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METAL CONCENTRATION IN CHILLI *(CAPSICUM ANNUM L.)* IN SINDH, PAKISTAN

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خلاصہ

مرچ کو پاکستان کے پکوانوں کا اہم جز سمجھا جاتا ہے یہ ان چند غذ آئی اجناس میں سے ہے جسکی تجارت بڑے پیمانے پر اندرون اور بیرون ملک کی جاتی ہے۔ پاکستان مرچ کی تجارت کے اعتبار سے دنیا کے 7.2 فیصد حصے کا شراکت دار ہے۔ مرچ میں چند زہریلے مادوں مثلاً ایفلاٹاکسن، ہیوی میٹل کی موجودگی کی وجہ سے یورپی ممالک اور جاپان نے پاکستان سے جانے والی برآمدات روک دی ہیں اب ہماری برآمدات صرف UAE, USA, Mexico, Canda، چند افریقی اور ایشیائی ممالک تک محدود ہو کر رہ گئی ہے لہذا ہمیں اپنے کاشت کاری کے تمام مراحل جن میں بیج کی کوالٹی سے لیکر انکی بوائی، کٹائی اور پھر مارکیٹ تک انکی رسائی کے طور طریقوں پر نظر ثانی کرنے کی اہمیت نمایاں طور پر اجاگر ہوتی ہے۔ مندرجہ ذیل تجربہ میں تیار شدہ فصل کی کٹائی کے دوران استعمال ہونے والے آلات اور نقل و حمل کے ذریعے میٹل کی مقدار پر پڑنے والے اثرات کا جائزہ لیا گیا۔ کنری شہر کے تین مختلف گاؤں اور مارکیٹ سے مرچ کے نمونے حاصل کئے گئے جن میں نور ہیلی پوتو، ایم۔ایچ چانڈیو اور صدیق کپری کے علاقے شامل ہیں۔ نتیجہ سے معلوم ہوا کہ Fe, Cu, Zn, Pb, Cd اور Mn کی اوسطاً مقدار نمونوں میں بالترتیب 0.026 177 0.003, 0.085 177 0.008, 16.68 177 0.66, 9.65 177 0.98, 128.50 177 1.88 and 30.20 177 1.25 ugg-1 ہے Cd اور Pb کی مقدار نمونوں میں WHO/FAO کے مقرر کردہ جائز حد تک پائی گئی۔ مرچ میں دھاتوں کے جمع ہونے کا پیٹرن Fe > Mn > Zn > Cu > Pb > Cd پایا گیا۔ نتیجہ کے طور پر یہ بات بھی سامنے آئی کہ چند پوسٹ ہارویسٹ کی تکنیک اور روایتی نقل و حمل کے طریقے مرچ کے نمونوں میں دھاتوں کی مقدار بڑھا سکتے ہیں۔ آلے کی کارکردگی linear calibration curve کے ذریعے معلوم کی گئی جو کہ ہر دھات کے لئے R<0.99 تھی۔

Abstract

A comparative study was carried out to assess the effect on heavy metal concentration in fruits of major variety of Dandicut chilli (*Capsicum annum L.)* between field and market samples. Field samples were collected from Kunri city while markets of Noor helepoto, M.H Chandio and Siddiq kapri were analyzed for heavy metal contamination. In Farmer's field Cd, Pb, Zn, Cu, Fe and Mn contents (mean ±SD) were found to be 0.029 ± 0.003, 0.061 ± 0.005, 20.196 ± 1.094, 10.156 ± 0.812, 111.01 ± 7.206 and 30.766 ± 1.872 µg g^{-1} while samples from local market showed 0.030 ± 0.0292, 0.089 ± 0.002, 19.071 ± 1.906, 12.261 ± 1.292, 126.84 ± 1.829 and 32.791 ± 1.828 µg g^{-1} respectively. Cadmium and Lead contents in all samples were within the permissible limits by W.H.O/F.A.O standard. The order of accumulation of metals in both sampling location was found to be Fe > Mn > Zn > Cu > Pb > Cd.

