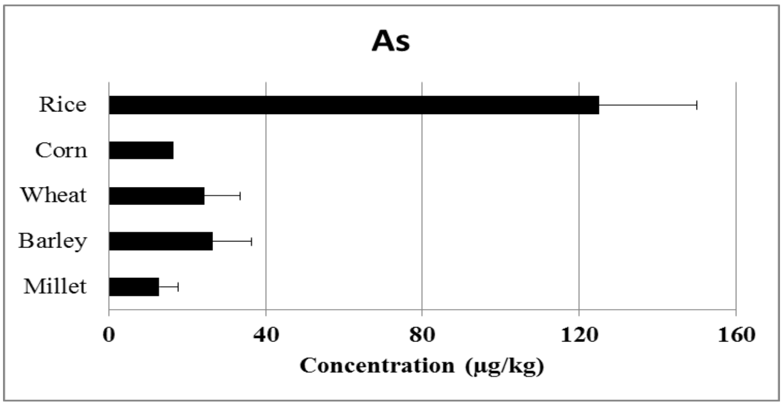

Figure1: Concentrations (µg/kg) of arsenic in Libyan Cereals (as mean and standard divisions).

For wheat grains, the mean concentrations of As, Cd, Pb and U (± SD) were 34.3 ± 9.3 µg/kg, 12.5 ± 3.3 µg/kg, 58 ± 45 µg/kg and 1.5 ± 1.2 µg/kg, respectively (Fig. 1 - 4). On the other hands, the lowest levels of As, Cd and U elements among cereals were detected in corn grain (Fig. 1, 2, 4). The mean concentrations of these elements were 16.4, 2.8 and 1.14 µg/kg for As, Cd and U in corn grain, respectively (Fig. 1, 2, 4). However, Pb level in corn grain was 105 µg/kg (Fig. 3). Millet grains has high concentrations of Cd and U compared with other cereals, mean concentrations were 33.6 and 2.42 µg/kg for Cd and U, respectively (Fig. 2, 4). Barley is another cereal that consume from Libyan population, the mean concentrations of As, Cd, Pb and U (± SD) were 26.5 ± 9.9 µg/kg, 5.6 ± 2.8 µg/kg, 50.8 ± 9.3 µg/kg and 1.94 ± 0.55 µg/kg, respectively (Fig. 1 - 4).

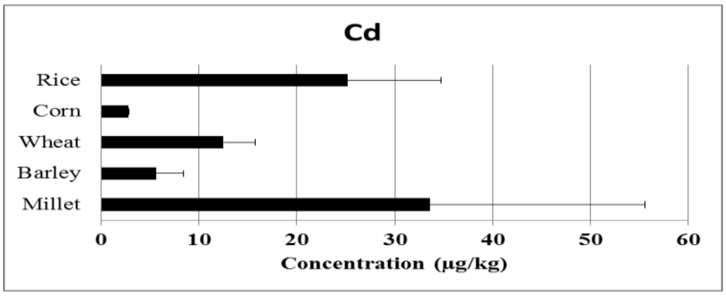

Figure 2: Concentrations (µg/kg) of cadmium in Libyan Cereals (as mean and standard divisions).

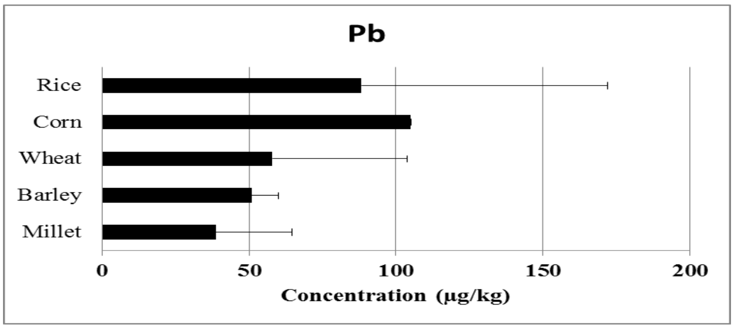

Figure 3: Concentrations (µg/kg) of lead in Libyan Cereals (as mean and standard divisions).

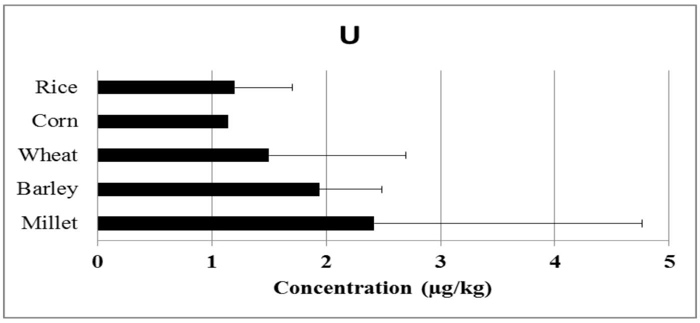

Figure 4: Concentrations (µg/kg) of uranium in Libyan Cereals (as mean and standard divisions).

