

Determination of Trace Metals in the Vegetables Procured from Local Markets of Karachi City by Atomic Absorption Spectrophotometry

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Summary: A study was carried out to determine the accumulation of heavy metals in the vegetables by Atomic Absorption Spectrophotometry. Eighteen varieties of vegetables (belonging to nine different families), were procured from Federal B Area, Landhi and Korangi markets of Karachi city. The metals investigated were Fe, Cu, Mn, Zn and Cr. The level of Fe was found to be highest, whereas the level of Cr was lowest. The maximum concentration of Fe, Mn, Zn, Cu and Cr were found to be 65.63, 42.40, 31.50, 2.51 and 1.08 $\mu\text{g/g}$ in Spinach, ginger, potato, mustard and spinach, respectively. The overall contents of these trace metals in the vegetables investigated were found to be within the permissible limits recommended by the Food and Nutrition Board, USA. The results show that the accumulation of trace metals in these vegetables is of nutritional interest.

Introduction

Pollution due to heavy metals is now a worldwide phenomenon. Heavy metals are discharged into the environment through industrial activities, automobile exhaust, heavy duty electric power generators, refuse burning and pesticides used in agriculture, etc. Heavy metals play an important role in body metabolism. The deficiency of trace metals also cause diseases, whereas their excess presence cause toxicity to human life.

Food is the major intake source of toxic metals by human beings. Among different food systems, vegetables are most exposed food to environmental pollution due to aerial burden. Vegetables are consumed enormously in many countries and thus constitute one of the important food sources. It is therefore necessary to assess the level of trace metal contents in different varieties of vegetables.

Owing to their traditional food habit and economic considerations, a significant amount of vegetables is consumed by the people in Pakistan belonging to the middle and low income groups. Vegetables are considered as "Protective supplementary food" as they contain large quantities of minerals, vitamins, carbohydrates, essential amino acid and dietary fibers, which are required for normal functioning of human metabolic processes. Besides

being useful "roughage" they are also important to neutralize the acid produce during digestion.

Vegetables are staple part of food and are taken both in cooked and raw forms. The required amount of vegetables in our daily diet must be 300 to 350g per person has been suggested by WHO guidelines [1], whereas Butt and Haq [2] have estimated that only 80-90g of vegetable per person is being used in daily diet by our population. Therefore, determination of metal content in vegetables is important from the view point of crop yield technology, food nutrition and health impacts. In event of their presence in excess, these metals enters into the body and may disturb the normal functions of central nervous system, liver, lungs, heart, kidney and brain, produce hypertension, abdominal pain, skin eruptions, intestinal ulcer and different types of cancer [3].

Studies on the estimation of heavy metal content in the vegetables grown in different areas of Pakistan have been reported by some other worker [4-8]. The main aim of this study was to assess the present status of trace metals pollution in vegetables, procured from local markets of different localities of Karachi city. This paper reports the level of Fe, Cu, Mn, Zn and Cr studied in eighteen varieties of vegetables (belonging to nine different families)

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abundantly consumed by local population. The analysis was carried out using Atomic Absorption Spectrophotometry techniques.

Results and Discussion

The average concentration of Fe, Cu, Mn, Zn and Cr observed in 5 varieties of fruit vegetables are given in Table-1, 4 varieties of root vegetables are in Table-2, 4 varieties of stem vegetables are in Table-3, 5 varieties of leafy vegetables are given in Table-4. The data have been presented at 99 % ($\pm 2S$) confidence level for triplicate measurements in each of the case whereas, Table-5 shows the daily dietary allowance for the selected trace elements, recommended by National Research Council, USA [9].

Table-1 gives the concentration of trace metals observed in fruit vegetables. The Table shows that the maximum concentration of Fe was recorded 18.05 $\mu\text{g/g}$ in ladyfinger, Cu (2.48 $\mu\text{g/g}$) in tomato, Mn (2.86 $\mu\text{g/g}$) in Brinjal, Zn 7.24 $\mu\text{g/g}$ and Cr (0.70 $\mu\text{g/g}$) in tomato. Minimum concentration of Fe, Mn and Zn was found to be 10.14, 1.04 and 3.31 $\mu\text{g/g}$ respectively in pumpkin, Cu (1.41 $\mu\text{g/g}$) in Brinjal and Tori, and Cr (0.32 $\mu\text{g/g}$) in Tori.

