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Research Article

DETERMINATION OF CONCENTRATION OF HEAVY METALS AND TRACE MINERALS IN SELECTED FRUIT AND VEGETABLES FROM DELHI NCR REGION

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ABSTRACT

The objective of the current research was to determine the concentration of heavy metals and trace minerals in six fruit and vegetable samples (Cucumber, Cauliflower, Watermelon, Apple Gourd and Onion) collected from different sources in the Delhi-NCR region. The concentration was analyzed for eight metals: Sodium, Calcium, Magnesium, Potassium, Zinc, Lead, Cadmium and Mercury by using ICP-MS whereas iron concentration was analysed by Thiocyanate calorimetry. The samples were prepared by dry ashing method. The analysis results for the heavy metals (Zinc, Cadmium, Mercury and Lead) were found to be below 1ppm level which is the legal limit as per Food safety and standards (contaminants, toxins and residues) regulation, 2011. The trace minerals were also found to be below their toxic dosage which may cause any harm to body upon ingestion. The results of analysis of trace minerals showed that that although there was variation in concentration of four trace metals namely: Sodium, Magnesium, Potassium and Calcium in fruit and vegetable samples collected from different sources of the same species yet the concentration of the trace metals was below the toxicity dosage. Therefore the fruit and vegetables samples under study will not cause any harm to the consumer in relation to the trace minerals content upon ingestion.

INTRODUCTION

Indian dietary pattern varies widely according to the geographical conditions yet vegetables and fruits form a significant portion of the people's diet. Nutritional awareness among people has led to gradual increase in the consumption of vegetables due to their high nutritive value (Sridhara Chary, Kamala, & Samuel Suman Raj, 2008) (SONG *et al*., 2009). Due to traditional irrigational practices and lack of awareness among farmers, a significant portion of fruits and vegetable cultivation is irrigated by wastewater from sources such as municipal waste, agricultural waste, etc. (Alam, Snow, & Tanaka, 2003)(SONG *et al*., 2009) (Sridhara Chary *et al*., 2008) (Chopra & Pathak, 2012) (Chang *et al*., 2014). Wastewater is preferred for irrigation by farmers as it is abundant in organic matter which serves as a ready source of nutrients (SONG *et al*., 2009) (Chopra & Pathak, 2012) (Chang *et al*., 2014). The continued use of wastewater along with the atmospheric deposition on plants surface due to industrial soot, automobiles' smoke among others has led to heavy metals accumulation in the fruits and vegetables via root uptake or foliage. According to (Luo *et al*., 2011), broccoli cultivated in areas of electronic waste processing sites in China was found to be contaminated by Cd (0.79 mg/kg) and lettuce was contaminated by high Pb levels (0.38 mg/kg). The radish cultivated in Titagarh, India was found to be contaminated by Cd (17.79 mg/kg) and Pb (57.63 mg/kg) (Gupta, Khan, & Santra, 2008). Some of the heavy metals (Fe, Cu, Zn, etc.) etc are considered essential for human body as they serve as micro nutrients at low concentration but become toxic at elevated concentration (Singh, Mohan, Sinha, & Dalwani, 2004). Vegetables and fruits when contaminated with heavy metals if consumed can lead to various diseases and disorders like diminished immunity, intra uterine growth retardation, weak psycho-social behavior, cardiovascular, nephratic, malnutritional disorders, bone disorders, etc. (SONG *et al*., 2009) (Chang *et al*., 2014) (Gebrekidan, Weldegebriel, Hadera, & Van der Bruggen, 2013). Heavy metals accumulated in vegetables may lead to neurotoxic, carcinogenic, teratogenic and mutagenic effects causing a number of diseases (Patra, Wagh, Jain, & Hegde, 2010). Vegetables contaminated with heavy metals can lead to serious health problems (SONG *et al*., 2009). Fruits serve as significant source of essential minerals. Many fruits being low in Sodium content serve beneficial to people having high blood pressure problem. Some fruits are rich in Magnesium which has potential anticancer effects (AOAC, 1999).

