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Potential Health Risk Assay of Major and Trace Metals *via* Consumption of Wastewater Irrigated Vegetables

FARIA NISAR[1,*], MUHAMMAD ASLAM MIRZA[1,*], RIFFAT NASEEM MALIK[2], MUHAMMAD AZIZ CH.[1] and SOMIA QAYYUM[1]

[1]Department of Chemistry, Mirpur University of Science and Technology, Mirpur-10250, Pakistan
[2]Environmental Biology and Ecotoxicology Laboratory, Department of Environmental Sciences, Quaid-i-Azam University, Islamabad, Pakistan

*Corresponding authors: Tel: +92 5827 961100; E-mail: fari.raja_77@yahoo.com; ma_mirza64@yahoo.com

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This study determines the potential health risk of metals to human health through consumption of fresh and waste water irrigated vegetables in the district Bhimber, Pakistan. Five samples of fresh and waste water vegetables *e.g.*, *Brassica oleracea capitata* (cabbage), *Coriandrum sativum* (coriander), *Brassica rapa* (turnip), *Raphanus sativus* (radish), *Spinacia oleracea* (spinach) and soil samples were collected and analyzed by atomic absorption spectroscopy (AA-240FS) for metals. Soil of waste water vegetables showed elevated levels of metals. Health risk index was evaluated which depicted the higher levels of heavy metal contents through consumption of waste water vegetables. The health risk index value for each fresh water vegetable was less than one indicating no threat for the consumers. However, the health risk index for each of the selected waste water vegetables was > 1. Therefore, consumption of waste water vegetables indicated a potential threat to the study area. Multivariate cluster analysis of selected metals indicated the common association of Ni-Pb with Fe-Ca and Cr-Zn. Correlation investigation depicted the positive association of K-Cu, Ca-Fe and Zn-Cr. Negative correlation such as K-Fe (-0.835), K-Ca (-0.956), Mg-Fe (-0.861) revealed the opposite distribution of metals in vegetables. Lead showed higher accumulation factor or translocation factor values both in fresh water and waste water irrigated vegetables thereby forecasting about the serious threat to the vegetable consumers.

Keywords: ***Brassica oleracea capitata, Coriandrum sativum, Brassica rapa, Raphanus sativus, Spinacia oleracea,*** **Toxicity.**

INTRODUCTION

Vegetables are rich in nutrients and energy. Most of the vegetables are rich in essential pigments, glycosides and oils *etc*. for the preparation of mixture of food. For the preparation of food, enormous number of species and varieties of vegetables are used as a raw material. Most of the vegetables are rich in carbohydrates [1].

Vegetables also contain mineral deposits such as, sodium, magnesium, iron, manganese, calcium, potassium and trace metals. Health reimbursement involves the vegetable utilization. It helps in lessening of diseases and control of body weight and these vegetables have little contented fats. Though quantity of sodium is less in vegetables but it helps to gain water. Within intestinal areas of body, sodium helps in water holding. Many vegetables are natural cancer fighter, like *Brassica oleracea capitata* [2].

In soil metals are present in different forms like exchangeable, dissolved, residual insoluble and structural constituents [3,4]. Availability and mobility of metals in soil determines their uptake to the plants [5]. Different soil factors such as pH, organic carbon *etc.* affect the mobility and availability of metals [6,7]. Among these, pH is an important factor that affects the solubility of metals in soil [8,9]. Lower pH increases the solubility of metals in soil thus causing the serious threat to human health as a result of consumption of the plants having higher uptake of metals [5,10]. The farming fields receive metals from different sources such as pesticides application, waste dumping, industrial wastes and fertilizer contamination [11,12].

However, irrigation of agricultural fields with waste water is of serious ecological alarm due to deposition of metals and their accumulation in soil and vegetables [13,14]. Due to toxic, non-biodegradability and accumulative nature of heavy metals, these are considered as fatal and toxic to environment and human beings [13,15-18]. Toxicity of metals affects human health like retardation of growth, increased abnormalities, mutagenic effects, mortality and impaired nervous system [19-21]. Therefore, present study is focused on determining the accumulation of metals in selected vegetables and their effects to local people *via* health risk index assessment.

EXPERIMENTAL

Sampling and digestion: The area under investigation was Bhimber city (Pakistan) covering about 15-20 Km^2. Samples were collected from two different irrigation zones, one from waste water irrigated zone and other from fresh water irrigated zone. Fresh water as well as waste water samples were collected. Samples were labelled and preserved in polythene bags and brought to Laboratory of Chemistry at Mirpur University of Science and Technology for analysis.

