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Determination of Heavy Metal Contents of Some Over the Counter Staple Food Items

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The contents of some heavy metals *i.e.* iron, copper, chromium, lead, cadmium and cobalt were determined in some over the counter food items by atomic absorption spectroscopy. Pulses, rice, wheat and their processed products contribute to a major portion of daily food intake by a very large segment of population of Pakistan. There was variation in metal contents in the same kind of variety purchased from different food stores which can be attributed to the soil conditions, water sources, manure and pesticides and processes used. The concentration of Fe(II) ranged from 78-118 mg kg^{-1} on dry weight basis, where as that of Cu(II) ranged from 9.0-21.5 mg kg^{-1}. The concentration level of Cr(III) was from 115.0-368.0 mg kg^{-1}. While concentration of Co(II) and Cd(II) and Pb(II) varied slightly from sample to sample and ranged between 11.5-15.0 mg kg^{-1}, 0.5-2.0 mg kg^{-1} and 1.1-1.5 mg kg^{-1}, respectively. Daily intake limits were calculated and compared with MRL (minimum risk level) values given by ATSDR (2001). Results showed that the concentrations of Cr(III) and Pb(II) of all samples under study were much higher than those of MRL values. Thus intake of these food items in excessive amounts can cause accumulation of these hazardous metals in the body and pose a great health risk.

Key Words: Heavy metals, Spices, Atomic absorption spectroscopy.

INTRODUCTION

Trace metals composition of foods is of interest because of their essential or toxic nature[1]. The accumulation of heavy metals can have middle-term and long term health risks and strict periodic surveillance of these contaminants is therefore advisable[2]. Micronutrients constitute a small fraction of the entire diet but play important roles in different metabolic processes[3].

Food composition data is important in nutritional planning and provides data for epidemiological studies[4]. Environmental pollution is the main cause of heavy metal contamination in food chain. The trace metal contents of individual foods varies and is dependent upon the trace metals introduced in the growing, transport, processing and fortification of food[5]. The other technological processes used to bring the food to the consumer can significantly increase the total trace metal contents of the food[6,7].

Staple food: According to Wikipedia a staple food is a food that can be stored for use throughout the year and forms the basis of a traditional diet. Staple foods vary from place to place, but are typically inexpensive starchy foods of vegetable origin that are high in food energy (calories) and carbohydrate. Most staple foods derive either from cereals such as wheat, barley, rye, maize, or rice or starchy root vegetables such as potatoes, yams, taro and cassava. Other staple foods include pulses (dried legumes), sago (derived from the pith of the sago palm tree) and fruits such as bread fruit and plantains[8].

Pulses: Pulses (dried grains) are a rich source of proteins. These form an essential part of the vegetarian diet of the people of Pakistan. They are cultivated on 5 % of the total cropped area. Their use ranges from baby food to delicacies of the rich and the poor. Because of the population growth, demand for pulses is increasing day by day. Natural pulses have been reported to contain significant quantities of some trace metals. These trace metals in pulses play vital role as structural and functional components of metallo-proteins and enzymes in living cells[9]. Use of pulses contaminated with trace and heavy metals, may result in accumulation of these metals in human organs. Subjecting to trace and heavy metals above the permissible limits can affect the human health and may result in ill effects on human fetus, abortion, preterm labor and mental retardation to children. Adults also may experience high blood pressure, fatigue and kidney and brain damages.

Wheat: Wheat (*Triticum aestivum*) is the staple food crop of the Pakistani nation, supplying 72 % of energy and protein in the average daily diet. Wheat provides more nourishment than any other food grains. Per capita wheat consumption in Pakistan is around 120 kg/year which is highest in the world[10].

There is little information available about the safety of crops and staple food obtained from them with respect to heavy metal contamination. Wheat rice and pulses are major source of staple food in Pakistan. Due to the use of enormous amount of staple food daily, it is important to know the toxic metal contents in them. The objective of the present research work is to determine the levels of some heavy metals contents (lead, cadmium, cobalt, iron, copper and chromium) in 17 items forming a major part of staple food in Pakistan and to compare these levels with MRL (minimum risk level) values given by ATSDR (2001) so as to create awareness about high levels of toxic metals consumed daily and to provide a basis for future mitigation options.

EXPERIMENTAL

Sample collection and processing: Various pulses including Bengal gram, black gram, black eyed beans, chickpeas (brown), chickpeas (white), green gram, red kidney beans, split red gram, rice, split Bengal gram, split black gram, split green gram, red lentil, semolina, wheat flour and gram flour were purchased from different markets of different areas in Lahore. These pulses and their products constituted the major part of total food intake of people of Pakistan. A total of 51 samples were collected (three of each type) and analyzed by FAAS (Hitachi Z-5000). Acids were analytical grade (Merck) and metal contents given on the label were calculated in the amounts used for digestion and corrections made by subtraction. The method used for AA analysis was wet process.

