

## DETERMINATION OF TRACE HEAVY METALS IN DIFFERENT VARIETIES OF VEGETABLES AND FRUITS AVAILABLE IN LOCAL MARKET OF SHORKOT PAKISTAN

IFTIKHAR HUSSAIN BUKHARI\*, MUHAMMAD RAMZAN, MUHAMMAD RIAZ, TANVEER HUSSAIN BOKHARI, GHANA REHMAN, SHAHIDA MUNIR

Department of Chemistry, Government College University, Faisalabad 38000 Pakistan. Email: pdiftikhar@yahoo.com

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### ABSTRACT

Heavy metals determination in food stuffs is of vital interest because of their essential or toxic nature. In order to assess the levels and impact of different trace metals on human health, a study was carried out to determine the levels of different trace heavy metals present in commonly edible vegetables and fruits which are available in local market of Shorkot City. For this purpose, total of eleven samples of different varieties of vegetables and fruits were purchased from the market and then were analyzed for trace levels of seven essential heavy metals including Fe, Mn, Cu, Co, Ni, Cr and Zn and two toxic metals Pb and Cd. Dried samples were digested by wet digestion method in the mixture of Hydrogen peroxide ( $H_2O_2$ ) and Nitric acid ( $HNO_3$ ) and then were taken to the Atomic Absorption Spectroscopy for the metal determination. Perusal of the results obtained showed that Mn was analyzed as 0.220-3.334; Ni, 0.117-1.190; Zn, 0.245-3.873; Cu, 0.109-0.401; Co, 0.007-0.462; Cr, 0.211-1.298; Fe, 3.447-41.283; Cd, 0.002-0.627 and Pb was analyzed as 0.046-1.159mg/100g of sample dry weight. These values were found to be comparable with the literature values. The determined concentrations of metals in vegetables and fruits under investigation illustrated that these do not cause any major health hazards for the local consumers.

### INTRODUCTION

Micronutrients are necessary for a living thing to continue its life, but only in minor concentrations (vitamins and minerals). Specific nourishing demands of a living body are fulfilled through a combination of all types of macro and micronutrients [1]. Micronutrients cover the wide range of trace elements. These are chemical constituents that are found in plants, soil and living things naturally in minor amounts. Due the variation of the atmospheric condition their uptake varies through root to the shoot. Trace elements are also known as trace minerals. Healthy immune system, reproduction and optimum cell metabolic rate in human body depend upon 72 trace elements. Trace elements are the natural constituents of the soil [2]. Metals are categorized into four classes on the basis of their needs for the body. Some are required in greater amounts which include magnesium, sodium, zinc, potassium, copper, iron and calcium. Trace metals include chromium, lithium, vanadium, germanium, selenium, manganese, molybdenum, cobalt and others. Possible essential trace metals include rubidium, strontium, niobium, tin, arsenic, nickel, gold and silver [3]. Many other metals are xenobiotics because these have no beneficial role in body functioning and even very harmful in minor concentrations e.g., mercury and lead. Even those metals which are essential for body turn to toxic at high levels of exposure. Cadmium, beryllium, aluminum, uranium, mercury, lead, bismuth, barium, antimony etc. are included in toxic metals [4,5].

Copper (Cu) is an essential trace metal required for proper human health in an appropriate limit. Iron (Fe) is required for various highly complex actions that continuously happens on a molecular level and that are much needed for human life e.g. the transport of oxygen to the body [6]. Manganese (Mn) is very important for normal functioning of different body parts like brain and nerves [7]. Cobalt (Co) is another necessary heavy metal needed for the synthesis of vitamin B-12[8] Nickel (Ni) is considered as mandatory for number of different metabolic reactions in living beings[9]. Zinc (Zn) acts as coenzyme for about 200 enzymes. Lead (Pb) is a very dangerous poison and there is no safe level of Pb for human body. Cadmium (Cd) is one more toxic heavy metal in foodstuffs and natural world. It acts like a poison when exposed in considerable amount[10].