Introduction

In Pakistan 88 percent of chili is grown in Sindh including the areas of Kunri, Umerkot, and MirpurKhas which produce around 130,350 tons of chillies annually. By far, the major crop cultivated in the area is red chilli comprising varieties of Maxi, Desi and Nageena (Arisar, 2011; Memon, 2015). In the past few years a decline of about 49% in production of chilli has been recorded as farmers' are sowing less chilli due to its low returns, resulting a decreased in 14% land area used to cultivate chilli.

Main factors which are responsible in produce losses include some pre-harvesting errors such as old and poor production techniques, improper harvesting and care. Imbalance in use of nutrients, insect pest and disease infestation and cultivation of varieties of low shelf life are also contributing factors for low production. Post-harvest practices like drying, carriage and storage and loading unloading etc are processes starting soon after harvest of crop. The farmers are using iron tools and other apparatus for drying of Chili and basic principles of post-harvest handling for most crops is to avoid all type of contamination, damages and maintenance of quality of produce. Postharvest processes determine the quality whether the edible portion of produce may contain sufficient level of essential mineral nutrients or may have not been contaminated by excess concentration incorporated by tools commonly used in the fields and storage sites while drying and storages. Also post-harvest problems include non-removal of field heat, poor handling of produce, humidity causing pathogen infestation, packaging in bulk without sorting and grading of produce, improper transportation and storage, and distant and time consuming market distribution.

Zurea-Cosano *et.al*, (1984) and Sabukola *et. al.*, (2010) have reported contamination of metals in vegetables due to polluted environment which necessitates to check the accumulation of metals in different food stuffs. (Cabrera *et al.*, 1993); Memon, 2015). Estimates of the post-harvest losses of food grains in the developing world from mishandling are around 25 percent (John and Wills 1989).

Present study thus was conducted to determine the post-harvest variability of metal content in chilies produce in Sindh (Pakistan). The study covers metal contents (increase and decrease due to post-harvest processes viz drying, transportation and storage etc.) in the catchment. Samples from farmer's field before drying and from market after completion of drying, were collected just to investigate variance between and to assess metal contamination pathway. It's worth mentioning that overall variance of metal accumulation and contamination levels between field and market is studied. The objective of the study is to disseminate information among farming community about pathway of metal contamination in Chili after using tools and conventional post-harvest practices.

Materials and Methods

One hundred and twenty samples of chilli Dandicut varieties were taken from farmers' field and from local market of each of village Noor Halepoto, SiddiqKapri, and M.H Chandio in Kunri town, Umerkot, Sindh. Twenty samples from field and another twenty from the local market of each village around the town were collected. Representative samples then were preserved into polyethylene bags and brought to laboratory for analysis.

Sample Preparation

0.5g of dried, ground and homogenized sample of each from farmer's filed and from market samples in triplicate were taken into the tubes. 20 mL of concentrated HNO_3 (65%) were added and digested on microwave on temperature 200°C for 20 minutes at 800 psi pressure (Gawalko *et.al*, 1997). Samples were allowed to predigest by keeping them in fuming hood for 15 minutes. Then sampling tubes were sealed and samples were digested following heating program as given in Table-1. Flame atomic absorption spectrophotometer Model FS-220 coupled with graphite tube atomizer and vapor generation assay with deuterium correction background were used for the analysis of the samples. Cadmium and lead were analyzed by Graphite Tube Atomizer (GTA) while Zinc, Copper, Iron and Manganese were analyzed on Flame-AAS. Instrument parameter settings are given in Table-2 and 3.

Results and Discussion

In fruits and vegetables, the quality of produce starts deteriorating right after their harvest. It is necessary to adopt some standard prescribed method to store/transport the produce which do not affect their quality and quantity. Comparison of metal content in chilli between the samples of field and market is shown in (Fig. 1). It is reveled from the result that metal content in all the market sample has been increased as compare to field samples.