Sample preparation: Staple food items (17) were bought each from markets of 5 different areas of Lahore (for statistical calculations). The samples were carefully opened and dried to constant weight. Samples (1 g each) were digested with 20 mL of 2:1 $HNO_3/HClO_4$ (Anal. grade) and heated until evolution of white fumes. Where necessary more acid mixture was added and the sample digested until evolution of white fumes marking the end of the digestion process. The digests were filtered into standard 50 mL volumetric flask and made up to mark with distilled water. This was subsequently analyzed for Pb, Cd, Cu, Cr, Co and Fe by air-acetylene flame atomic absorption spectrometry (Hitachi Z-5000) by the standard calibration technique. The instrumental parameters used by FFAAS (Hitachi Z-500) are given in Table-1. Calibration standards were prepared by dilution of the high purity commercial metal standards (applichem) for atomic absorption analysis. Adequate quality assurance measures were carried out to ensure reliability of results. Glassware was properly cleaned and reagents (HNO_3, $HClO_4$ and distilled water) were of analytical grade. Spikes and blanks were also introduced. Each sample was analyzed three times and average results were reported. The daily intake (mg kg^{-1} day^{-1}) was calculated taking average body weight 50 kg and daily intake of all 17 items combined equal to 300 g.

The daily intake (mg $kg^{-1}day^{-1}$)

$$= \text{metal concentration in food items} \times 20/1000/50 \quad (1)$$

TABLE-1
MULTIPLE METAL CORRELATION COEFFICIENT MATRIXES FOR VARIOUS METALS IN STAPLE FOOD ITEM SAMPLES

	Fe	Cu	Cr	Co	Cd	Pb
Fe	1.0	0.023	0.026	0.349	0.0088	0.0564
Cu		1.000	0.1187	0.0406	0.0475	0.0014
Cr			1.0000	0.0294	0.0048	0.1603
Co				1.0000	0.0804	0.0845
Cd					1.0000	0.2181
Pb						1.0000

RESULTS AND DISCUSSION

Samples (17 × 5) were analyzed for iron, copper, chromium, cobalt, cadmium and lead by AAS. Of the total samples analyzed all the six metals were detected in each sample Iron was present in highest amounts followed by Cr(III) and Pb(II). Metal to metal correlation showed that no elements were strongly correlated in staple food samples (Table-2). Some correlation was found between Co(II) and Fe(II), Pb(II) and Cd(II), Pb(II) and Cr(III).

TABLE-2
INSTRUMENTAL PARAMETERS USED BY FAAS (HITACHI Z - 5000)

Metal	Wavelength (nm)	Slit width (nm)	Air: acetylene (L min^{-1})	Upper measurable limit (mgL^{-1})
Fe	248.3	0.2	2.0	20
Cu	324.8	1.3	2.2	30
Cr	359.3	1.3	2.8	100
Co	240.7	0.2	2.2	10
Cd	228.8	1.3	2.0	6
Pb	283.3	1.3	2.2	200

Iron: Fe(II) is an essential element. Analytical results (Table-2) showed iron content in staple food items ranged between 78.0-118.0 mg kg^{-1}. The highest mean level of Fe(II) was found in wheat flour. On the other hand, lowest mean value was found in rice and split black gram.

Although Fe(II) were relatively high in all the samples (Table-2), but daily intake was less then MRL (minimal risk level) value (Fig. 1). So Fe(II) intake by staple food items was lower then recommended uptake and needed fortification to avoid nutritional deficiency.

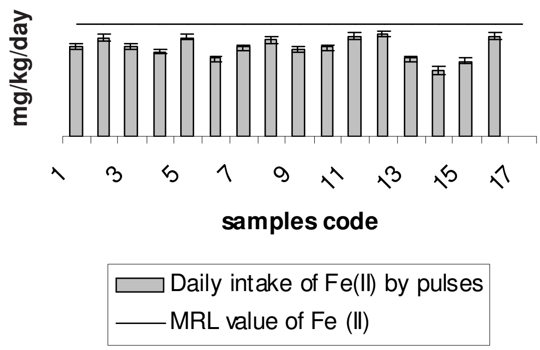

Fig. 1. Comparison of MRL (minimum risk level) values with daily intake to assess health effect of Fe(II) assuming daily intake of staple food items at 300 g/day/body wt. (50 kg)

Copper: Although copper is an essential element in trace amount but can be toxic at excess level. Copper build can result in a tendency for hyperactivity in autistic children. An excess of copper can cause oily skin loss of skin tone (due to ability to block vitamin C) and cause a dark pigmentation of skin specially, around face. It can attribute to hair loss specially, in women. The results (Table-3) showed copper content of staple food items ranged between 9.0-20.0 mg kg^{-1}. The highest mean level of copper was found in black gram and lowest mean value was found in semolina. Daily intake was much less then MRL (minimal risk level) value in all samples (Fig. 2) hence all the items were safe for human consumption.