MATERIAL AND METHODS

Sample procurement

For the present study five vegetables and one fruit were taken namely: Cauliflower, Cucumber, Onion, Water melon, Tinda (Apple Gourd) and Orange. The vegetable samples were taken

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from three sources: 1) From the fields around Sonepat city. 2) From the Supermarket of Rohini, New Delhi (Reliance Fresh). 3) From Azadpur vegetable market at New Delhi. The Fruit samples of orange were taken from three sources from local vendors of Sonepat city, Supermarket of Rohini, New Delhi (Reliance Fresh) and from Azadpur vegetable market at New Delhi. From the fields, samples were taken by representative sampling by taking from four corners of the field as well as from the center of the field and then the samples were intermixed for each vegetable and final sample taken at random from the total lot. The samples from the rest two sources were taken by representative sampling. The samples were then analyzed for the presence of heavy metals namely: Lead, Cadmium, Mercury and trace metals like Iron, Sodium, Magnesium, Potassium, Calcium and Iron. The supermarket fruits and vegetables are grown by employing organic farming and claim to be free from chemical fertilizers, pesticides and heavy metal contaminants.

The reagents used for the experiment were of AR (Analytical Reagent) grade. Nitric acid (concentrated) and Hydrochloric acid (concentrated) were bought from Fischer Scientific Ltd. The concentration used for the experiment was made up by using MilliQ ultrapure water. Ferric ammonium sulfate and ammonium thiocyanate for iron determination by colorimetric method were brought from Fischer Scientific Ltd.

Sample preparation

Each fruit and vegetable sample from all the sources were washed thoroughly under running tap water followed by rinsing with distilled water. The samples were then chopped into fine pieces, kept in moisture dishes and then dried at 65°C for 48 hours in a Heat Pump Dryer. After 48 hours the moisture dishes were cooled in a moisture free environment in a Heat desiccator. 1gm of sample was then taken in a crucible and placed in a preheated muffle furnace at 200–250°C for 30 minutes.

The samples in crucibles were ashed for 4 h at 480°C. The samples were then removed from the furnace and cooled down. 2 ml of 5 M HNO_3 was added to the samples and evaporated to dryness on a sand bath.

The samples were placed in a cool furnace and heated to 400°C for 15 min, before being removed (from the furnace, cooled and moistened with four drops of distilled water). 2 ml of concentrated HCl was then added to the samples and the samples were evaporated to dryness, removed, and 5 ml of 2 M HCl was added and the crucibles were swirled gently. The solution was then sequentially filtered through Whatman No. 42 filter paper and <0.45 µm Millipore filter paper, and then transferred quantitatively to a 15 ml Centrifuge tube and total volume was made 15 ml exactly by using measuring cylinder by adding distilled water.

Sample Analysis

The project was carried out in two phases. The first phase involved the sample preparation from the vegetables and fruit for application into ICP-MS. This phase was carried out at NIFTEM's Chemistry Laboratory. The Second phase involved the analysis of fruit and vegetables sample for heavy metals and trace metals concentration by ICP-MS. This phase also included the determination of iron by thiocyanate colorimetry using UV-VIS Spectrophotometer.

Statistical Analysis

All analysis was carried out in triplicate. Results are expressed as mean±standard deviation. The analysis was carried out using analysis of variance (ANOVA) and Duncan's Test using SPSS. The results were considered significant at the level of $p<0.05$.