In order to remove soil particles and dust, samples of fresh and waste water irrigated vegetables were washed carefully with tap water and then rinsed with distilled water. Then, the samples were ground to fine powder. The powdered samples were stored in plastic bags for further analysis. Added 15 mL of mixture of acids (HNO_3, $HClO_4$ and H_2SO_4) in the ratio 5:1:1 into about 2 g of powdered sample in a beaker. The solution was heated slowly on hot plate to avoid the evaporation of contents of metals. When solution was about to dryness then added 10 mL of 0.5 N HNO_3 and the solution was filtered with Whatman filter paper No. 41. Made the level upto 30 mL with 0.5 N HNO_3 solution and stored in plastic bottles [22].

The samples of the soil were air dried and crushed into fine powder. Added 15 mL of aqua regia into 1 g of grinded soil and the solution was heated on hot plate. When solution was near dryness, filtered this solution and made the volume upto 30 mL with 0.5 N HNO_3 solution [23]. Metals were analyzed by flame atomic absorption spectrophotometer (AA-240FS).

Arithmetic analysis: Arithmetic analysis includes maximum, minimum, median, mean, standard error, standard deviation and Skewness. In order to determine concentration of metals, arithmetic analysis was done [24]. Correlation studies were done in order to determine the relationship between the metals explored [25]. Minitab software was used in order to analyze the basics and correlation study and also multivariate cluster analysis. To make molds on experimental data and levitating the knowledge on the concentration of different metals, arithmetic analysis was done [26].

Accumulation factor (AF): From soil, plants generally have different tendency to gather metals in their parts which can be shown by accumulation factor or translocation factor. Accumulation factor (AF) of metals was revealed as:

$$AF = \frac{\text{Metal concentration in the vegetables}}{\text{Metal concentration in the root soil}}$$

Risk assessment: Interview was conducted to local people including men, women, children and adults of Bhimber city and their data such as, diseases history, daily consumption of food and weight of body was composed.

Daily intake of metals (DIM): Average daily intake of vegetables was collected from data during survey.

$$DIM = \frac{C_{metal} \times C_{food\ intake} \times C_{Factor}}{B_{avg.\ wt}}$$

C_{metal} represents the concentration of metal in vegetables, $C_{food\ intake}$ shows daily consumption of vegetables which is 100 mg person^{-1} day^{-1}, C_{Factor} indicates the conversion factor (to convert dry weight into fresh weight, its value is 0.083).

Health risk index (HRI): Health risk index represents the human health risk index from contaminated vegetables consumption, which is expressed as:

$$HRI = DIM/RfD$$

RfD denotes the reference oral dose.

RESULTS AND DISCUSSION

Distribution of metals in vegetables: The distribution of metals in fresh and waste water vegetables is revealed in Tables 1 and 2. Prevailing mean levels of metals in fresh water vegetables are shown as: Na (1675.5 mg/Kg), Mg (879.0 mg/Kg), Ca (878.4 mg/Kg), Fe (342.4 mg/Kg) and K (302.0 mg/Kg). The decreasing trend of average metal levels in fresh water vegetables is Na > Mg > Ca > Fe > K > Zn > Ni > Pb > Mn > Cr > Cu. In waste water vegetables, the increasing trend of average metal levels is as follows: Cr < Cu < Mn < Pb < Ni < Zn < K< Fe < Ca < Mg < Na. In vegetables irrigated with fresh water, Zn, Pb and Fe indicated quartile dissemination whereas symmetric distribution of Ni, Pb and Zn was shown by the waste water irrigated vegetables (Figs. 1 and 2).

Correlation study of selected metals: To determine the common associations of metals, correlation study was done. Table-3 revealed the correlation study of fresh water vegetables. Very strong positive correlations are shown by K-Cu (0.972), Ca-Fe (0.842) and Zn-Cr (0.720). Opposite distribution of metals in vegetables revealed the negative correlation such as K-Fe (-0.835), K-Ca (-0.956), Mg-Fe (-0.861). Correlation study of wastewater vegetables was revealed in Table-4. A strong correlation was observed for following pairs; Ca-Ni (0.995), Cr-Cu (0.868) and Zn-Ni (0.754). Other metal pairs show very weak or negative correlation.

