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ASSESSMENT OF HEAVY METALS CONCENTRATION IN INDIAN AND PAKISTANI VEGETABLES

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ABSTRACT: The current research was conducted to quantify the heavy metals accumulation in vegetables imported from India and compared with same vegetables collected from vegetable market in Pakistan. Green chili, capsicum, tomato and ginger were selected to analyze their heavy metal contents by atomic absorption spectrophotometer. Samples were prepared by dry ash method and wet digestion method to find out the efficient method for heavy metals analysis. Maximum concentration of heavy metals detected by dry ash method in Indian vegetables were of Cu (0.34ppm) in capsicum, Cd (0.0ppm) in capsicum, Cr (0.22ppm) in Ginger, Pb (0.22ppm) in ginger and Ni (0.14ppm) in Ginger while in Pakistani vegetables, it were of Cu (0.62ppm) in Tomato, Cd (0.04ppm) in Capsicum, Cr (0.17ppm) in Tomato, Pb (0.36ppm) in Ginger. Heavy metal contents determined by wet digestion method were of Cu (0.57ppm) in Ginger, Cd (0.01ppm) in capsicum, Cr (0.17ppm) in Ginger, Pb (0.27ppm) in capsicum while in Pakistani vegetables these were of Cu (0.19ppm) in Ginger, Cd (0.04ppm) in green chili, Cr (0.09ppm) in Tomato, Pb (0.25ppm) in Ginger. It was found that the concentrations of these heavy metals in vegetables of both the countries were within WHO/FAO permissible limits so at present these are not hazardous but long term use of these vegetables can magnify heavy metals contents in human body. For statistical analysis two factor ANOVA was run, which indicated that almost all the vegetables had accumulated heavy metals but there was a difference in the uptake of Indian and Pakistani vegetables.

Keywords: Heavy metals, Vegetables, Green chili, Capsicum, Ginger.

I. INTRODUCTION

In Pakistan industrial effluent and untreated sewage are being discharged into surface water bodies. The water deficiency in country, forces the farmers to use wastewater for irrigation of their crops and vegetables fields. Sewage water disposal in big cities of Pakistan and its hazardous effects are worsen with the passage of time because untreated sewage water is used for growing crops in the surroundings of urban areas [1]. Sewage and industrial wastewater contains high level of organic matter and nutrients along with heavy metals like Fe, Mn, Cu, Zn, Pb, Cr, Ni, Cd and Co. Plants have high capacity for accumulation of the heavy metal contents, some species accumulate specific heavy metals while other accumulate all heavy metals, which cause detrimental effects on human health. Leafy vegetables accumulate more concentration of heavy metals when grown in contaminated soil and water [2].It has been widely reported that health problems occurred due to heavy metals contamination of soil [3]. Metals such as iron, copper, zinc and manganese are essential metals but they may produce toxic effects when their levels exceed certain limits in organisms. High level of copper may produce toxic effects such as dermatitis and liver cirrhosis when consumed in excessive amounts in foods [4]. The objectives of this study were to estimate heavy metal concentration in vegetables imported from India and to compare the heavy metal contents of Indian vegetable with Pakistani vegetables collected from vegetable and fruit market.

II. MATERIALS AND METHODS

The present study was carried out to analyze the contamination of the heavy metals concentration in vegetables imported from India and compared with vegetables grown in Pakistan.

A. *Collection of samples:*

The samples of vegetables i.e. Tomatoes (*lycopersicon esculentum*), Ginger (*Zingiber officinale*), Green chilli (*Capsicum frutescens*), Capsicum (*capsicum annum*) that imported from India to Pakistan were collected from trucks which were shifting the vegetables from Wagha border to vegetable market. Same Pakistani vegetable samples were collected from Lari Adda Mandi and Iqbal Town market Lahore. The samples were taken in winter season in the month of December.

B. *Pretreatment of vegetable samples:*

The vegetables that collected from different sites coming from Wagha border were individually washed by distilled water to remove dust particles and non-edible parts were removed from them. After washing and cutting, the vegetables were dried in open air and then these vegetables were placed in an oven for 2-3 days at 80 °C. The hard dried vegetables were broken into small pieces by hammer and then these pieces were grinded into a fine powder (80 mesh) using a commercial blender (TSK-West point, France). The powdered material was stored in polythene bags and placed aside until further procedure was done.