Table-2 presents the concentration of trace metals observed in root vegetables. Table-2 shows that the maximum concentration of Fe, Cu and Mn was found 57.05, 1.58 and 7.81 $\mu\text{g/g}$ respectively in beet, whereas Zn and Cr 8.67 and 0.95 $\mu\text{g/g}$ respectively in carrot. Minimum concentration of Fe and Mn was found to be 12.91 and 1.2 $\mu\text{g/g}$ respectively in turnip, Cu, Zn and Cr (0.80, 2.90 and 0.70 $\mu\text{g/g}$ respectively) in radish,

Table-3 shows the concentration of trace metals in the stem-vegetables. Highest concentration of Fe was found to be 36.54 $\mu\text{g/g}$ in potato, Cu (1.73 $\mu\text{g/g}$) in garlic, Mn and Zn (5.26 and 7.94 $\mu\text{g/g}$ respectively) in ginger and Cr (1.0 $\mu\text{g/g}$) in onion. Minimum concentration of Fe and Cu was observed 10.88 and 1.06 $\mu\text{g/g}$ respectively in onion, Mn (1.30 $\mu\text{g/g}$) in potato, Zn (3.27 $\mu\text{g/g}$) in garlic and Cr (0.47 $\mu\text{g/g}$) in ginger.

Table-4 shows the concentration of trace elements in the leafy vegetables. This group of vegetables shows the highest concentration of Fe as compared to fruit, root and stem. The maximum concentration of Fe was found to be 65.63 $\mu\text{g/g}$ in

TABLE-1: Concentration of Heavy Metals ($\mu\text{g/g}$) observed in five varieties of Fruit Vegetables

| S. No | Vegetables | Family | Fe | Cu | Mn | Zn | Cr |
|-------|-------------|---------------|-----------------|----------------|----------------|----------------|----------------|
| 1 | Lady finger | Malvaceae | 18.05 \pm .05 | 2.47 \pm .01 | 2.65 \pm .00 | 6.99 \pm .01 | 0.51 \pm .01 |
| 2 | Pumpkin | Cucurbitaceae | 10.14 \pm .03 | 1.49 \pm .03 | 1.04 \pm .00 | 3.31 \pm .01 | 0.45 \pm .01 |
| 3 | Tomato | Solanaceae | 13.41 \pm .03 | 2.48 \pm .01 | 1.75 \pm .02 | 7.24 \pm .01 | 0.70 \pm .02 |
| 4 | Brinjal | Solanaceae | 14.10 \pm .01 | 1.41 \pm .02 | 2.86 \pm .01 | 3.79 \pm .02 | 0.69 \pm .02 |
| 5 | Tori | Cucurbitaceae | 11.87 \pm .04 | 1.41 \pm .01 | 1.15 \pm .00 | 6.02 \pm .02 | 0.32 \pm .01 |

Table-2: Concentration of Heavy Metals ($\mu\text{g/g}$) in four varieties of Root Vegetables

| S. No | Vegetables | Family | Fe | Cu | Mn | Zn | Cr |
|-------|------------|----------------|-----------------|----------------|----------------|----------------|----------------|
| 1 | Beet | Chenopodiaceae | 57.05 \pm .05 | 1.58 \pm .03 | 7.81 \pm .01 | 9.23 \pm .02 | 0.71 \pm .01 |
| 2 | Radish | Crucifereae | 18.41 \pm .03 | 0.80 \pm .01 | 1.40 \pm .02 | 2.90 \pm .25 | 0.70 \pm .01 |
| 3 | Carrot | Umbilifereae | 20.26 \pm .07 | 0.90 \pm .02 | 1.54 \pm .01 | 8.67 \pm .01 | 0.95 \pm .01 |
| 4 | Turnip | Crucifereae | 12.91 \pm .35 | 1.11 \pm .05 | 1.22 \pm .02 | 3.15 \pm .01 | 0.93 \pm .01 |

Table-3: Concentration of Heavy Metals ($\mu\text{g/g}$) in four varieties of Stem Vegetables

| S. No | Vegetables | Family | Fe | Cu | Mn | Zn | Cr |
|-------|------------|---------------|-----------------|----------------|----------------|----------------|----------------|
| 1 | Potato | Solanaceae | 36.54 \pm .11 | 1.17 \pm .03 | 1.30 \pm .00 | 3.35 \pm .01 | 0.51 \pm .01 |
| 2 | Ginger | Zingaberaceae | 13.27 \pm .14 | 1.26 \pm .02 | 5.26 \pm .02 | 7.94 \pm .02 | 0.47 \pm .01 |
| 3 | Garlic | Liliaceae | 18.77 \pm .07 | 1.75 \pm .02 | 4.21 \pm .00 | 3.27 \pm .02 | 0.50 \pm .00 |
| 4 | Onion | Liliaceae | 10.88 \pm .06 | 1.06 \pm .01 | 1.56 \pm .01 | 5.83 \pm .02 | 1.00 \pm .01 |