TABLE 1
STATISTICAL DISTRIBUTION PARAMETERS FOR SELECTED METALS (mg/kg) IN SOIL OF FRESH WATER IRRIGATED VEGETABLES

	Minimum	Maximum	Mean	Median	SD	SE	Skew
Cu	1.350	4.410	3.540	3.930	1.249	0.559	-2.02
Ni	1.590	47.940	33.770	37.830	18.560	8.300	-1.90
Mn	2.250	13.950	6.140	2.880	5.190	2.320	1.08
Cr	3.240	5.580	4.524	4.620	0.878	0.393	-0.54
Zn	72.20	176.300	110.500	101.900	43.900	19.600	0.89
Pb	4.200	50.700	24.160	28.800	19.410	8.680	0.29
Fe	303.500	387.500	342.400	346.900	32.700	14.600	0.27
Ca	760.500	1152.000	878.400	804.600	162.500	72.700	1.68
Mg	112.000	1498.000	879.000	1130.000	557.000	249.000	-0.55
K	214.800	338.500	302.000	317.800	49.500	22.200	-2.06
Na	1432.200	1865.900	1675.500	1723.100	164.300	73.500	-0.68

TABLE 2
STATISTICAL DISTRIBUTION PARAMETERS FOR SELECTED METALS (mg/kg)
IN SOIL OF WASTEWATER IRRIGATED VEGETABLES

	Minimum	Maximum	Mean	Median	SD	SE	Skew
Cu	3.930	10.080	5.595	4.965	2.235	0.912	2.260
Ni	42.000	60.240	51.300	49.090	7.400	3.020	0.039
Mn	6.930	48.300	29.430	30.180	15.240	6.230	-0.330
Cr	4.650	6.040	5.312	5.265	0.452	0.184	0.310
Zn	130.400	268.600	212.800	214.50	54.300	22.200	-0.450
Pb	41.400	66.000	51.450	50.400	8.000	3.270	1.200
Fe	368.200	512.500	456.700	470.500	52.100	21.300	-1.010
Ca	392.000	884.300	646.600	596.500	200.000	81.700	0.300
Mg	340.000	950.000	764.000	891.000	254.000	104.000	-1.240
K	216.700	313.400	279.800	287.300	36.700	15.000	-1.100
Na	1177.400	1602.600	1447.700	1455.300	160.100	65.400	-0.910

TABLE-3
CORRELATION COEFFICIENT OF SELECTED METALS IN SOIL OF FRESH WATER IRRIGATED VEGETABLES

	Cu	Ni	Mn	Cr	Zn	Pb	Fe	Ca	Mg	K
Ni	-0.161									
Mn	0.510	0.476								
Cr	-0.606	-0.239	-0.081							
Zn	-0.295	-0.117	-0.031	**0.720**						
Pb	-0.267	0.666	-0.149	-0.563	-0.613					
Fe	-0.750	0.653	-0.031	0.203	-0.175	0.669				
Ca	-0.873	0.273	-0.103	0.682	0.173	0.185	**0.842**			
Mg	0.843	-0.541	0.416	-0.126	0.004	-0.714	-0.861	-0.672		
K	**0.972**	-0.283	0.304	-0.647	-0.273	-0.263	-0.835	-0.956	0.816	
Na	0.906	-0.026	0.794	-0.331	-0.167	-0.390	-0.579	-0.604	0.849	0.789

$P \leq 0.05$ Significant

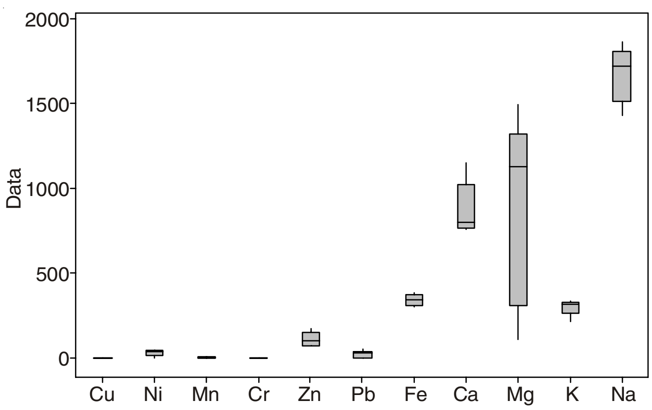

Fig. 1. Quartile distribution of selected metals in the soil of fresh water irrigated vegetables