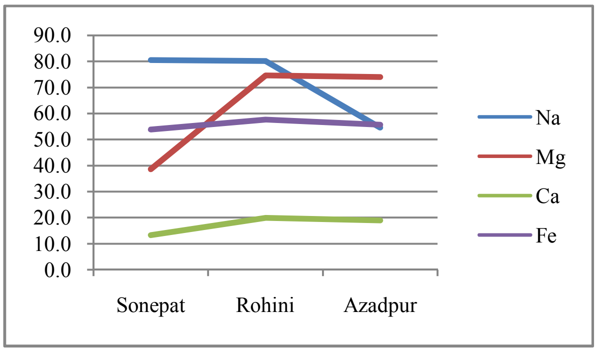
RESULTS AND DISCUSSION

The results for metal analysis of fruit and vegetables obtained from Delhi NCR are shown in table 3.1. Results showed that Na content in cucumber from the three different regions was not significantly different with a range of 54.57 ppm from Azadpur Market Delhi to 80.53 ppm from Sonepat region. The Na content in onion ranged from 30.07 ppm (Rohini supermarket) to 30.87 ppm (Azadpur market) with no significant difference among the three regions.

Table 1 Mineral content in fruit and vegetables

Sample	Na (ppm)	Mg (ppm)	K (ppm)	Ca (ppm)	Fe (ppm)
Cucumber.S	80.53±5.95	38.63±15.21	529.00±192.19	13.27±5.95	53.90±1.18
Cucumber-R	80.13±21.15	74.63±22.25	977.30±70.54	20.00±2.49	57.60±0.79
Cucumber-A	54.57±10.60	73.97±3.84	773.20±20.42	19.03±2.57	55.70±0.20
Onion-S	30.30±3.22	12.70±1.11	172.63±19.44	8.67±0.76	26.10±0.62
Onion-R	30.07±9.15	67.83±28.46	711.60±224.84	17.33±8.25	23.20±0.98
Onion-A	30.87±10.97	47.07±10.61	459.43±59.07	12.40±4.63	26.10±0.46
Orange-S	8.70±0.46	45.57±2.15	725.33±87.40	9.27±2.14	27.70±0.43
Orange-R	33.23±20.67	29.93±7.86	456.83±51.60	10.73±12.74	33.80±1.48
Orange-A	8.27±±1.21	26.70±7.93	350.77±30.85	18.83±3.32	31.40±0.46
Apple Gourd-S	82.63±6.35	38.00±12.64	457.47±133.81	12.70±7.82	24.50±0.72
Apple Gourd-R	132.67±45.19	42.23±29.59	387.00±17.32	7.50±7.22	23.40±0.98
Apple Gourd-A	82.03±20.59	20.93±10.74	299.23±66.80	4.67±2.71	25.80±0.75
Watermelon-S	30.63±5.34	18.07±3.25	174.80±25.15	7.33±1.95	39.90±1.06
Watermelon-R	25.63±5.20	75.73±12.22	662.30±74.54	11.73±1.44	43.60±0.53
Watermelon-A	50.50±18.76	85.23±21.42	645.27±116.78	14.37±5.44	41.70±0.81
Cauliflower-S	157.40±68.90	61.30±30.47	686.33±347.12	9.77±4.64	24.00±0.82
Cauliflower-R	175.77±100.12	94.17±6.34	1149.97±244.03	17.17±5.06	27.10±0.96
Cauliflower-A	181.77±114.40	81.47±16.48	1091.97±486.06	17.57±7.34	26.10±0.69

The Orange sample Na concentration ranged from 8.27 ppm to 33.23 ppm in Azadpur market sample and Rohini supermarket respectively.



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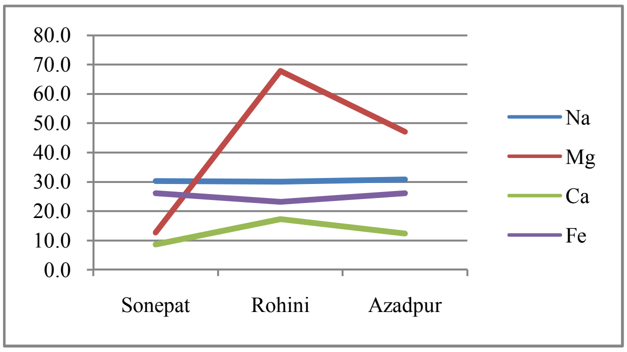