C. *Heavy metal analysis:*

Samples were prepared for the analysis of heavy metals by dry ash method and wet digestion method to measure the process efficiency.

D. *Dry ash method:*

Electronic balance was used to weigh 1g powered sample of each vegetable in boron free silica crucibles then these samples were placed in the muffle furnace at 450 ^{0}C for at least two hours until ash was formed. Furnace was left for some time to get cool. Samples were removed from furnace and added 10ml of 0.7N H_2SO_4. Mixed the samples thoroughly and left the samples for one hour. A conical flask of 500ml was used to filter the samples with Whatmann filter paper no.42 and washed two to three times by using 5.0ml of 0.7N H_2SO_4. Samples were filtered again in volumetric flasks were used for heavy metal analysis.

E. Wet digestion method:

In wet digestion method, 0.5g sample of each vegetable was weighed by weighing balance and 5ml of concentrated HNO_3 was added into digestion flasks. Same quantity of HNO_3 was also added into empty digestion flask to run the blank sample. Kjeldahl digestion unit was used to digest samples at 80-90ºC for two hours. Temperature increased to 150ºC (boiling point) and 3 to 5ml of 30%H_2O_2 along with concentrated HNO_3 were added to start and continued the digestion until the clean solution obtained. Samples were cooled at room temperature. Solutions were filtered by Whatmann filter paper no. 42. Final volume was made to 25ml by using distilled water. Samples of both dry ash method and wet digestion method were put in an analyzer for the analysis of heavy metals by Atomic Absorption Spectrophotometer (FAAS, Shimadzu AA-7000F).

F. Statistical Analysis:

Concentrations of metals in various vegetables dry ash method and wet digestion method were compared by SPSS version-19.

II. RESULTS AND DISCUSSION

Deposition of heavy metals are associated with a wide range of sources such as brick kilns, small level industries (metal smelting, metal products, battery production, cable coating industries), suspended road dust, vehicular emission, diesel generators and coal combustion. Indian coal has poor quality and high concentration of heavy metals. These are all important contributor of heavy metals present in vegetables. Another source of heavy metal contamination in vegetables is the wastewater produced from domestic and industrial areas and used for irrigation purpose. This wastewater not only contaminates soil but also contaminate crops and vegetables grown in those fields containing contaminated soil. Other sources include excessive use of pesticides, fertilizers and sewage sludge. Industrial wastewater used for irrigation could be the major reason of heavy metal accumulation in vegetables. Cadmium can easily be taken up by the food crops especially leafy vegetables. Different vegetable species contain different heavy metals concentration depending on environmental conditions such as plant availability, metal species and type of irrigation practice. Heavy metal concentrations of plants is directly associated with their concentrations in soils, but their levels significantly differ with plant species [5].

A. Comparison of Pakistan and Indian Vegetables by Dry Ash Method:

1. Heavy metal concentration in Green chili

The heavy metal concentration of Cu and Pb obtained by dry ash method in Indian vegetables was 0.29ppm and 0.11ppm respectively and value of Cd, Cr and Ni were below detection limit. The value of Cu and Pb obtained in Pakistani vegetables by dry ash method was 0.07ppm and 0.18ppm and value of Cd, Cr and Ni were below detection limit (Fig. 1). It have been reported that local residents of an area near a smelter in Nanning, China have been exposed to Cd and Pb through consumption of vegetables but no risk was found for Cu and Zn [6, 7].

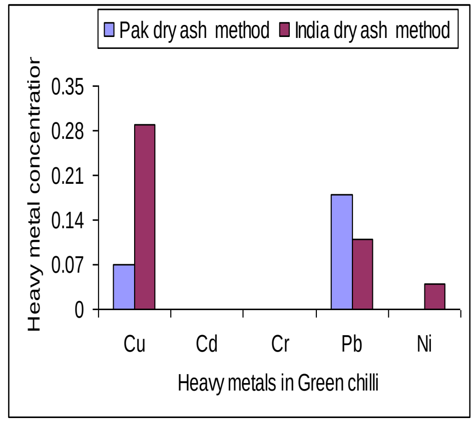

Fig. 1: Heavy metal concentration in Indian and Pakistani Green chili by dry ash method.