It is literated that contents of naturally available ionic cadmium (Cd^{2+}) in soil vary from $1.6x10^{-9}$ M (Mitchell, 1997) to $9x10^{-8}$ M (Keller, 1995) could be a reason that M.H Chandio's field chilli has more cadmium then other two village's fruit. It is also evident that field management practice and post -harvest practices shown no significant impact on uptake on cadmium.

Pb in samples of present study collected from markets of selected villages showed significant difference (P>0.05) than fields, which reflects the efficient uptake of lead by first barriers epidermis during transportation. Lead is added in environment by anthropogenic activities like, gasoline, mining, smelting, paints, explosives etc. (Meyers *et. al.*, 1982). The increase in lead contents of all three samples collected from market is believed to be due to atmospheric emission as the samples are brought to local market via open carriers and stored on sides of roads and in open environment (Table 4). The contents though increased were found within allowable limits 0.3 μgg^{-1} given by (FAO/WHO, 2007).

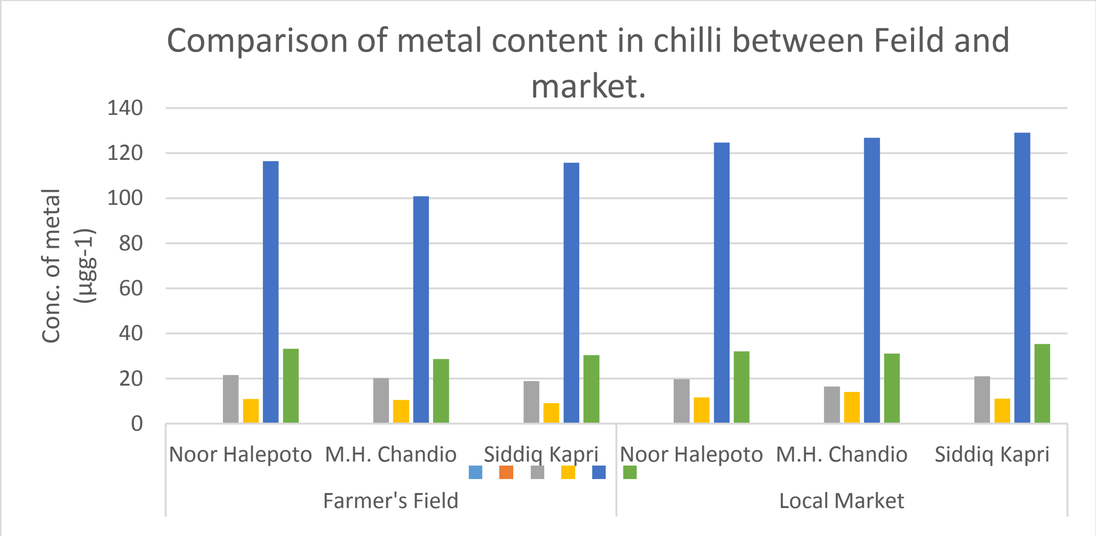

Fig-1. Comparison of metal content in chilli between the samples of Field and market.