Food is the main source of uptake of toxic trace metals for human beings. Vegetables are taken as necessary portion of food either in cooked or raw form. The individuals of Pakistan, especially those of mediocre and low-income groups utilize a considerable quantity of vegetables and fruits. The requisite quantity of vegetables and fruits

in our routine diet should be 300-350 gm per individual whereas only 80 to 90 gm of vegetable and fruit per person is being utilized in routine diet by our inhabitants. Vegetables and fruits are called the Protective supplementary food. They are composed of high amounts of minerals, carbohydrates, vitamins, dietary fibers and essential amino acid, which are needed for healthy working of human metabolic reactions. They are also vital to neutralize the acid formed in stomach during digestion, besides being useful fibre according to food experts [11]. A complete profile of mineral and heavy metals must be available for the nutritionist and consumers. A lot of work has been done on metal determination in food stuffs. Data regarding the mineral contents is still lacking in developing countries like Pakistan. The present research work was designed to analyse the commonly edible vegetables and fruits available in local market of Shorkot, a city in Jhang District Punjab in Pakistan. Shorkot City is a pure agricultural area and soil is so fertile. Fields are irrigated with canal water. Vegetable and fruits cultivated in the city were never analysed before for metals. It was therefore necessary to analyse the level of trace elements concentration in different varieties of vegetables and fruits. The main aim of this research work was to assess the contents of trace heavy metals in different eight varieties of vegetables and three varieties of fruits available in local market for the consumers in Shorkot City, Pakistan.

### MATERIALS AND METHODS

Fresh samples of different varieties of commonly edible vegetables and fruits were collected from local market of Shorkot City, Pakistan. A total of eight varieties of vegetable including radish, carrot, spinach, garlic, methi (leaves), turnip, coriander (leaves) and greens (saag) and three varieties of fruits including oranges (pulp), berry fruits and guava were taken for the study. Firstly, samples were thoroughly washed to remove mud and dust and then rinsed with distilled water. Garlic, oranges, radish, turnip were peeled out. All fruit and vegetable samples were then sliced with the help of knife into small pieces. After that the samples were dried in air for few days and then in microwave oven at the temperature between 45 to 80°C till the constant weight was obtained. After drying, they were ground by electric grinder to tiny particle size and directly stored in fresh plastic containers for further analysis.

Wet acid digestion was done by standard methods reported by AOAC, 1990. 1.0 gm of each dried sample was added to 10 ml of conc.  $HNO_3$  in 50 ml beaker and placed on the electric hot plate for 1 hour to get semi dried sample. Again 10 ml of conc.  $HNO_3$  and 4ml of  $H_2O_2$  were added and again kept on hot plate and heated vigorously. Addition of  $HNO_3$  and  $H_2O_2$  was continued till to colorless solution

and its volume reduced up to 2-3ml. It was cooled and filtered with the help of Whatmann filter paper. The filtrate was stored in 10 ml sample bottles or vials. It was diluted up to 25 ml by de-ionized water before taking to Atomic Absorption Spectrometer.

Metal contents in the prepared samples were analyzed using Atomic Absorption Spectrophotometer (Hitachi Polarized Zeeman AAS, Z-8200, Japan) following the conditions described in AOAC (1990). Selected metals included Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Iron (Fe), Lead (Pb), Manganese (Mn), Nickel (Ni) and Zinc (Zn).

Calibrated standards were prepared from the commercially available stock solution in the form of an aqueous solution (1000 ppm). Highly purified de-ionized water was used for the preparation of working standards. All the glass apparatus used throughout the process of analytical work were immersed in 8N HNO<sub>3</sub> overnight and washed with several changes of de-ionized water prior to use.

## RESULTS AND DISCUSSION

Concentration of trace heavy metals in fruits and vegetables plants depends upon the soil of the cultivated area, the atmospheric condition and the irrigated water. In this study trace minerals such as Fe, Mn, Cu, Co, Ni, Cr and Zn and two toxic metals Pb and Cd were done by atomic absorption spectroscopy in mg/100 gm.

A thorough survey of data had shown in Fig. 1-9 shows that the heavy metal contents in analyzed samples were found in wide range. The levels of Mn were ranged from 0.220 to 3.334mg/100g of sample dry weight. The highest level was observed in saag while lowest in oranges. Concentration of Ni was ranged from maximum 1.190 in turnip to minimum 0.117mg/100g in bair. Levels of Pb were in range from 0.046-1.159mg/100g. Maximum level was found in methi while minimum in guava. Zn was ranged between 0.245 and

3.873mg/100g. Maximum concentration appeared in carrot while minimum in guava. Cu contents in vegetables and fruits varied in narrow range of 0.109 in bair to 0.401mg/100g in methi. The range of Cd was from 0.002-0.627mg/100g. Coriander showed maximum level of Cd while minimum level was found in bair. It was non-detectable in guava. Level of Co was ranged from 0.007-0.462mg/100g. It was observed maximum in saag and minimum in bair. In oranges, Co was non-detectable. Cr was observed in range of 1.298 in turnip to 0.211mg/100g in bair and guava together. Fe was ranged from 3.447 to 41.283mg/100g. Fe was observed maximum in spinach while minimum in guava. The contents of Mn, Cu, Cr, Ni, and Zn in all samples are similar. But slightly lower levels of Co and Cd were observed. The level of Fe was much higher in all samples followed by Pb which showed slightly higher contents.