2. Heavy metal concentration in Capsicum:

The heavy metal concentration of Cu, Cd, Cr, Pb and Ni obtained by dry ash method in Indian vegetables was 0.34ppm, 0.01ppm, 0.09ppm, 0.12ppm and 0.13ppm respectively and values of Cu, Cd, Cr, Pb and Ni obtained in Pakistani vegetables by dry ash method were 0.08ppm, 0.04ppm, below detection limit, 0.07ppm and below detection limit respectively (Fig. 2). It have been studied the heavy metal contents in different vegetables grown in the lands irrigated by wastewater and noted the concentration of Cr to be within the safe limits [8].

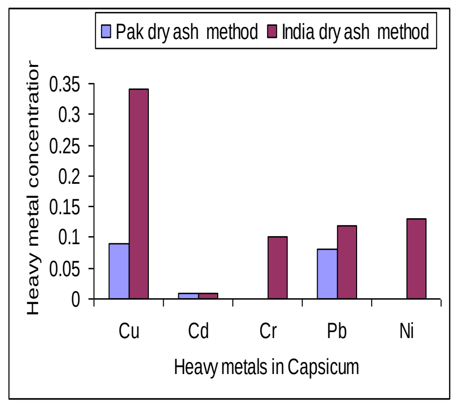

Fig. 2: Heavy metal concentration in Indian and Pakistani Capsicum by dry ash method.

3. Heavy metal concentration in Tomato:

The heavy metal concentration of Cu, Cd, Cr, Pb and Ni obtained by dry ash method in Indian vegetables was 1.27ppm, below detection limit, 0.18ppm, 0.13ppm and 0.05ppm respectively and values of Cu, Cd, Cr, Pb and Ni obtained in Pakistani vegetables by dry ash method were 0.62ppm, below detection limit, 0.17ppm, 0.23ppm and below detection limit respectively (Fig. 3). It have been analyzed various vegetables (cucumber, tomato, green pepper, lettuce, parsley, onion, bean, eggplant, pepper mint, pumpkin and okra) and reported that the Zn concentration (3.56–4.592 mg kg^{-1}) was within the recommended international standards[9].

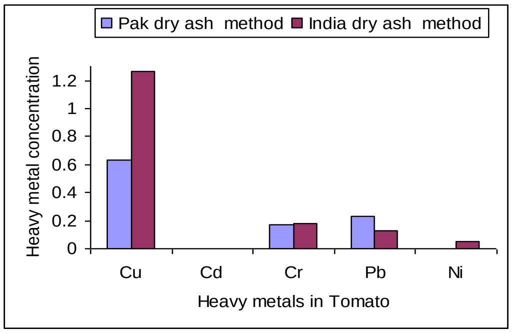

Fig. 3: Heavy metal concentration in Indian and Pakistani Tomato by dry ash method.

4. Heavy metal concentration in Ginger:

The heavy metal concentration of Cu, Cd, Cr, Pb and Ni obtained by dry ash method in Indian vegetables was 1.13ppm, below detection limit, 0.22ppm, 0.22ppm and 0.14ppm respectively and values of Cu, Cd, Cr, Pb and Ni obtained in Pakistani vegetables by dry ash method were 0.39ppm, below detection limit, 0.09ppm, and 0.36ppm and below detection limit respectively (Fig. 4).

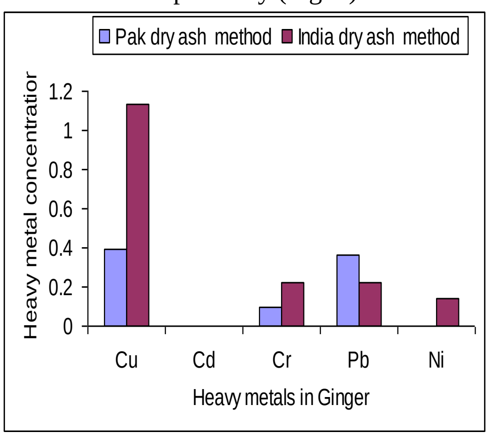

Fig. 4: Heavy metal concentration in Indian and Pakistani Ginger by dry ash method.