Table-4: Concentration of Heavy Metals ($\mu\text{g/g}$) in five varieties of Leafy Vegetables

| S. No | Vegetables | Family | Fe | Cu | Mn | Zn | Cr |
|-------|------------|----------------|-----------------|----------------|-----------------|-----------------|----------------|
| 1 | Mustard | Crucifereae | 40.50 \pm .04 | 2.51 \pm .21 | 16.42 \pm .01 | 6.76 \pm .00 | 1.05 \pm .01 |
| 2 | Cabbage | Crucifereae | 14.80 \pm .04 | 0.72 \pm .02 | 2.30 \pm .04 | 2.83 \pm .02 | 1.01 \pm .01 |
| 3 | Spinach | Chenopodiaceae | 65.63 \pm .02 | 2.12 \pm .03 | 13.45 \pm .02 | 10.38 \pm .01 | 1.08 \pm .01 |
| 4 | Coriander | Umbellifereae | 52.00 \pm .10 | 2.51 \pm .03 | 8.63 \pm .01 | 7.29 \pm .02 | 0.96 \pm .00 |
| 5 | Mint | Labiataee | 57.00 \pm .08 | 2.41 \pm .02 | 9.00 \pm .01 | 5.76 \pm .03 | 0.89 \pm .01 |

spinach, Cu (2.51 $\mu\text{g/g}$) in mustard and coriander, Mn (16.42 $\mu\text{g/g}$) in mustard, Zn (10.38 $\mu\text{g/g}$) in spinach and Cr (1.08 $\mu\text{g/g}$) in spinach. Minimum concentration of Fe, Cu, Mn and was found to be 14.8, 0.72, 2.30 and 2.83 $\mu\text{g/g}$ respectively in cabbage and Cr (0.89 $\mu\text{g/g}$) in mint.

Trace elements are present in the body in very low amounts, usually less than 1 micro-organism per gram of the tissue [9]. Iron plays an important role in human body metabolism. It acts as a catalyst and is present in amount greater than that of any other trace element. According to an estimate, 57.6% of the body iron in human being is contained in hemoglobin and 8.9 % in myoglobin. Approximately 33% in non-heme iron complexes including ferritin and hemosiderin. The cytochrome and catalase enzyme contains about 0.5 % of iron [10]. The heme pigments, hemoglobin in erythrocytes and myoglobin in muscles function as oxygen carriers. The maximum concentration of iron was found to be 65.6 $\mu\text{g/g}$ in spinach. National Research Council recommended the dietary allowance of iron for male is 10 -12 mg and 15 mg for female during pregnancy and the recommended limit of iron is upto 30 mg [9].

Copper is an essential trace element for normal biological activities of aminoxide and tyrosinase enzymes. Excessive intake of copper may cause hemolysis, hepatotoxic and nephrotoxic effects. The maximum concentration of copper 2.51 $\mu\text{g/g}$ found in coriander and mustard (leafy vegetables) as the leaves are the most exposed part of the plant from aerial burden. The mean daily intake of copper from UK Total Diet Study (TDS) fell from 2.3 mg/person to < 1.6 mg/person [11], whereas, according to an estimate 1.5 to 3.0 mg/day of dietary copper has been determined to be safe and adequate for human consumption [9].

Manganese is essential for normal growth, skeletal formation and for normal reproductive function in mammals and poultry. The estimated safe and adequate daily dietary intake (upper limit) in adults is 11mg/day [9]. The maximum concentration of manganese 16.42 $\mu\text{g/g}$ found in Mustard used as leafy vegetable. According to Schroeder and his coworkers, manganese deficiency causes diabetes, nervous instability, disorder of bony cartilaginous, growth in infant and children and rheumatic arthritis in adults [12].

Zinc is an intercellular cat-ion present in all body tissues and fluids and next to iron, is the second most abundant of the trace metals in humans. Zinc is important for enzymatic function. It takes part in the synthesis of DNA, protein and insulin. It is also essential for normal functioning of the cell including protein synthesis, carbohydrate metabolism, cell growth and cell division. The maximum concentration of zinc 10.38 $\mu\text{g/g}$ found in spinach also used as leafy vegetable. A normal body contains 1.4 to 2.3 g of zinc and it is present in all body cells. Recommended daily dietary intake of zinc is about 15 mg for adult males and 12 mg for females. An increase in intake to 30 mg/day is recommended during pregnancy [9].

Chromium is present in human tissues in variable concentration and its deficiency is characterized by disturbance in glucose, lipids and protein metabolism [13]. The maximum concentration of chromium 1.05 $\mu\text{g/g}$ was found in Mustard. The daily chromium intake of 50 to 200 μg has been recommended for adults by the US National Academy of Sciences. Whereas, from the TDS the weighted mean upper intake limit of chromium was 136 $\mu\text{g/person /day}$ and lower intake limit were 111 $\mu\text{g/person /day}$ [11].