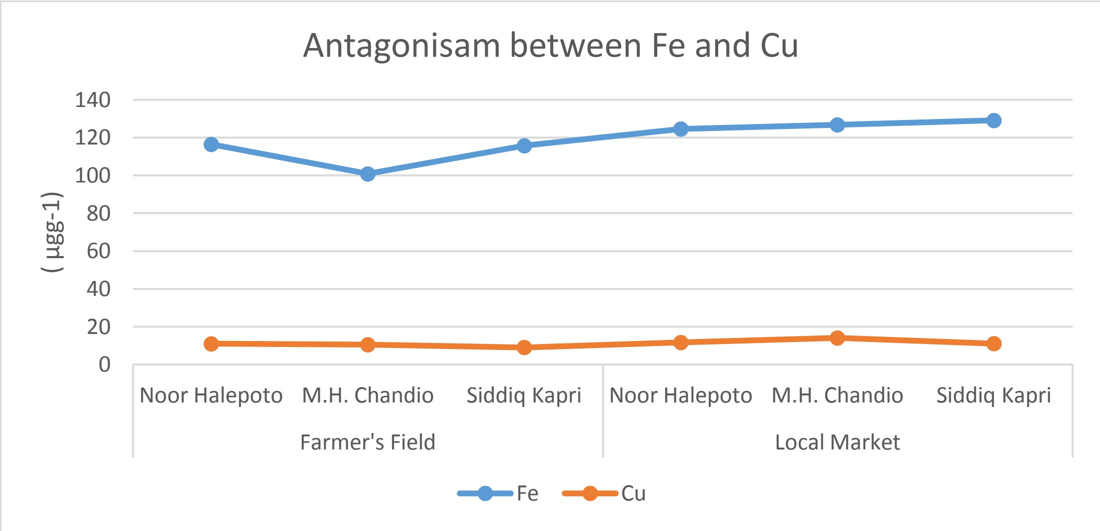

Fig-.2. Antagonism between Iron and Copper

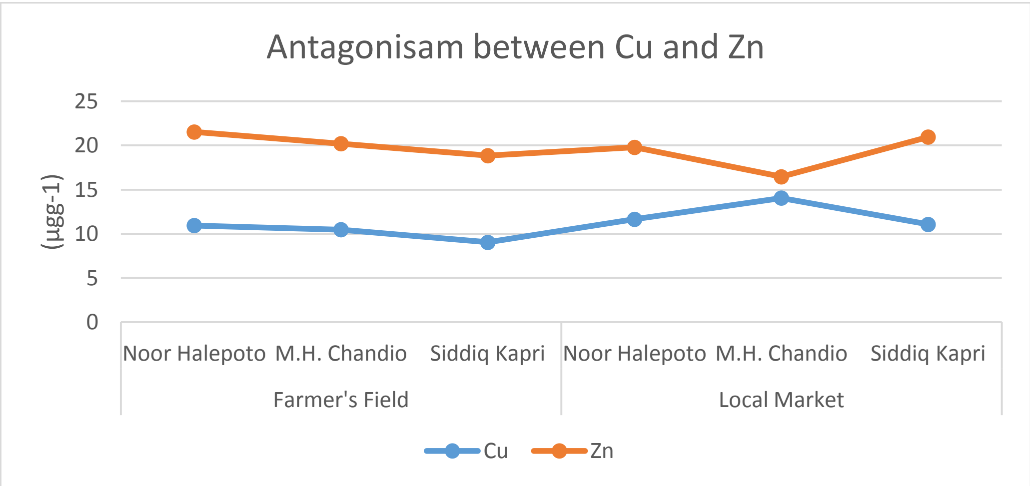

Fig.3. Antagonism between Copper and Zinc.

Table-1: Microwave Heating Program

Control Style : Ramp to Temperature Stage	Power		Ramp Time	Pressure	Temp	Stir	Hold Time
	Level	%	mm:ss	(psi - limit)	°C		mm:ss
1	400W	100	15:00	800	200	Off	15:00

Table-2: GTA Parameter for Cadmium and Lead

Metal	Temperature (^{o} C)		Auto-Sampler Volume (ml)		
	Ashing	**Atomization**	**Sample**	**Modifier**	**No. of Injections**
Cd	600	2500	15	5	3
Pb	400	2200	15	5	3

Table-3: Flame AA Parameters for Trace Metals:

Parameters	FLAME			
	Cu	**Zn**	**Fe**	**Mn**
Concentration Unit	mg/L	mg/L	mg/L	mg/L
Measurement mode	Integration	Integration	Integration	Integration
Wave Length (mm)	324.8	213.9	248.3	279.5
Slit Width (nm)	0.5	1.0	0.2	0.25.
Lamp Current (mA)	4.0	5.0	5.0	5.0
Background Correction	On	On	On	On

Table-4: Average metal contents in Dandicut chili samples in field and market.