B. Comparison of Pakistan and Indian Vegetables by wet digestion Method:

1. Heavy metal concentration in Green chili:

The heavy metal concentration of Cu, Cd, Cr, Pb and Ni obtained by wet digestion method in Indian vegetables was 0.24ppm, below detection limit, below detection limit, 0.13ppm and below detection limit respectively and values of Cu, Cd, Cr, Pb and Ni obtained in Pakistani vegetables by wet digestion method were 0.06ppm, 0.02ppm, 0.07ppm, 0.20ppm and below detection limit respectively (Fig. 5). The estimated intake rates of Cu and Zn suggested that the contribution of vegetables to the intake of these heavy metals is low and does not pose potential health risk to consumers of vegetables [10].

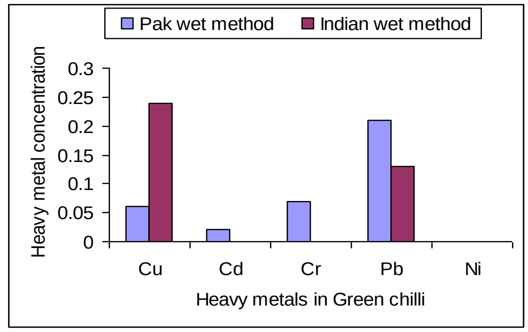

Fig. 5: Heavy metal concentration in Indian and Pakistani Green chili by wet digestion method.

2. Heavy metal concentration in Capsicum:

The heavy metal concentration of Cu, Cd, Cr, Pb and Ni obtained by wet digestion method in Indian vegetables was 0.43ppm, 0.01ppm, below detection limit, 0.27ppm and below detection limit respectively and values of Cu, Cd, Cr, Pb and Ni obtained in Pakistani vegetables by wet digestion method were 0.10ppm, 0.01ppm, 0.08ppm, 0.17ppm and below detection limit respectively (Fig. 6).

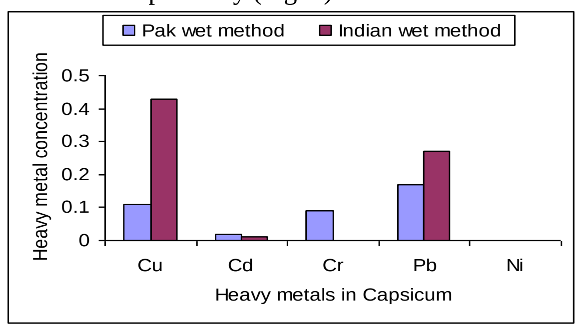

Fig. 6: Heavy metal concentration in Indian and Pakistani Capsicum by wet digestion method.

3. Heavy metal concentration in Tomato:

The heavy metal concentration of Cu, Cd, Cr, Pb and Ni obtained by wet digestion method in Indian vegetables was 0.28ppm, below detection limit, 0.10ppm, 0.15ppm and below detection limit respectively and value of Cu, Cd, Cr, Pb and Ni obtained in Pakistani vegetables by wet digestion method were 0.14ppm, 0.01ppm, 0.09ppm, 0.25ppm and below detection limit respectively (Fig. 7).

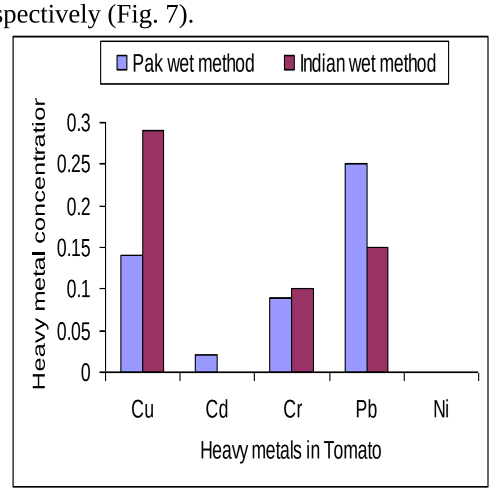

Fig. 7: Heavy metal concentration in Indian and Pakistani Tomato by wet digestion method.

