▼ Journal of Research (Science), Bahauddin Zakariya University, Multan, Pakistan.
Vol. 18, No. 2, April 2007, pp. 53-59 ISSN 1021-1012

DETERMINATION OF TRACE AND TOXIC ELEMENTS IN FOUR PAKISTANI BARLEY (*HORDEUM VULGARE* L.) VARIETIES AND ITS SOIL COLLECTED FROM PIRSABAK (NWFP), PAKISTAN

G. Q. Shar, L. A. Shar
Department of Chemistry, Shah Abdul Latif University,
Khairpur (Sindh), Pakistan.
T. G. Kazi*, H. I. Afridi, M. B. Arain
Centre of Excellence in Analytical Chemistry, University of Sindh,
Jamshoro, 76080, Pakistan.
email: tgkazi@yahoo.com
M. K. Jamali
Government Degree College Usta Mohammad Balochistan, Pakistan

Abstract

A study was conducted to determine the concentration of trace and toxic metal accumulation in barley varieties and soil grown at Cereal Crop Research Institute (CCRI), Faisalabad using flame atomic absorption spectrophotometer. In this connection wet ashing method used to destroy the organic matrix. The highest level in (mg/kg) of trace and toxic metals determined in barley varieties and its soil were found 5.75-7.57 (Cu), 3.21 – 3.79 (Co), 0.75 – 1.13 (Cr), 1.68 – 5.67 (Ni), 2.19 – 6.76 (Ba), 16.71 – 29.28 (Al), 1.01 – 1.46 (Pb) and 0.18 – 0.44 (Cd). The concentration in (mg kg^{-1}) of the soil of that specific plot was observed 14.74 ± 1.39 (Cu), 6.07 ± 0.81 (Co), 7.09 ± 0.65 (Cr), 8.39 ± 1.29 (Ni), 116.74 ± 8.02 (Ba), 18821.4 ±1583.8 (Al), 3.88 ± 0.45 (Pb) and 1.25 ± 0.16 (Cd). Using reference material checked the validity of digestion method.

Keywords: Absorption spectrophotometer, barley, toxic elements, wet ashing method.

INTRODUCTION

Barley grains have a hull of adherent paleas, which are removable only with difficulty in hulled forms. In naked forms, the hull is readily lost during threshing. The hull amounts to about 13% of the grain (by weight) on average, the proportion ranging from 7 to 25% according to type, variety, grain size, and latitude where the barley is grown.

---

* Author for Correspondence,
Tel: 022- 2771379, Fax: 022- 2771560

Blue color may be present due to anthocyandin pigmentation. In the starchy endosperm 2 populations of starch granules are present in most types, though in some mutants, exploited for their chemically different starch, only one population may be present [Evers 1990]. The variables were tested in artificially salinized soil for four different electrical conductivity levels (1.25, 4, 8 and 12dsm^{-1}) to assess the contents of various ions (Na, Ca, Mg) in plants and grains [Sial 1988]. Cadmium and lead were determined by electrothermal atomic absorption spectrometry [Correia 2000]. Multi-elements determined by inductively coupled plasma mass [Kang and Sugimoto 1985]. Juwarkar and Shiende [Wu *et al* 1997] observed that the lengths of ear head and grain yield of barely were reduced due to combine treatment of cadmium and lead [Rashid and Mukherji 1993, Mukherji and Banerjee 1980]. A pot experiment was conducted to study forage yield and quality of barley when harvested at different times and grown under three-nitrogen dose [PSI 1962]. Elemental content of Vietnamese food studied [Ayub *et al.* 1999]. The factors, which regulate the growth of plants are depend on a number of a biochemical processes involving various inorganic elements present in the soil. Large variation in mineral content of different crops [Phung *et al.* 1999, Ansari *et al.* 1999, Kishkan 1986] depends upon plants species, soil and climate. The plant species vary widely in tolerance to toxic metals and varieties with a species can also vary three to ten folds. Variation in mineral content of different plant species grown on the same soil have also been reported [Reddy 1986].