Heavy metals affect the nutritive values of agricultural and food materials and also have harmful effects on human beings. National and international regulations on food quality set up the maximum permissible and acceptable levels of essential as well as toxic metals in human food. Hence an increasingly important aspect of food quality should be to control the concentrations of heavy metals in food stuffs.

Mn is an essential trace metal. Concentration of manganese in the vegetables and fruits studied was found to be in the range of 0.220-3.334mg/100g (Fig. 1). The study revealed that all the samples (except methi) contained less contents of Mn than the reported required intake. This might occur due to deficiency of Mn in the cultivated soils. Different studies showed different levels of Mn in carrot (1.2), spinach (1.001), orange (0.3), turnip (1.0), radish (1.0), guava (1.086), garlic (0.1152) [12][13]. No reliable data was found about coriander, methi, saag and bair. The difference in Mn contents could be due to difference in environmental and soil conditions.

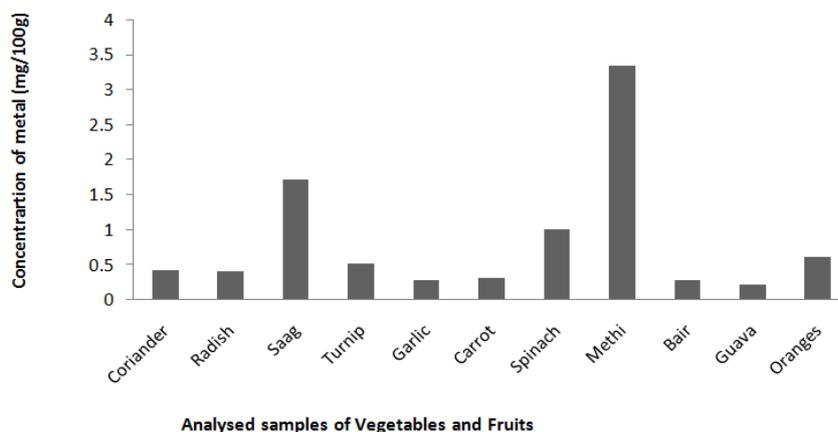


Fig. 1: Manganese level in vegetables and fruits

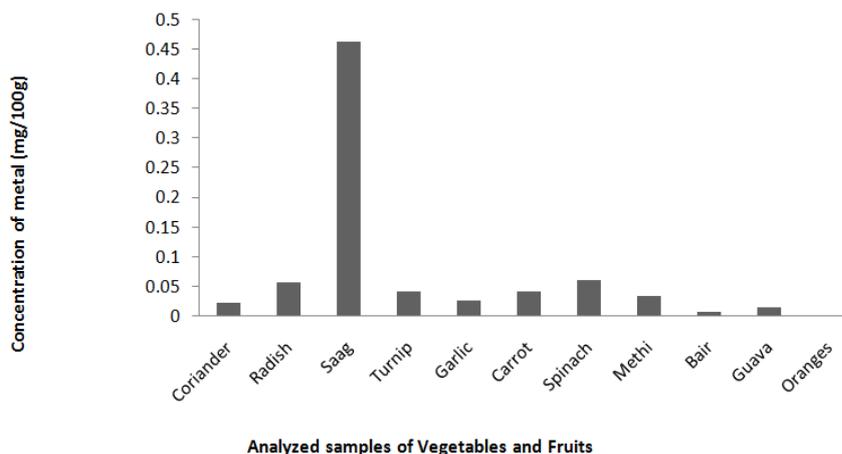
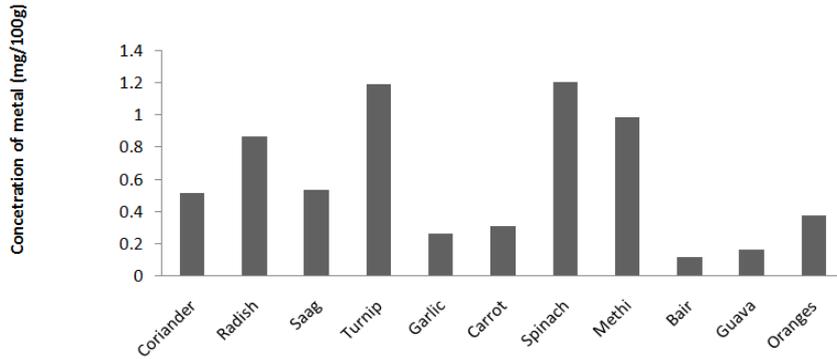
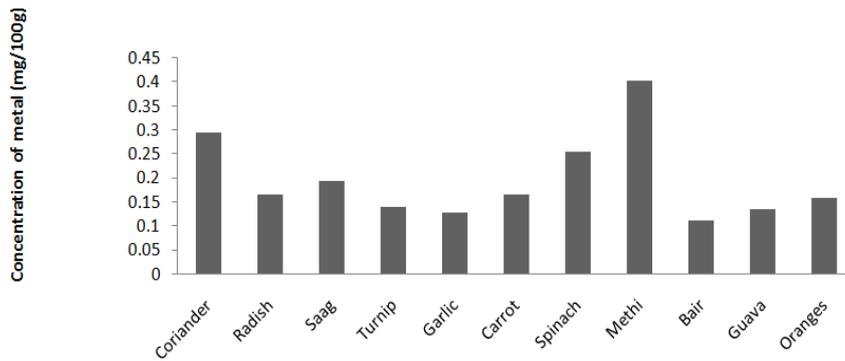


Fig. 2: Cobalt level in vegetables and fruits



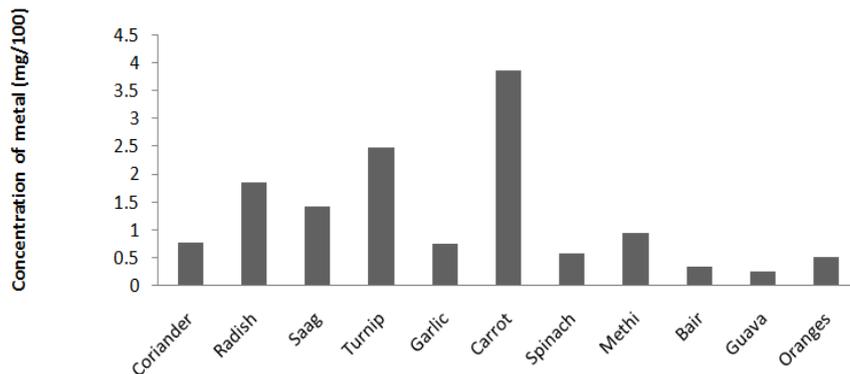
Analyzed samples of Vegetables and Fruits

Fig. 3: Nickel level in vegetables and fruits



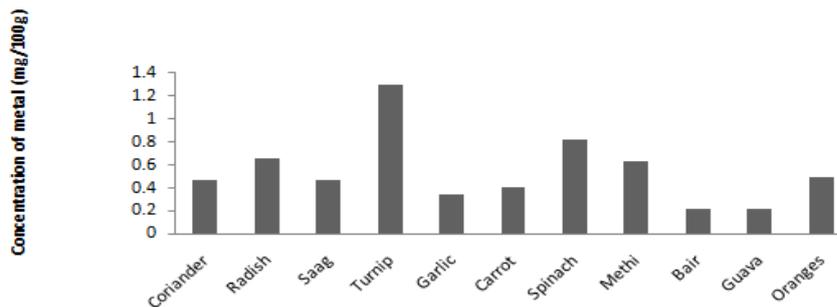
Analyzed samples of Vegetables and Fruits

