MONITORING OF HEAVY AND ESSENTIAL TRACE METALS CONTENTS IN WHEAT PROCURED FROM VARIOUS COUNTRIES BY THE GOVERNMENT OF PAKISTAN IN THE YEAR 2008-09

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ABSRACT

Government of Pakistan confined importers of wheat, both public and private to ensure acceptable quality of wheat meeting FAO and WHO standard. Monitoring of wheat quality i.e. physical, chemical and biological was carried out at Grain Quality Testing Laboratory, Karachi, Pakistan. The contents of heavy and essential trace metals were also assessed. Samples of wheat from various countries were imported through TCP (Trading Corporation of Pakistan). These samples were packed properly and forwarded to laboratory for analysis of some heavy (Cd, Pb, As, Hg) and essential trace metals (Zn, Cu, Fe, Mn, and Mg) contents. The metals concentrations found in the samples were in order of Mg >Fe > Cu > Zn > Mn > Pb > Cd > Hg > As. The metals contents found were under the permissible limits.

Key Words: Wheat quality Monitoring, Heavy & Trace Metals concentrations, Wheat, Pakistan

INTRODUCTION

Essential trace nutrients, micronutrients such as Zinc, Copper, Iron, Manganese, Boron and Molybdenum etc. are as important as primary and secondary nutrients in plant nutrition. Optimal concentration of essential trace metals is required for various physiological and metabolic processes taking place in the body of organism (McDowel, 2003 and Koike *et al.*, 2004). Amounts of these metals required for optimum nutrition are much lower. Solid phase of soil is the main reservoirs of these essential metals (Davendra, 1993). However the concentration of these metals if exceed the maximum permissible limits it becomes toxic.

Heavy metals such as Cadmium (Cd), Lead (Pb), Arsenic (As), Thallium (Tm) and Chromium (Cr) are the metallic elements with relatively higher densities ($>5g/cm^3$) and are toxic and poisonous even at very low concentrations (Alberti *et.al.*, 2002) . These metals are the primary constituent of the earth's crust and are present in soils where as their concentration is increased by improper fertilization application, spray of metallic pesticides on soil and crops, industrial effluent and sewage discharge into irrigation channels etc. (Jabbar and Innayatullah 1990, Perry *et al.* 1988, Van Bruggen 1999, Pinomonti *et al.* 1996). Over a period of time   these metals are deposited into soil and ultimately transported from soil solution to plant system. Higher accumulation of these toxic metals has direct and indirect effects on soil organisms, nutrients availability, and crop production and on human health (Bhaskar and Lena, 2003)

Thus the Present research was carried out to assess the essential and heavy metal contents in wheat procured from Russia and Australia by the government through Trading Corporation of Pakistan in the year 2008-9.

MATERIALS AND METHODS

Forty-three (43) samples of wheat grain procured from various countries (i.e. Russia and Australia) by Trading Corporation of Pakistan were forwarded to Grain Quality Testing Laboratory Karachi in the year 2008-9 for analysis of some heavy and essential trace metal contents. Samples were processed to get flour using laboratory mill and were homogenized. One gram of wheat flour from each sample was taken into digestion tubes, 30ml of nitric acid (65%) were added and were left for overnight. The next day, samples were digested first at 80^oC for an hour. When samples cooled down, 2ml of Perchloric acid (70%) were added and digested again at 250^oC until white fumes appear and solution become light colored or colorless and sample volume reduced to 2-5ml. On cooling, 20ml, 0.1M nitric acid were added and filtered with Wattman filter paper No. 542. Samples again were diluted with 0.1M nitric acid solution into the 100ml volumetric flask up- to- mark. Sample preparation was done following the recognized methods of (AOAC Method No. 999.10), Horwitz (2000) and Ahmed *et al.* (1994). The standard solutions of the studied metals ions for calibration procedure as well as for accuracy of the instrument and the method is shown in table 3 were prepared by diluting a stock solution of 1000ppm of the investigated metals supplied by "SCP Science (Traceable to NIST)". All dilutions of secondary and working standards were made up with 0.1M nitric acid. Zinc,

Copper, Iron, Manganese and Magnesium were analyzed using flame atomic absorption spectrophotometer   (FS-220, Varian). Cadmium and Lead using graphite furnace (GTA-110, Varian) and Arsenic and Mercury using vapor hydride and vapor generation assay (HVGA-77, Varian). Instrument conditions used, are given in Table 1 & 2. All the required glassware used in the analysis were washed with standard detergent following with tap water then soaked in acid (30% nitric acid) and placed in fuming hood. After soaking they were rinsed with distil water.