Table 2 shows the daily intakes (DIs) of As, Cd, Pb and U elements (mean concentrations of elements were used). Generally, consumption of wheat can result in high daily intakes of As, Cd, Pb and Zn compared to consumption of other cereals. Wheat has the highest arsenic intake (11.37 µg/day) for someone consuming 468 g of wheat (this quantity was adapted from FAOSTAT) [20], however, daily intakes of Cd (5.85 µg/day), Pb (27.15 µg/day) and U (0.70 µg/day) (table 2). Rice also can be another high source of intake of As and Pb of Libyan population. Consumption of 60.3g of rice per day can reach the daily intake of arsenic to be (7.54 µg/day) and Pb (5.32 µg/day), otherwise, daily intake of Cd and U were 1.52 and 0.07 µg/day respectively (table 2).

Table 2: Daily intake (µg/day) in cereals for Libyan Population.

Elements	Wheat (n=4) (468g/capita/day)*	Barley (n=6) (33.6g/capita/day)	Rice (n=4) (60.3g/capita/day)	Corn (n=1) (2.8g/capita/day)	All cereals
As	11.37	0.89	7.54	0.05	19.85
Cd	5.85	0.19	1.52	0.01	7.57
Pb	27.15	1.71	5.32	0.29	34.47
U	0.70	0.07	0.07	0.001	0.84

* Food supply quantity (g/capita/day) for period from 1997 to 2007 was adapted from FAOSTAT [20].

Corn grain was the lowest daily intake of toxic elements, because it is low consumption by Libyan population (2.8g/day). Barley has low daily intakes of toxic elements as well compared with wheat and rice (table 2).

Wheat and rice can be major sources of dietary intake of As and Pb. As already mentioned, average daily intake of wheat (468g of wheat/day, FAOSTAT) can provide an estimated As and Pb intake of 11.37µg/day (7.74% of PMTDI) and 27.15 µg/day (10.77% of PMTDI), respectively (table 2 and 3). Mean concentrations of As and Pb content in Libyan wheat measured in the current study were 24.3 and 58 µg/kg, respectively (Fig. 1 and 3). However, average daily intake of rice (60.3g of rice/day, FAOSTAT) can provide an estimated As and Pb intake of 7.54 µg/day (5.13% of PMTDI) and 5.32 µg/day (2.11% of PMTDI), respectively (table 2 and 3). High intake of wheat and rice is clearly a major factor for the elevated exposure to As and Pb in the Libyan population. From the results, it is clear that wheat is the main source of cadmium and uranium in Libyan population compared with other cereals.

Table 3: The PMTDIs of Libyan cereals[a]

Cereals	As[b]	Cd	Pb	U
Wheat	7.74	8.36	10.77	3.58
Barley	0.61	0.27	0.68	0.33
Rice	5.13	2.17	2.11	0.37
Corn	0.03	0.01	0.12	0.02
All cereals	13.50	10.81	13.68	4.30

[a] the PMTDI: The Provisional Maximum Tolerable Daily Intake, assuming the body weight for adult is 70kg. PMTDIs of toxic elements in cereals defined by Joint FAO/WHO Expert Committee on Food Additives (JECFA) (FSA, 2009) [18], however, for lead EFSA, (EFSA, 2010) [19]. [b] total mean concentrations were used to calculate daily intake (assuming 100% of the total arsenic is present as inorganic arsenic.

Some studies have been reported concentrations of trace elements including toxic elements including Cd and Pb elements in cereals [8-9]. Latvia study reported that the mean concentrations of Cd and Pb were detected in barley and wheat, concentrations were Cd (9.5 µg/kg) and Pb (23 µg/kg) for barley, however, Cd (23.1-30.6 µg/kg) and Pb (21.8-34.6 µg/kg) for wheat, respectively [9]. Compared to these, mean concentrations of Cd in the current study are lower, however, Pb are higher for both barley and wheat. On the other hand, Bangladeshi study reported the mean concentrations of As, Cd and Pb were detected in rice and wheat, concentrations were As (321 µg/kg), Cd (88 µg/kg) and Pb (713 µg/kg) for rice, however, As (281 µg/kg), Cd (11 µg/kg) and Pb (221 µg/kg) for wheat, respectively [8]. Also compared to the Bangladeshi study, mean concentrations of As, Pb in the current study are very lower for both rice and wheat, however, Cd is similar for wheat. Bangladesh is very well known as a arsenic contaminated country, and these results are expected data from Bangladesh. Results from our study showed that cereals grown in Libya are not contaminated and the levels of toxic elements are similar to Latvia study but very low compare with Bangladeshi study.

Markedly, daily intake study in our paper revealed that consumption of Libyan cereals does not reach to the risk. Daily intakes of toxic elements from consuming cereals in Libya were less than the PMTDI of these elements, and no risk was detected from the present study. We concluded that Libyan population may not expose to high levels of toxic elements from cereals consumption, however, more study should be done for total daily intakes of toxic elements from consumption of different types of foods and to have complete sight of Libyan situation, also and to assess the risk of these elements amongst Libyan population.

Acknowledgment

I would like to thank research staff at De Montfort University, and I would like to thank Dr. Scott Young (Nottingham University) for his help with ICP-MS analysis.

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