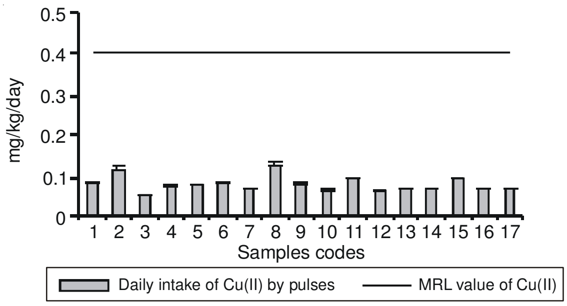

Fig. 2. Comparison of MRL (minimum risk level) values with daily intake to assess health effect of Cu(II) (assuming daily intake of staple food items 300 g/day/human body (50 kg)

TABLE-3
CONTENTS OF LEAD, CADMIUM, COBALT, IRON, COPPER AND CHROMIUM PRESENT IN STAPLE FOOD SAMPLES FROM MARKETS OF FIVE DIFFERENT AREAS OF LAHORE

Staple food items/ Names and codes		Fe(II) (mg kg^{-1})	Cu(II) (mg kg^{-1})	Cr(III) (mg kg^{-1})	Co(II) (mg kg^{-1})	Cd(II) (mg kg^{-1})	Pb(II) (mg kg^{-1})
1	Bengal gram	1061.0	14.0	5.75	0.700	2.0	1.5
2	Black gram	116.0	20.0	5.40	0.620	1.0	1.1
3	Black eyed beans	106.0	9.0	5.50	0.650	1.0	1.5
4	Chickpeas (brown)	99.5	12.5	6.15	0.650	0.5	1.2
5	Chickpeas (white)	117.0	13.0	6.50	0.650	1.0	1.2
6	Green gram	92.0	14.0	5.40	0.650	1.0	1.2
7	Red kidney beans	105.0	9.0	6.20	0.620	0.5	1.2
8	Red lentil	114.0	11.5	4.20	0.650	1.0	1.5
9	Semolina	103.0	21.6	7.80	0.650	1.0	1.5
10	Split bengal gram	105.0	13.5	5.20	0.650	1.0	1.2
11	Split black gram	118.0	11.0	5.20	0.700	1.0	1.1
12	Split green gram	121.0	16.0	5.20	0.710	0.5	1.2
13	Split red gram	92.0	10.5	5.20	0.620	1.0	1.4
14	Split red lentil	99.0	11.5	6.50	0.650	1.0	1.3
15	Rice	78.0	11.5	7.30	0.623	1.0	1.2
16	Gram flour	89.0	16.5	5.50	0.658	1.0	1.2
17	Wheat flour	118.0	11.5	7.00	0.620	0.8	1.1

Chromium: Chromium particularly Cr(III) plays an important role in the body function in trace amount but it is toxic in excess amount. Analysis for Cr(III) revealed that daily intake values were higher than those required. In case of chromium highest mean concentration was found in sample semolina and lowest mean concentration in red lentil (Fig. 3). MRL values were not a bright line for health risk but as the distance of experimental daily intake increases from MRL increased risk level also increases. So all the samples under study were source of Cr accumulation in body and were thus health hazards.

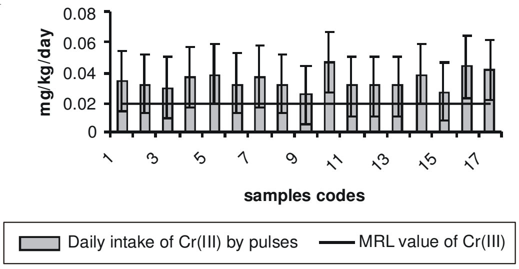

Fig. 3. Comparison of MRL (minimum risk level) values with daily intake to assess health effect of Cr(III) (assuming daily intake of staple food items 300 g/day/human body (50 kg)

Cobalt: In case of cobalt there was a small variation in concentration for all samples ranging from 0.6-0.7 g kg^{-1}. Daily intake values were found to be much lower than MRL values (Fig. 4). So these staple food samples were risk free of cobalt contamination. Cobalt is toxic at elevated levels. However the body needs small amounts of it in the form of vitamin B_{12}, an active physiological form containing Co(II).