Sampling Location	Villages	No. of sample	Replicates	Metals (μgg^{-1})					
				Cd	Pb	Zn	Cu	Fe	Mn
Farmer's Field	Noor Halepoto	20	3	0.028 ± 0.04	0.062 ± 0.05	21.53 ± 5.62	10.95 ± 0.61	116.47 ± 6.91	33.24 ± 2.65
	M.H. Chandio	20	3	0.026 ± 0.08	0.067 ± 0.04	20.21 ± 4.41	10.48 ± 0.91	100.83 ± 5.32	28.71 ± 0.81
	Siddiq Kapri	20	3	0.034 ± 0.06	0.054 ± 0.03	18.85 ± 2.81	9.04 ± 0.52	115.74 ± 4.18	30.35 ± 0.95
Local Market	Noor Halepoto	20	3	0.031 ± 0.02	0.091 ± 0.04	19.79 ± 1.92	11.65 ± 1.06	124.62 ± 6.22	32.03 ± 2.53
	M.H. Chandio	20	3	0.029 ± 0.01	0.091 ± 0.01	16.46 ± 0.51	14.06 ±2.17	126.8 ± 2.86	31.03 ± 0.56
	Siddiq Kapri	20	3	0.030 ± 0.03	0.085 ± 0.07	20.96 ± 1.93	11.07 ± 1.23	129.10 ± 1.46	35.31 ± 4.55
W.H.O Limits (μgg^{-1})				<0.10	<0.30	<100	<73	<425	<500

Zn contents in samples collected from all the villages were fond very low indicate either fields may be deficient or uptake and translocation may have been disturbed. Total amounts of zinc within healthy plants vary from 20- 100μgg^{-1} depending upon the contents of availability in soils. Market samples of Noor Halepoto and M.H Chandio showed an increase in zinc content while decrease in Siddiq Kapri's market sample was noted. Overall impact of post-harvest practices on Zn content was found non-significant.

Cu in samples collected field and market of M.S Chandio and Siddiq Kapri showed non-significant difference (p>0.05). Post-harvest practices; picking, drying, transportation and storage showed no influence and the safe levels of Cu was found. Concentration of manganese in chilli market were slightly high in two sample as compare to their field chilli. It is assumed that lower and higher concentration of Mn is due to the contents of these metals present in the soil in that particular growing season and uptake behavior of Chilli plant roots. Significant difference ($p>0.05$) in contents of field and market samples of M.H Chandio and Sidiq Kapri may be due to use of iron containing tools at drying and storage level (Table 4). Sufficient levels of Fe found in all studied samples.

Linearity of the system

These results were obtained on the bases of linear calibration line for each of the nutrient trace metals and heavy metals. The calibration lines for known concentration (at four levels of concentration) of each individual metal were plotted against their respective absorbance. These calibration curves for each studied metals represent the regression of determination are R^2= 0.996, 0.999, 0.998, 0.997, 0.994, 0.992 for Zn, Cu, Fe, Mn, Pb and Cd respectively. That reflects the good performance of the instrument and accuracy of the results of the analyzed metals.