The concentration of heavy metal accumulation, in food and soil at sewerage farm in Sindh Industrial Trading Estate (SITE), Karachi studied [Tahir *et al.* 1986]. The study was carried out to investigate the levels of heavy metals Cu, Fe, Mn, Zn, Cd, Co, Ni, Mo, Cr and Pb in soils of Peshawar and Nowshera district [Yousufzai and Hashmi 2001]. Variation in uptake of essential and trace elements of different varieties of wheat grown in same agricultural plot of Balochistan, Pakistan was carried out [Mohammadzai and Khan 2001]. Variations in Ca, P, Fe, Cu, Zn and Mn contents of six wheat and six rice varieties under salt stress were investigated [Shar *et al.* 2002]. Uptake of various trace elements during germination of wheat, buckwheat and quinoa were studied [Alpaslan 1998]. Strategy of analysis for the estimation of the bioavailability of zinc in foodstuffs reported [Lintschinger *et al.* 1997]. Many heavy metals were determined by flame atomic absorption spectrometry in foods and biological sample [Schwedt *et al.* 1998]. Determination of Cr, Zn, Cd and Pb in food studied [Miller-Ihli 1996].

The purpose of this research was to examine the concentration of trace and toxic metals in barley cultivars and their source i.e., soil, in order to improve their nutritional role as a source of bioavailability of trace and toxic metals. This study would be highly significant for the nutritive purpose for the human being as well as for animals.

MATERIALS AND METHODS

MATERIALS

The experiment was conducted at Cereal Crop Research Institute (CCRI) Pirsabak, Nowshoro province NWFP of Pakistan during normal barley growing season (November 2000 to April, 2001) for two years. Four varieties (i.e. Jau-83, Jau-87, Haider-93 and Quina) were grown at Cereal Crop Research Institute

(CCRI) Pirsabak, Nowshoro province NWFP. The varieties were harvested at maturity stage and randomly collected to make representative samples of each variety.

Soil samples were collected from the above agricultural research institute where varieties grown by the usual procedure, i.e., from 0 to 15-cm depth. Soil samples were collected in the sunny days of the month of November 2000 to April 2001, with the help of a wooden tool to avoid contamination of the soils with any of the element being studied.

The soil samples were air dried, ground with a wooden mortar and sieved (<0.5mm). The samples were Stoppard tightly in plastic bottles and labeled. These samples were then used for further investigation.

METHODS

All four barley (i.e. Jau-83, Jau-87, Haider-93 and Quina) varieties and soil samples were dried at 105 ^{0}C in oven till constant weight. Replicate 1g samples of dried soil and 2g of each barley cultivar were weighed in to 100ml conical flasks and treated with 5ml of nitric acid. 5ml of nitric acid were also added to empty conical flask serving as a blank [Ho *et al.* 2002]. The flasks were covered with watch glasses, and their contents were heated to reflux gently on an electric plate. After refluxing for one hour the contents of flasks were treated with 5ml more of nitric, 2ml of 35% hydrogen peroxide was added, and the heating at gentle reflux was continued for another hour. The watch glasses were removed from the flasks, and the heating was continued until the volumes of their contents were reduced to 2-3ml. The contents of flasks were cooled, diluted with high purity water, and filtered through Whatman # 42 paper in to 25ml volumetric flasks. The contents of the flasks were brought to volume with high purity water and examined by atomic absorption spectrometry for their copper, cobalt, chromium, nickel, barium, aluminum, and lead and cadmium levels. Total mineral content was determined by the wet digestion method. The above-mentioned analyses were performed according to the standard Official Methods of Analysis of the Association of Official Analytical Chemists [FNB 1989, AOAC 1995]. Total insoluble minerals were determined using Flame Atomic Absorption Spectrophotometer (FAAS), according to Approved Methods of the American Association of Cereal Chemists [AACC 2000]. The results of these measurements are presented in Table 1.

Table 1: Determination of Trace and Toxic Elements in four Barley (Hordeum Vulgae L.) Cultivars and their Soil grown at CCRI , (NWFP) Pirsabak, Nowshoro.