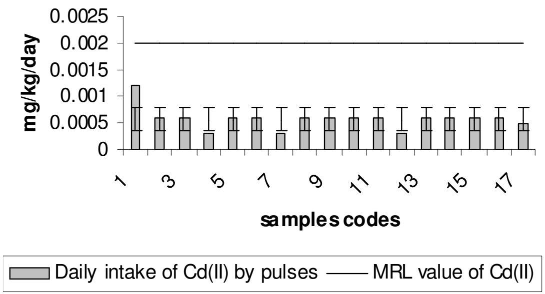

Fig. 4. Comparison of MRL (minimum risk level) values with daily intake to assess health effect of Co(II) (assuming daily intake of staple food items 300 g/day/human body (50 kg)

Cadmium: There was a little variation in case of cadmium. The concentration (0.5-2.0 mg kg^{-1}) was within permissible limit of 6 mg kg^{-1} for all foods in Pakistan[11,12]. Daily intake values were much lower than MRL values (Fig. 5).

Lead: As revealed by the analytical data concentration of Pb ranged between 1.1-1.5 mg kg^{-1} *i.e.*, greater than permissible standard limit of Pb (0.3 mg kg^{-1}). Daily intake was much higher than MRL values (Fig. 6) and posed a great health hazard as all staple foods under study constitute about 70 % of the total energy requirements of population of Pakistan. Lead(II) is a heavy metal poison which forms complexes with oxo-groups in enzymes to affect virtually all steps in the processes of hemoglobin synthesis and porphyrin metabolism[13]. Toxic levels of Pb(II) in man have been associated with encephalopathy seizures and mental retardation[14].

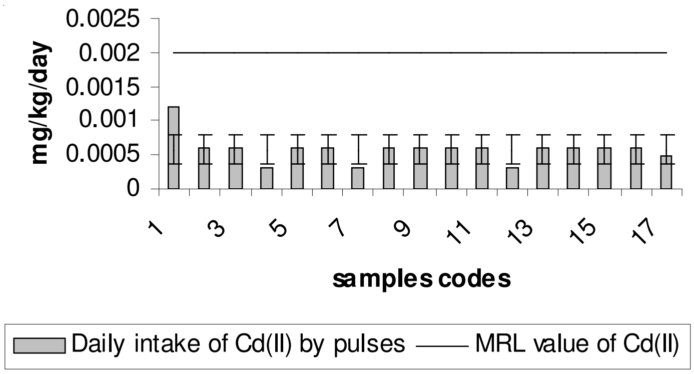

Fig. 5. Comparison of MRL (minimum risk level) values with daily intake to assess health effect of Cd(II) (assuming daily intake of staple food items 300 g/day/human body (50kg)

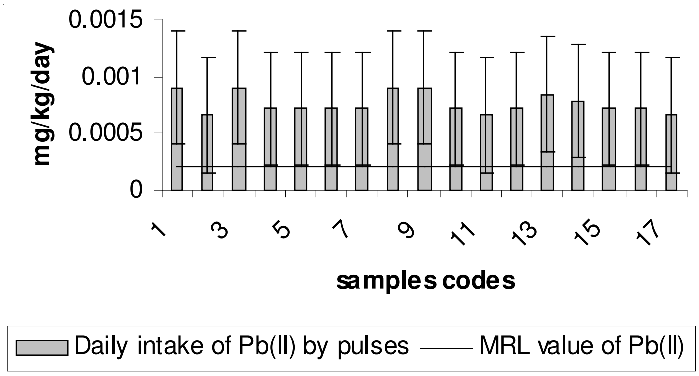

Fig. 6. Comparison of MRL (minimum risk level) values with daily intake to assess health effect of Pb(II) (assuming daily intake of staple food items 300 g/day/human body (50 kg)

Conclusion

On the basis of results obtained, it can be concluded that the staple food items widely used in Pakistan were not only source of trace metals but also source of contamination of toxic heavy metals especially Pb(II) and Cr(III). Thus excessive use of these pulses in foods was a health hazard especially for poor population as their all daily food intake mainly consists of .these staple food items because they can ill afford to include meat and poultry for their energy and protein requirements.

Mitigation options: The only option is to avoid deleterious effects of lead and chromium hazards is to remove anthropogenic sources causing increased levels of these toxic heavy metals in environment and by saving soil and ground water sources from waste waters from industries by bioremedial measures.

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