Trace elements are present in human body in very low amount, some elements are essential trace elements and some are not essential but have well defined evidence in human metabolism. Fe and Zn are the essential trace elements for human metabolism and have recommended dietary allowance (RDA), Whereas Cu, Mn and Cr which have defined evidence for the essentiality in human metabolism but RDA has not yet been established; only the estimated safe dietary daily intake limits have been established. The comparison of recommended dietary allowance and safe daily dietary intake of trace elements with our analyzed values of trace elements are given in Table-5.

Table-6 shows the approximate daily intake of metals by human beings from mixed vegetables. The intake values are calculated by taking the average value of metals in all the eighteen varieties of the vegetables and considering that each person consumes approximately 200g (fresh weight) and 50g (dry weight) of vegetables per day. Although different vegetables are consumed variably by different segments of population at different time

Table-5: Recommended Dietary Allowance and Estimated Safe Daily Dietary Intake of Trace Elements for Human Beings

| S. No. | Elements | Maximum Concentration of Elements in the analyzed vegetables in $\mu\text{g/g}$ | | | | Recommended Dietary Allowance (RDA) | Estimated Adequate Intake | Safe Daily Dietary Intake |
|--------|----------|---|-------|-------|--------|---------------------------------------|---------------------------|---------------------------|
| | | Fruit | Root | Stem | Leaves | | | |
| 1 | Fe | 18.05 | 57.05 | 36.54 | 65.6 | 15 mg for Female 10-12 mg for Male | Nil | Nil |
| 2 | Zn | 7.24 | 9.23 | 7.94 | 10.38 | 12-15 mg for Female 15 mg for Male | Nil | Nil |
| 3 | Cu | 2.48 | 1.58 | 1.75 | 2.51 | Nil | 0.9mg | |
| 4 | Mn | 2.86 | 7.81 | 5.26 | 16.42 | Nil | 11mg | |
| 5 | Cr | 0.70 | 0.95 | 1.00 | 1.08 | Nil | 25-35 μg | |

Table -6: Estimated Daily Intake of Fe, Cu, Mn, Zn and Cr through vegetables

| S. No | Trace Element | Average conc. of 18 vegetables (mg/g) | Intake by human being (mg/g) | WHO Limits for Human consumption |
|-------|---------------|---------------------------------------|------------------------------|----------------------------------|
| 1 | Fe | 26.42 | 1320.5 | 10-60 mg/day |
| 2 | Cu | 1.60 | 80.5 | 2-3 mg/day |
| 3 | Mn | 6.70 | 335.0 | 0.5 5.0 mg/day |
| 4 | Zn | 7.36 | 368.0 | 15 mg/day |
| 5 | Cr | 1.23 | 61.5 | 50-80 $\mu\text{g/day}$ |

throughout the year, yet it may be a realistic estimate for the average intake of metals from vegetables. It may however be seen in Table-6 that intake of toxic metals from vegetable is not high and is within the permissible limits recommended by WHO [14].

Experimental

All the vegetable samples were randomly collected from different market located in Landhi, Korangi and Federal B Area of Karachi city in 2004. Three samples of each variety of vegetable were collected from each area and hence nine samples of each variety of vegetables were studied. All the samples were separately washed with distilled water and air-dried. The dried samples were then cut into the pieces with Teflon knife and further dried at $80 \pm 1^\circ\text{C}$ for 1h.

Known amount of dried samples were wet ashed with 5 - 10 ml (1:1) $\text{HNO}_3 - \text{HClO}_4$ mixture and heated near to dryness in a platinum crucible, few drops of hydrofluoric acid were added and heating was continued to dryness. The residue was then treated with 10 ml concentrated HCl and after boiling for 30 minutes, 20 ml distilled water was added and the solution was further heated for 15 minutes, after that filter the solution and made up to 50 ml [15]. Analysis of Fe, Cu, Mn and Zn were carried out by flame (FAAS) and Cr by flameless (ETAAS) Atomic Absorption Spectrophotometer

(Hitachi Z-800), with Zeeman Effect back ground correction, using standard addition method. All reagents used for the preparation of samples for analysis were of ultra high purity grade. BDH, Spectrosol standard stock solutions were used for calibrations. The purity of distilled water used for the preparation of all the reagents and calibration standards was equivalent to ASTM Specification Type II reagent water [16].

Conclusions

Among all the vegetables investigated, leafy vegetables showed the highest concentration of Iron metal. The overall zinc concentration remained up to $10 \mu\text{g/g}$. The concentration of copper and chromium were quite lower in all types of vegetables, whereas manganese showed slightly higher concentration, but was found within permissible limits. This study concludes that almost all the groups of vegetables investigated, the heavy metal contents were found within acceptable limits and are safe for human consumption.

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