Parameters	GTA		VGA		FLAME	
	Cd	Pb	As	Hg	Cu	Zn
Concentration Unit	µg/L	µg/L	µg/L	µg/L	mg/L	mg/L
Measurement mode	Peak Height	Peak Height	Integration	Integration	Integration	Integration
Wave Length (mm)	228.8	217.0	193.7	253.7	324.8	213.9
Slit Width (nm)	0.5	1.0	0.5	0.5	0.5	1.0
Lamp Current (mA)	4.0	10.0	10.0	4.0	4.0	5.0
Background Correction	On	On	On	On	On	On

Table 1. Flame AA, Graphite Furnace and Vapor Generation Assay Parameters.

Table 2. Temperature, Retention time, Argon Gas flow for Lead (Pb) & Cadmium (Cd).

Lead (Pb)					
Step	**Temp (^{o}C)**	**Time (s)**	**Flow (L/min)**	**Read**	**Signal Storage**
1	85	5.0	3.0	No	No
2	95	40.0	3.0	No	No
3	120	10.0	3.0	No	No
4	400	5.0	3.0	No	No
5	400	1.0	3.0	No	No
6	400	2.0	0.0	No	Yes
7	2100	1.0	0.0	Yes	Yes
8	2100	2.0	0.0	Yes	Yes
9	2100	2.0	3.0	No	Yes
Cadmium (Cd)					
Step	**Temp (^{o}C)**	**Time (s)**	**Flow (L/min)**	**Read**	**Signal storage**
1	85	5.0	3.0	No	No
2	95	40.0	3.0	No	No
3	120	10.0	3.0	No	No
4	250	5.0	3.0	No	No
5	250	1.0	3.0	No	No
6	250	2.0	0.0	No	Yes
7	1800	0.8	0.0	Yes	Yes
8	1800	2.0	0.0	Yes	Yes
9	1800	2.0	3.0	No	Yes

RESULT DISCUSSION

Heavy Metals:

Cadmium in the samples ranged between 2×10^{-6} - 9.6×10^{-5} with an average concentration of 3.48×10^{-5} µg/g, lead (Pb) ranged between 7.8×10^{-6} - 2.7×10^{-4} with an average content of 6.2×10^{-5} µg/g and concentration of Mercury (Hg) were very low ranging from 3×10^{-6} - 1×10^{-5} with mean value of 5.5×10^{-6} µg/g (as shown in Table-

3). Similar study was conducted by Ahmed *et al.,* (1994), who reported that average cadmium, lead and mercury contents was 0.31 µg/g, 1.03 µg/g and 0.0196 µg/g respectively in wheat samples collected from local markets of Pakistan. Present study shows lower concentration of these metals than the previous one. USDA Agricultural Services has reported the maximum permissible limits of Cd, Pb and Hg to be 0.1 µg/g, 0.2 µg/g and 0.02 µg/g, respectively.

Essential Trace Metals:

In wheat flour samples Zinc ranged between 8.6 - 22.60 with an average concentration of 16.50 µg/g, Copper ranged between 6.80 - 18.88 with mean contents of 18.40 µg/g, Iron ranged between 12.0 - 77.60 with an average of 24.60 µg/g, Manganese ranged 6.0 - 20.0 with mean of 10.20 µg/g and Magnesium ranged between 778.21 - 924.20 with mean concentration of 922.64 µg/g. present study results are comparable to some extent except (Cu & Mn) with the results of Ahmed *et.al.*, 1994 who reported that Zn, Cu, Fe and Mn in wheat flour samples collected from local markets of Pakistan was 19.10 µg/g, 2.17 µg/g, 32.40 µg/g, 28.20 µg/g respectively. On the basis of nutritional value 122.9 µg/g, 62.26 µg/g, 133.01 µg/g, 2390 µg/g, respectively for Zn, Fe, Mn and Mg given by USDA Nutrient Data base, flour samples of procured wheat in 2008-09 by TCP contained low contents of Zn and Fe where as Cu and Mg was present in sufficient quantities.