Elements	Barley varieties / cultivars				Soil	C at 450g/d/p	
	Jau-83	Jau-87	Haider-93	Quina		Exp.	P.L
Cu	7.57±0.32	5.75±0.59	6.70±0.30	6.77±0.14	14.74±1.39	3.46	2.0-3.0
Co	3.60±0.20	3.74±0.41	3.79±0.20	3.21±0.34	6.07±0.81	1.48	0.15-0.5
Cr	1.13±0.19	1.03±0.11	0.75±0.06	1.00±0.16	7.09±0.65	0.46	0.05-0.2
Ni	4.22±0.19	4.86±0.54	5.67±0.42	1.68±0.28	8.39±1.29	1.04	0.16-0.25
Ba	6.76±0.88	5.52±0.88	2.78±0.35	2.19±0.31	116.74± 8.02	3.65	0.41-0.48
Al	16.71±1.11	29.28±3.34	13.56±1.1	28.50±2.22	18821.4± 1583.8	9.9	8.6-13.6
Pb	1.04±0.13	1.01±0.18	1.22±0.05	1.46±0.11	3.88±0.45	0.38	3.6
Cd	0.43±0.04	0.39±0.05	0.18±0.00	0.44±0.02	1.25±0.16	0.25	0.27

Exp.= Experimental value, P.L.= Permissible Limit, C = Consumption,
C at 450g/d/p= Consumption at 450g per day per person

INSTRUMENTATION

A Hitachi Model 180-50 atomic absorption spectrophotometer was used for the determination of elements such as, copper, cobalt, chromium, nickel, barium, aluminum, lead and cadmium as given in Table 1. The hollow-cathode lamps (made by Mitorika company) of all above elements were operated at lamps current 9.5, 9.5, 6.0, 9.5, 9.5, 9.5, 7.0, and 7.0 mA respectively. The flow-rate for fuel 2.30 Lmin^{-1} for Cr and Cd; 2.0 Lmin^{-1} for Cu, Co, Ni, and Pb; 5.61 Lmin^{-1} for Ba and Al. Similarly flow rate of air 9.40 Lmin^{-1} for Cu, Co, Cr, Ni, Pb, and Cd whereas 5.91 Lmin^{-1} for Ba and Al was used respectively to obtain a clear yellow flame (reducing condition). The spectrophotometer out put was connected to a Hitachi recorder 056 with a range of 5mV. The signals measured were the heights of the absorbance/division peaks. All instrumental parameters are given in Table 2.

Table 2: Instrumental conditions for the AAS measurement of Cu, Co, Cr, Ni, Ba, Al, Pb, and Cd.

Elements	Wave length (nm)	Slit width (nm)	Lamp current (mA)	Fuel flow (acetylene) (l min^{-1})	Flow rate (Air) (l min^{-1})	Burner height (mm)	Oxidant (Air) kg cm^{-2}	Fuel (Acetylene) Kg cm^{-2}	Signal out put
Cu	325.0	1.3	9.5	2.0	9.4	7.5	1.60	0.2	100%
Co	250.0	0.2	9.5	2.0	9.4	10.0	1.60	0.35	100%
Cr	358.2	1.3	6.0	2.30	9.4	7.0	1.60	0.30	100%
Ni	232.3	0.2	9.5	2.0	9.4	7.5	1.60	0.2	100%
Ba	553.8	1.3	9.5	5.61	5.91(N_2O)	7.5	1.60(N_2O)	0.45	100%
Al	309.5	1.3	9.5	5.61	5.91(N_2O)	12.5	1.60(N_2O)	0.45	100%
Pb	232.3	1.3	7.0	2.0	9.4	7.5	1.60	0.2	100%
Cd	229.0	1.3	7.0	2.30	9.4	7.5	1.60	0.30	100%

REAGENTS AND CALIBRATION

The supra pure nitric acid (65% w/v) and hydrogen peroxide (35% w/v) reagents (Merck), high-purity water (electrical resistivity 〉10mΩ cm) was produced with a Milli-Q system Millipore, MA, USA).