Fig. 4: Copper level in vegetables and fruits



Analyzed samples of Vegetables and Fruits

Fig. 5: Zinc level in vegetables and fruits



Analyzed samples of Vegetables and Fruits

Fig. 6: Chromium level in vegetables and fruits

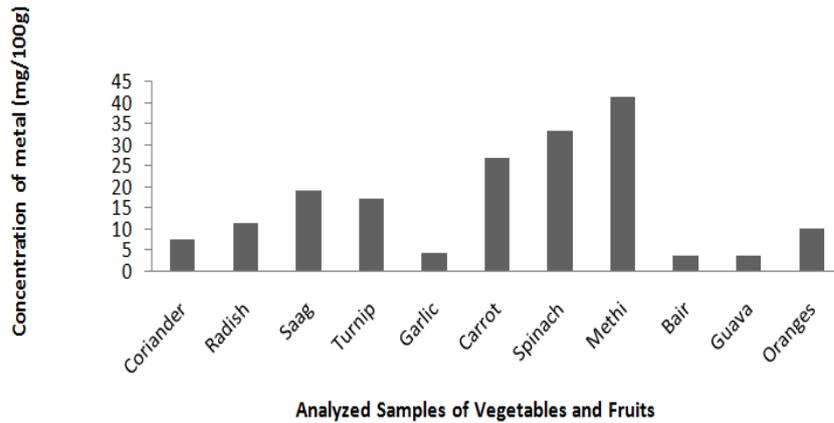


Fig. 7: Iron level in vegetables and fruits

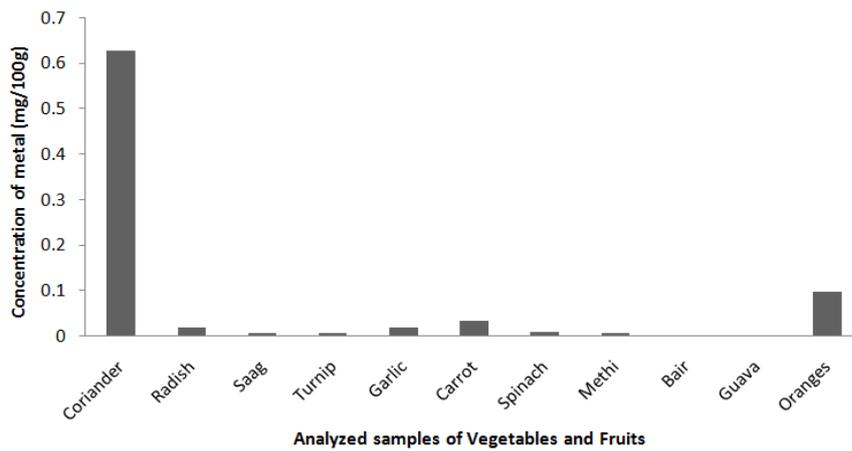


Fig. 8: Cadmium level in vegetables and fruits

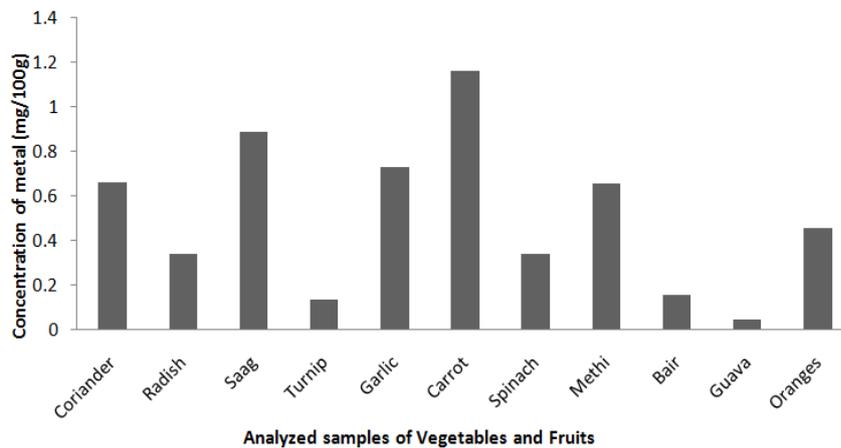


Fig. 9: Lead level in vegetables and fruits

Co contents were ranged from ND-0.462mg/100g (Fig. 2). In the past research studies a very little information has been reported about Co concentrations in food materials. Cobalt was found higher in saag as 0.462mg/100gm and lower concentration as 0.007mg/100g in bair. It was non-detectable in oranges. According to a study carried on Cobalt in different foods, Co variation in vegetables and fruits is 0.006-0.009mg/kg [14]. Analysis of data expressed that concentrations of Co in investigated samples of vegetables and fruits in the current study was within permissible range of safe limit.

The samples under investigation in the research work contained the level of Ni in the range of 0.117-1.201mg/100g (Fig. 3). Highest

concentration was present in spinach and lowest in bair. Our results reveal that the contents of Ni in some vegetables and fruits like spinach, radish, turnip and guava are slightly higher than the acceptable safe limit for the body. The elevated level of Ni may lead to the Nickel toxicity and potential health hazards for the local consumer.