Table 3. Analysis of metals Standards (As reference samples) & actual imported wheat samples.

Metals	Metal Standard (µg/ml)		Range with mean concentration of 43 imported samples (µg/g)
	Actual concentration	**Instrument detected concentration**	
Cd	0.007 ± 0.0005	0.0069 ± 0.00059	2×10^{-6}- 9.6×10^{-5} (**3.48×10^{-5}**)
Pb	0.2 ± 0.01	0.1945 ± 0.0055	7.8×10^{-6}-2.7×10^{-4} (**6.2×10^{-5}**)
Hg	0.023 ± 0.0005	0.0213 ± 0.0001	3×10^{-6}- 1×10^{-5} (**5.5×10^{-6}**)
Cu	10.0 ± 0.2	10.32 ± 1.2	6.8-18.88 (**18.40**)
Zn	10.0 ± 0.5	9.64 ± 0.7	8.6- 22.60 (**16.50**)
Fe	10 ± 0.5	9.8 ± 0.8	12.0- 77.6 (**24.60**)
Mn	10 ± 0.5	9.92 ± 0.6	6.0- 20.0 (**10.20**)
Mg	10 ± 0.5	9.63 ± 0.9	778.21-924.20 (**922.64**)

CONCLUSION

Results of present study show that Cd, Pb and Hg in majority of the samples were at lower side and within the permissible limits where as low contents of nutrient metals was found in the samples. Study reveals that wheat procured by TCP in 2008-09 was safe to consume and the toxic metals found were within the permissible limits (NHMRC, 1987). The levels of essential nutrient metals were low to sufficient found in the samples.

REFERENCE

Ahmed S., S. Waheed, A. Manan, I. Fatima and I.H. Qureshi (1994). Evaluation of trace metals in Wheat and Wheat By-products. *JOAC (Journal of Official Analytical Chemist*s), 77: 11-17

Alberti-Fidanza A, G. Burini and G. Perriello (2002). Trace elements in foods and meals consumed by students attending the faculty cafeteria. *Sci Total Environ.*, 287: 133-140

Bhaskar, R.B. and M.A. Lena (2003). *Tolerence of heavy metals in plants, Plants poisoning by heavy metals in the new millennium.* Kluwer Academic Publisher, Netherland, pp: 397-420.

Davendra, C. (1993). Trees and shrubs and sustainable sources. Proceedings of the world conference on Animal *Production. Endmonton*, 10: 119-136.

Horwitz, W. (2000). *Official method of analysis of AOAC International* (Association of Official Analytical Chemist), Vol-I, Method No. 999.10, Chapter-9, pp: 16.

Jabbar, A. and C. Innayatullah (1996). Environmental considerations of pesticide production, usage in Pakistan. *RENPAP Gazette-1* (1), pp: 15-24.

Koike, S., H. and Inoue D.Mizuno (2004). OsYSL2 is rice metal-nicotianamine transporter that is regulated by Iron

and expressed in phloem. *Plant J*., 39: 415-424.

McDowell, L.R. (2003). *Minerals in animals and human nutrition*. 2nd edition. pp: 144. Elsevier Science BV Amsterdam, Netherlands.

NHMRC (1987). *National Health and Medical Research Council*. Food Standard Code. pp: 68-71.

Perry, G.A., F.V. Robbins and P.L. Brans (1988). *Factors affecting leaching in agricultural Areas and assessment of agricultural chemicals in ground water of Texas*. Water resources investigation report, U.S. geological survey, Lawrence, Texas. pp: 1-55

Pinomonti, F., M. Stefin and A. Dalpiaz (1996). Soil management effects on nutritional status and grapevine performance. *Weins-Wiss* (51): 76-82.

Van Bruggen A.H., and A.M. Seminov (1999). New approach to the search for indicators of root disease suppression. *Australian plant pathology Journal,* 28: 4-10.

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