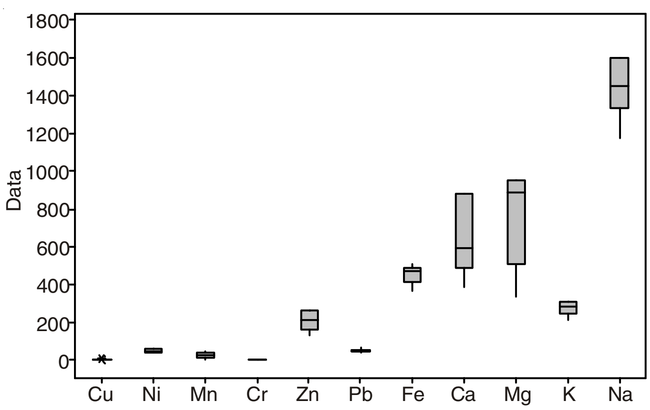

Fig. 2. Quartile distribution of selected metals in soil of wastewater irrigated vegetables

Multivariate cluster investigation of selected metals in vegetables: Multivariate statistics was done in order to govern the intricate nature of interrelation and distribution of metals. Figs. 3 and 4 represented the multivariate analysis by dendrogram. In Fig. 3, strongest cluster was shown by Ni-Pb which has common association with Fe-Ca and Cr-Zn, which were mostly paid by geogenic sources. Fig. 4 revealed the multivariate cluster analysis of waste water vegetables. Strongest cluster is shown by Fe-Pb which has common association with Mg-Mn revealed the anthropogenic contributions. Another cluster is shown by Cu-Cr followed by overwhelming contribution of Ni-Ca-Na-Zn-K.

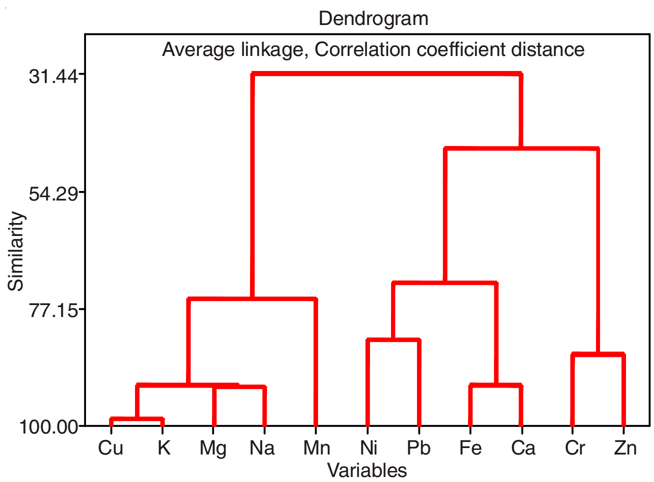

Fig. 3. Cluster analysis of selected metals in soil of fresh water irrigated vegetables

TABLE-4
CORRELATION COEFFICIENT OF SELECTED METALS IN SOIL OF WASTEWATER IRRIGATED VEGETABLES

	Cu	Ni	Mn	Cr	Zn	Pb	Fe	Ca	Mg	K
Ni	-0.045									
Mn	-0.815	-0.508								
Cr	**0.868**	-0.137	-0.734							
Zn	-0.137	**0.754**	-0.400	0.124						
Pb	-0.179	0.150	0.162	-0.131	0.199					
Fe	-0.315	**0.624**	0.066	-0.652	0.080	0.397				
Ca	0.053	**0.995**	-0.586	-0.062	**0.726**	0.106	0.598			
Mg	-0.787	0.318	0.442	-0.754	0.253	-0.351	0.307	0.256		
K	0.210	0.556	-0.564	0.118	0.371	-0.732	0.040	0.597	0.428	
Na	0.014	0.611	-0.499	0.299	0.913	-0.191	-0.206	0.605	0.285	0.610

$P \leq 0.05$ Significant

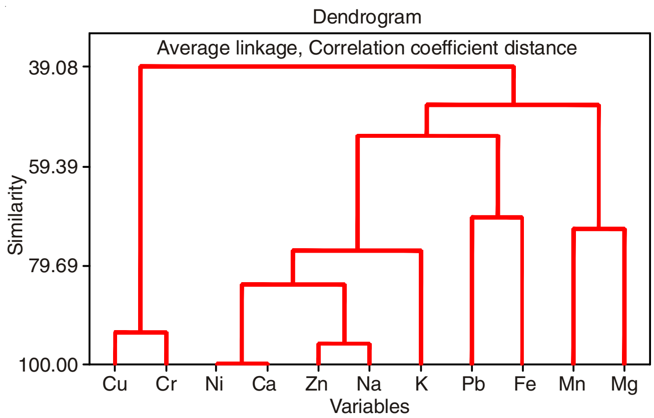

Fig. 4. Cluster analysis of selected metals in soil of wastewater irrigated vegetables

Accumulation factor (AF): Accumulation factor values of metals revealed that lead has highest level (2.8) in waste water vegetables (Fig. 5). The higher values of Pb both in fresh as well as waste water vegetables may be due to its higher mobility and load in waste water. Owing to different composition of soil, atmospheric composition and absorption capacity, metal concentration differs in various vegetables collected from same site. Accumulation factor is the best tool to evaluate the heavy metal level exposure through consumption of vegetables [21].