Antagonism in Metals

It is reported by McLaughlin (2010) that accumulation of metals and metalloids in edible vegetable tissues are govern by important processes such as root uptake, root selectivity, ion interactions, rhizosphere processes, leaf uptake from the atmosphere, and plant partitioning. Concentration of Cu in all samples collected from field and market chilli was found to be remain low as compare to iron and in (1978) Brar and Sekhon has concluded in their experiment of up taking of nutrient by plant that Concentration of Fe can reduce the concentration of Cu. (Fig. 2). Likewise (Arora and Sekhon, 1982) has found that copper behaves antagonistically with zinc. Finding of the experiment is in agreement of the statement for all 3 villages. (Fig. 3)

In order to promote horticultural industry, standardization of pre-harvest and post-harvest management technologies are required. On the basis of the results of the studied samples it may be concluded that ongoing post-harvest technique/practices exerted no or less impact on metal toxicity in dandicut chilli variety grown in Kunri and its vicinity of Umerkot districts and was safe for human consumption described by (USDA, 2010). But More Research & Development work has to be done on different aspects of post-harvest management of vegetables and fruits such as fungus, aflatoxin etc. which may restrict the export of the chilli samples and effect the economy of Pakistan.

Reference

Arisar, A. B. (2011) “Kunri man discovers technique to get rid chillies of fungus”. *The Dawn*. Feb 14.

Arora, C. L. and Sekhon, G. S. (1982). The effect of soil characteristics on the zinc-copper interaction in the nutrition of wheat. *Jour Agric. Sci*. 99(01) pp 185-189

Brar, M. S., and Sekhon, G. S. (1978). Effect of zinc and copper application on the yield and micronutrient content of wheat (*Triticum aestivum L.). Jour. Ind. Soc. Soil. Sci.* 26(1):84-86

Cabrera C, Gallego C, Lopez MC, Lorenzo ML, Lillo E. (1993) “Determination of levels of lead contamination in food and feed crops”. *J AOAC Int*. 77:1249 –1252.

Gawalko EJ, Nowicki TW, Babb J, Tkachuk R, Wu S. (1997). Comparison of closed-vessel and focused open-vessel microwave dissolution for determination of cadmium, copper, lead, and selenium in wheat, wheat products, corn bran, and rice flour by transverse-heated graphite furnace atomic absorption spectrometry. *J AOAC Int*. 80(2):379-87.

John, B. and Wills R. B. H. (1989). *Prevention of post-harvest food losses fruits, vegetables and root crops*. A training manual by FAO. Rome.

Joint FAO/WHO Food Standard Programme Codex Alimentarius Commission. (2007). *Report of 38th Session of the Codex Committee on Food Hygiene. Houston, United States of America*. ALINORM 07/30/13.

Keller, C. (1995). Application of centrifuging to heavy metal studies in soil solutions. *Commun. Soil Sci. Plant Anal.* 26: 1621–1636.

McLaughlin M.J., Smolders E., Degryse F., Rietra R. (2011) Uptake of Metals from Soil into Vegetation. In: Swartjes F (Ed.) Dealing with Contaminated Sites. From Theory towards Practical Application. *Springer*. Dordrecht. pp 325–367.

Meyers, M. W., Fricke, F. L., Holmgren, G. G. S., Kubota, J. and Chaney, R. L. (1982). Cadmium and lead in wheat grain and associated surface soils of major wheat production areas in the United States. *Agron. Abs.* p. 34.

Memon, A. N. (2015). “Export of red chillies decreased from Pakistan due to ban by EU and Japan”. *Pak. Food journ*. P 28-30.

Mitchell, L. G. (1997). Solubility and phytoavailability of cadmium in soils treated with nitrogen fertilizers. M.Sc. Thesis. Department of Soil Science, University of Manitoba, Winnipeg, MB. 90 pp.

Sabukola, O.P., O.M. Adeniran, A.A. Odedairo, O.E. Kajihausa. (2010). Heavy metal levels of some fruits and leafy vegetables from selected market in Logos, Nigeria. *African J. of Food Sci.*, 4(2): 389-393.

USDA. (2010). *Dietary guidelines for Americans.* U.S department of Health and Human Services.

Zurea-Cosano, G.R. Moreno-Rojas, J. Salmeron-Egea, R. Pozo Lora. (1984). Heavy metal uptake from green house border soil for edible vegetables. *J. Sci. Food Agric.*, 49 (3): 307-314.