4. Heavy metal concentration in Ginger:

The heavy metal concentration of Cu, Cd, Cr, Pb and Ni obtained by wet digestion method in Indian vegetables was 0.57ppm, below detection limit, 0.08ppm, 0.15ppm and below detection limit respectively and values of Cu, Cd, Cr, Pb and Ni obtained in Pakistani vegetables by wet digestion method were 0.14ppm, 0.02ppm, 0.17ppm, 0.25ppm and below detection limit respectively (Fig. 8). Heavy metals determined in different vegetables showed that the concentrations of Cu, Zn and Cd have often exceeded the safe limits of both Indian and FAO/WHO standards [11- 13]. However the concentration of Cu, Cd, Cr, Pb and Ni were lowered than given standard of WHO by both dry ash method and wet digestion methods but consumption of contaminated vegetables may pose risk to human health.

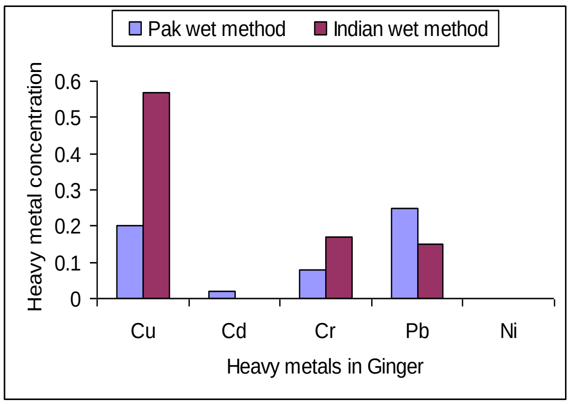

Fig. 8: Heavy metal concentration in Indian and Pakistani Capsicum by wet digestion method.

A. Statistical Analysis:

It was analyzed that the F value of Cu, Cd, Cr, Pb and Ni in vegetables were less than F Crit hence there were no difference in the uptake of Cu, Cd, Cr, Pb and Ni in different vegetables which means that all the vegetables contained Cu, Cd, Cr, Pb and Ni in it but the F value among the countries was more than F Crit value so there was a significant difference of concentration of Cu, Cd, Cr, Pb and Ni in vegetables of India and Pakistan (Table 1& 2).

Table 1: Relationship of copper, cadmium, chromium, lead and nickel uptake in various vegetables of India and Pakistan by wet digestion method.

	Concentration of metals in vegetables	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Wet Digestion Method	Copper	0.0595	3	0.019833	3.489736	0.166006	9.276628
	Cadmium	3.75	3	1.25	1	0.5	9.276628
	Chromium	0.0108	3	0.0036	1.064	0.4803	9.277
	Lead	0.00255	3	0.00085	0.180212	0.903481	9.276628
	Nickel	0	3	0	65535	----	9.276628

Table 2: Relationship of copper, cadmium, chromium, lead and nickel uptake in various vegetables of India and Pakistan by dry ash method.

	Concentration of metals in vegetables	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Dry Ash Method	Copper	0.901938	3	0.300646	8.489822	0.056199	9.276628
	Cadmium	0.00015	3	0.00005	2.77	1.17	9.276628
	Chromium	0.043338	3	0.014446	7.687361	0.063962	9.276628
	Lead	0.039438	3	0.013146	4.412587	0.127078	9.276628
	Nickel	0.0067	3	0.002233	1	0.5	9.276628

III. Conclusions

This research was conducted to quantify the heavy metals concentration in Pakistani and Indian vegetables. Samples were collected from the market. Pakistani vegetables were collected from vegetable market of Iqbal Town. Samples of Indian vegetables were collected from "lari adda mandi" from the trucks coming from Wagha Border. Samples of Indian and Pakistani vegetables were analyzed by using dry ash and wet digestion method. Heavy metals were analyzed both in Pakistani and Indian vegetables by using atomic absorption spectrophotometer. It was found that both Pakistani and Indian vegetables were contaminated with heavy metals but the concentration of these metals was not higher than WHO/FAO standards limits. As the long term usage of these contaminated vegetables may cause their accumulation in human body which can cause hazardous effects later in their lives. It was noted from the results that heavy metal contents were detected to be similar with both dry ash and wet methods except few in which concentration was detected to be more by dry ash method.

IV. Acknowledgements

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