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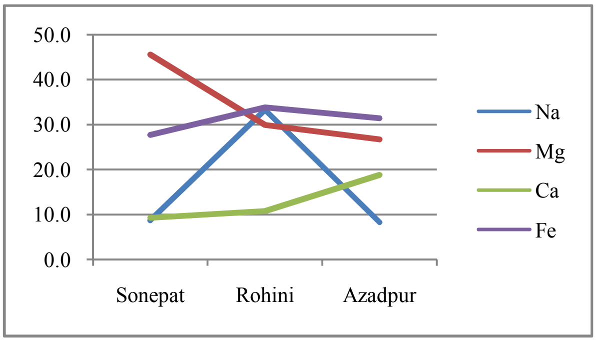

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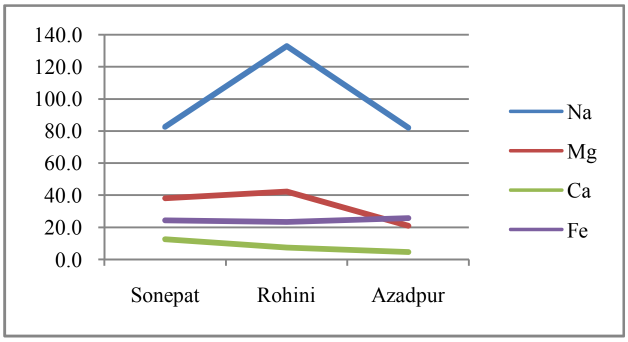

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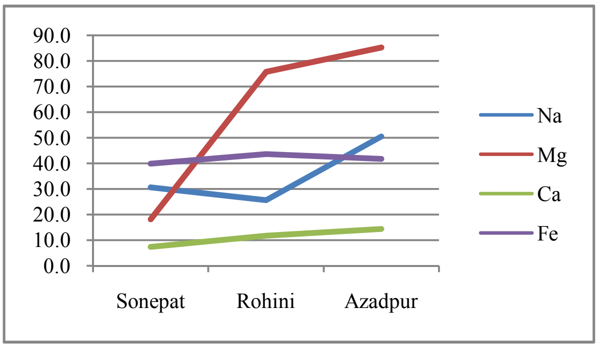

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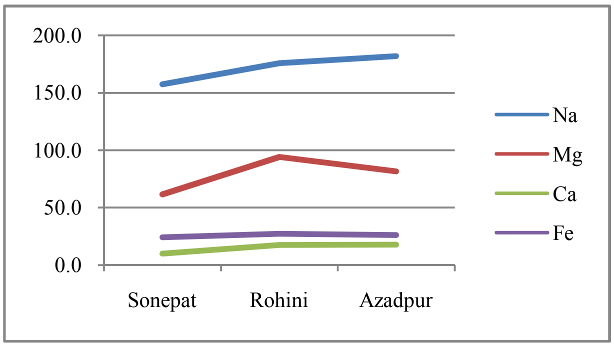

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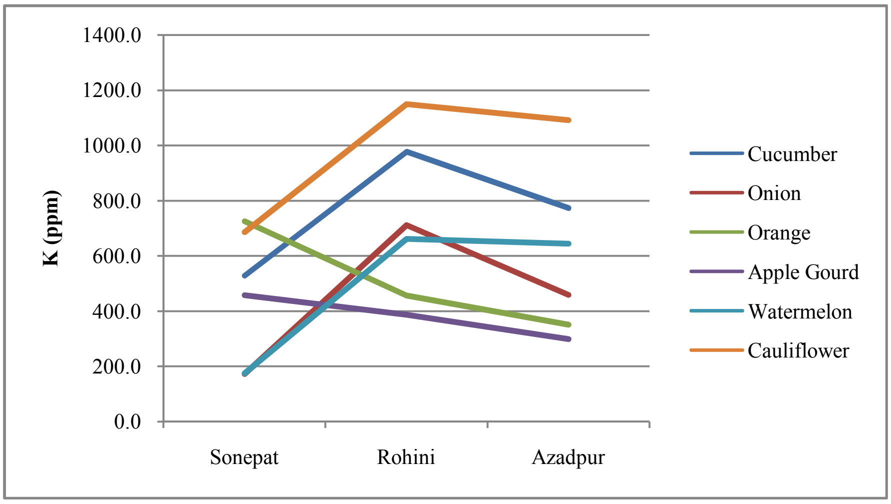