In the present analysis contents of Cu were found in range of 0.109-0.401mg/100g (Fig. 4). Higher concentration occurred in methi while lower in bair. The acceptable range for human intake is up to 1.0mg/100g [15] and the daily recommended limit is 2-3 mg/day. Currents results revealed that all the samples contain the Cu level within the permissible range of recommended uptake limit.

However, in comparison to the previous research studies, the overall contents of Cu were found to be much lower. The level is found to be within the safe range of use for the local consumers.

Zn level found in the study was ranged from 0.245 to 3.873mg/100g as highest found in carrot while lowest in guava (Fig. 4.5). Previous research studies showed that carrot, spinach, orange, turnip, radish, saag, bair, coriander and methi contained 2.1, 3.31, 0.2, 2.4, 3.1, 8.68, 8.01, 2.71 and 3.09mg/100g respectively [11]. In the present study, Zn uptake had been observed much higher in all samples of vegetables and fruits. Consumers of these vegetables and fruits might accumulate higher Zn contents in their body. The reason for higher level of Zn uptake might be due to the use of Zinc Sulphate salt powder by the farmer to enhance the growth of plants. In view of this the determined concentrations of metals in vegetables and fruits under investigation do not cause health hazards for consumers.

Cr contents in our research work were observed between 0.211-1.298mg/100g. Highest concentration was found in turnip while lowest concentration together in guava and bair (Fig. 6). Very little information was available about the level of Cr in vegetable and fruits. However some research studies revealed that carrot, radish, garlic contained 0.089mg/100g [16]; 0.031, 0.013mg/100g, respectively. Analysis of the data obtained in current research work concluded that Cr did not apparently cause any health threat in view of its concentration levels in the vegetables and fruits investigated.

In present research work, Fe level in tested samples was varied between 3.447-41.283mg/100g (Fig. 7). Fe has the highest concentration of all metals both in the vegetables and fruits samples. Maximum concentration was found in methi while lowest in guava. In previous literature survey it was found that carrot, spinach, orange, turnip, radish, bair, coriander and methi contained 3.4, 30.9, 1.1, 4.0, 6.5, 3.1, 31.3 and 43.9mg/100g respectively. The present results were found in closeness with the reported results. Current study revealed that Fe contents were found in normal safe limit and there is no potential health hazard for the consumers.

Cadmium is a non-essential toxic heavy metal in foods and natural waters. In all samples analyzed in the research work, its level was observed to be low varying between ND-0.627mg/100g (Fig. 8). It was non-detectable in guava but coriander contained much high concentration of Cd than its safe acceptable limit. Various values had been previously reported for Cd in vegetables and fruits. These included 0.012, <0.001, 0.012, 0.008, 0.19, <0.001mg/100g for carrot, orange, turnip, radish, saag, bair respectively [11][16]. Our results were comparable with the reported work and apparently pose no health hazards to human beings.

The results of the current analysis showed that the levels of Pb in all samples were between 1.159 and 0.046mg/100g (Fig. 9). Carrot accumulated highest level of Pb while guava contained the lowest among the analyzed samples of fruits and vegetables. Survey of available literature illustrated that carrot, spinach, orange, turnip, radish, garlic, saag, bair accumulated 0.01, 0.631, 0.014, 0.012, 0.012, 0.036, 0.142, 0.21, and 0.008mg/100g of Pb respectively. Results of our study were comparable with already available values.

## CONCLUSION

Several national and international health associations are working all over the world for creating novel health standards. But under developed countries like Pakistan still have a little information regarding maintaining the standard composition. According to the study minerals were found in different varieties of vegetables and fruits which are locally grown in the fields of Shorkot in comparatively low concentration, such as essential trace elements as Co, Zn, Cu, Ni, Fe, Mn, Cr and toxic metals Cd and Pb. Considering the current level of Cd and Pb pollution in the environment, the level of these elements in all vegetables and fruits is within safe limit. Slightly higher level of Zn is found in some fruit and vegetables. The necessity of Fe and Zn make it indispensable that their concentration should be high. As the vegetables and fruits are good source of essential trace elements, they may provide the required amount of

trace metals to our body. Therefore, it was concluded from the results of the study that the levels of trace metals are within limits set down for safe human consumption.

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