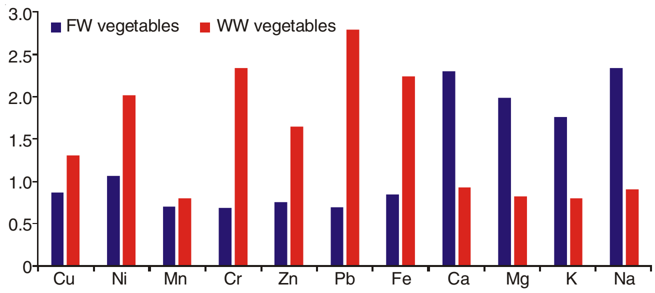

Fig. 5. Comparison of accumulation factor values of metals in fresh and wastewater

Daily intake of metal (DIM): Mean vegetable consumption indicated the daily intake of metals as represented in Fig. 6. The daily intake of metal values for Pb, Cr and Ni in wastewater vegetables is higher as compared to daily intake of metal values for these metals in vegetables irrigated with fresh water. It has been investigated through different researcher's reports that human toxicity is mainly attributed to their daily consumption of metal ions [13,27].

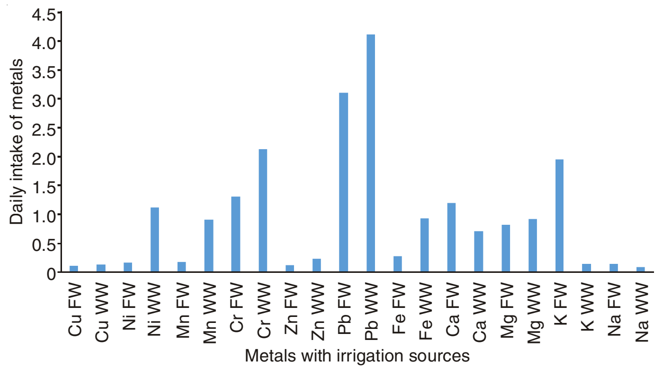

Fig. 6. Comparison of DIM values of metals in fresh and wastewater

Health risk index (HRI): Fig. 7 reveals the health risk index values of selected metals in fresh water (FW) and wastewater (WW) irrigated vegetables. The health risk index values of selected metals in fresh water irrigated vegetables were less than one indicating no threat to local consumers. However, health risk index of Pb, Cr and Ni was greater than unity in wastewater irrigated vegetables thereby posing a potential threat to local users.

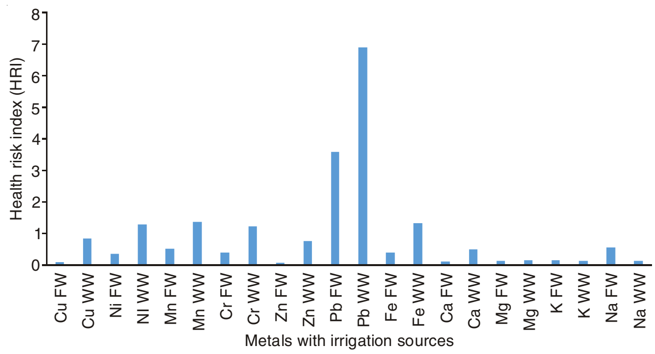

Fig. 7. Comparison of health risk index values of metals in fresh and wastewater

Conclusion

This study reveals that metal concentrations in wastewater irrigated vegetables were higher than those in fresh water vegetables; therefore, wastewater vegetables possess potential risk to residents of the studied area. The values of accumulation factor were higher in wastewater vegetables and in the order Pb > Cr > Ni > Fe. Results of health risk index disclosed that health risk index was > 1 for selected wastewater vegetables which were categorized as unsafe for the local consumers.

Quality control and safety rules for the consumption of waste water vegetables are considered unimportant in the study area. Therefore, awareness campaign regarding the consumption of food and regular monitoring in the study area are strongly recommended.

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