Calibration was obtained with external standards. The standards solutions were prepared by diluting a 1000 mg l^{-1} multi element solution (ICP Multi element standard iv, Merck, Darmstadt, FRG) with the same acid mixture used for sample dissolution. Glassware were cleaned by soaking with the contact over night in a 10 % (w/v) nitric acid solution and then rinsed with deionized water.

Table 3: Statistical data for standards of elements.

Elements	Concentration range ppm (x)	Absorbance/ Division (y)	Statistical calculation y = m x + c		
			m	c	r^2
Cu	0 – 1	0 –0.085*	0.0856	-0.0001	0.9995
Co	0 – 0.5	0 – 65 div.	130.29	-1	0.9982
Cr	0 – 0.125	0 – 24 div.	193.28	0.3479	0.9977
Ni	0 – 0.2	0 – 31div.	157	0.575	0.9991
Ba	0 - 2	0 – 40 div.	20.1	0.125	0.9992
Al	0 - 4	0 - 32	7.95	-0.125	0.9988
Pb	0 – 0.25	0 – 25 div.	99.604	-0.0428	0.9993
Cd	0 – 0.1	0 – 50 div.	502	-0.225	0.999

Absorbance*, div. =Divisions

Standards and sample solutions were aspirated into atomic absorption spectrophotometer and absorbance/divisions measurements were made for each element using optimum instrumental conditions for flame atomization mode.

Reference standards were also run in parallel for inter calibration of our own standards. Elemental concentration were computed on an IBM compatible PC using a excel computer program. The statistical calculations for standards are given in Table 3 above.

RESULTS AND DISCUSSION

The mineral content of four Pakistani barley varieties can be summarized in Table 1. The highest contents of Cu (7.57±0.32 mg kg^{-1}) was found in Jaw-83, while as lowest content (5.75±0.59 mg kg^{-1}) was detected in Jew-87 variety and its soil possesses 14.74±1.39 mg kg^{-1} of the Cu, which is approximately double to that of varieties. Maximum content of Co and Ni (3.79±0.20 and 5.67±0.42 mg kg^{-1} respectively) were observed in Haider variety while as lowest content of Co and Ni (3.21±0.34 and 1.68±0.28 respectively) were detected in Quina cultivar and its soil contains 6.07±0.81 and 8.39±1.29 mg kg^{-1} respectively. Similarly, the maximum absorption of Al (29.28±3.34 mg kg^{-1}) was found in Jew-87 variety and minimum absorption of Al (13.56±1.1 mg kg^{-1} detected in Haider-93 variety while soil of the crop keeps 18821.4±1583.8 mg kg^{-1}. It was found that highest absorption of Pb and Cd (1.46±0.11 and 0.44±0.02 mg kg^{-1}) takes place in Quina cultivar as compared to the rest of the varieties and soil of these elements possesses 3.88±0.45 and 1.25±0.16 mg kg^{-1} respectively.

It would be worthy of investigating the concentration levels of 8 elements among all the samples of the barley cultivars to gain some idea for the degree of variability in the uptake of different elements by different cultivars of barley grown on same agricultural plot in same season. The elemental concentrations were determined on dry weight basis. The data in Table 1 indicates the concentration of essential trace and toxic elements in different 4 cultivars of barley.

The experimental value of four varieties/cultivars of barley shows that Cu, Co, Cr, Ni, and Ba are higher and value of Pb is lower than permissible able limit values while as Al and Cd are found to be in within permissible limit on the basis of consumption at 450 grams/day/person, as recommended value [Shar *et al* 2002].

CONCLUSIONS

According to the data from Table 1, it was pointed out that highest uptake of Cu, Cr and Ba was found in Jew-83 variety. Maximum uptake of Al was detected in Jew-87 where as the highest absorption of Co and Ni was observed in Haider-93. In the same way highest uptake of Pb and Cd were detected in the Quina cultivar. It can be concluded that there were remarkable differences in up taking the 8 metals in different varieties/cultivars of barley even though; they can grow in the same soil and same climatic conditions. It may be due to some physiological, biochemical, anatomical and morphological, and genetic characters of the seed.

Acknowledgements

Ghulam Qadir Shar is thankful to Syed Iqrar Hussain Shah, Muhammed Aslam Nushad (Seed Certification Officers), Seed Certification & Registration

Department and Malik Azhar Ali for their co-operation in sampling of the Barley varieties from Cereal Crop Research Institute Pirsabak, Nowshera (NWFP). Thanks are also due to my parent institute Shah Abdul Latif University, Khairpur, Sindh, Pakistan for financial support and grant of study leave.

References

Alpaslan, Mehmet (**1998**) *Turk. Agric. J.,* **22(3)**

American Association of Cereal Chemists – AACC (**2000**) 10th ed., St. Paul AACC

Ansari, T.P., Kazi T.G. and Kazi, G.H. (**1999**) ACGC (Australia*) Chem. Res. Comm.,* **9**, 51-56.

Association of Official Analytical Chemists – AOAC (**1995**).

Ayub, M., Dewi, I.A.P., Tanveer, A. (**1999**) *Pak. J. Biol. Sci.,* **2 (4),** 1278-1282.

Correia, P.R.M. (**2000**) *Analytica Chimica Acta,* **405,** 205-211.

Evers, A.D. (**1990**) *Aust. J. Agric. Res*., **50,** 634-50.

Food and Nutrition Board, National Research Council 1989, “Recommended Dietary Allowances”, 10th ed., National Academy Press, Washington, DC.

Ho, C.Y., Jiang, S.J. (**2002**) *J. Anal. At. Spectrom*., **17 (7),** 688 – 692.

Kang, M.Y., Sugimoto, Y. (**1985**) *Agric. Biol. Chem.,* **49(5),** 1291-1297.

Kishkan, M.B. (**1986**) *Hot Sci.,* **21,** 24-27.

Lintschinger, J., Fuchs, N., Moser, H. (**1997**) *Plant Foods Hum. Nutr*. (Dordrecht, Neth.), **50(3),** 223-137.

Miller-Ihli, N.J. (**1996**) *Agric. J. Food Chem.,* **44 (9),** 2675-2679.

Mohammadzai, I. Khan, N. (**2001**) *J. Chem. Soc. Pak*., **23(1),** 23 – 30.

Mukherji, S., Banerjee, A. (**1980**) *Indian J. Expt. Biol.,* **18,** 428.

Pakistan Standard Institute, Standard for Nickel, PSI Standard No. 221, Government Printing Press (**1962**) p. 4.

Phung, Dong Tran, Kokot, S., Choung, Van Pham, TongKhim, D. (**1999**) *Analyst,* **124 (4),** 553-560.

Rashid, P., Mukherji, S. (**1993**) *Pak. J. Sci. Ind. Res.* **36,** 11.

Reddy, M.R. (**1986**) *J. Agric. Food, Chem*., **34,** 750-753.

Schwedt, G., Tawali, A.B., Koch, K., Fresenius (**1998**) *J. Anal. Chem.,* **360 (5),** 589 – 594.

Shar, G.Q., Kazi T.G.and Sahito, S.R. (**2002**) *Chem. J. Soc. Pak.,* **24 (2),** 258 – 261.

Shar. G.Q., Kazi, T.G., Sahito, S.R. (**2002**) *J. Chem. Soc. Pak.,* **24(4),** 258 – 261.

Sial, N.B. (**1988**) *Pak. J. Agric. Engg., vet.Sec,* **4(1-2),** 66-70.

Tahir, M., Kausar, M.A., Ahmad, R. and Bhatti, A.S. (**1986**) *Pak. J. Sci Ind. Res*., **29**, 6.

Wu, S., Feng, X., Wittmeier, A. (**1997**) *J. Anal. At. Spectrom.,* **12 (8),** 797 - 806.

Yousufzai, A.H.K., Hashmi, D.R. (**2001**) *Jour. Chem. Soc. Pak.,* **23(1**), 7 – 15.