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Graph 1 Mineral content of various fruit and vegetables from Delhi NCR region *(a)* cucumber *(b)* onion *(c)* orange *(d)* apple gourd *(e)* watermelon *(f)* cauliflower *(g)* K content of fruit and vegetables

The apple gourd Na concentration ranged from 82.03 ppm (Azadpur market) to 132.67 ppm (Rohini supermarket).

The Na concentration in watermelon ranged from 25.63 ppm (Rohini supermarket) to 50.50 ppm (Azadpur market). Cauliflower contained highest amount of Na among all the different fruit and vegetables with range from 157.40 ppm (Sonepat) to 181.77 ppm (Azadpur market) with no significant difference among the three regions.

The Magnesium concentration in Cucumber ranged from 38.63 ppm (Sonepat) to 74.63 ppm (Rohini supermarket). The onion sample Mg concentration was found ranging from 12.70 ppm (Sonepat) to 67.83 ppm (Rohini supermarket). Orange sample Mg concentration ranged from 26.70 ppm (Azadpur market) to 45.57 ppm (Sonepat). Mg concentration in Apple gourd was found to be ranging from 20.93 ppm (Azadpur market) to 42.23 ppm (Rohini supermarket). Watermelon sample Mg concentration ranged from 18.07 ppm (Sonepat) to 85.23 ppm (Azadpur market). Mg concentration in Cauliflower sample ranged from 61.30 ppm (Sonepat) to 94.17 ppm (Rohini supermarket).

(Rohini supermarket) to 26.10 ppm (Sonepat, Azadpur market). Orange sample Fe concentration ranged from 27.70 ppm (Sonepat) to 33.80 ppm (Rohini supermarket). Fe concentration in Apple gourd was found to be ranging from 23.40 ppm (Rohini supermarket) to 25.80 ppm (Azadpur market). Watermelon sample Fe concentration ranged from 39.90 ppm (Sonepat) to 43.60 ppm (Rohini supermarket). Fe concentration in Cauliflower sample ranged from 24.00 ppm (Sonepat) to 27.10 ppm (Rohini supermarket).

The heavy metals analysis of four heavy metals Zinc (Zn), Cadmium (Cd), Mercury (Hg), Lead (Pb) by ICP-MS (Table 2) did not show the presence of any of the four specified metals in all the vegetables and fruit samples analyzed for the study.

Table 2 Heavy metals concentration in fruit and vegetables samples

Sample	Zn (ppm)	Cd (ppm)	Hg (ppm)	Pb (ppm)
Cucumber.S	ND	ND	ND	ND
Cucumber-R	ND	ND	ND	ND
Cucumber-A	ND	ND	ND	ND
Onion-S	ND	ND	ND	ND
Onion-R	ND	ND	ND	ND
Onion-A	ND	ND	ND	ND
Orange-S	ND	ND	ND	ND
Orange-R	ND	ND	ND	ND
Orange-A	ND	ND	ND	ND
Apple Gourd-S	ND	ND	ND	ND
Apple Gourd-R	ND	ND	ND	ND
Apple Gourd-A	ND	ND	ND	ND
Watermelon-S	ND	ND	ND	ND
Watermelon-R	ND	ND	ND	ND
Watermelon-A	ND	ND	ND	ND
Cauliflower-S	ND	ND	ND	ND
Cauliflower-R	ND	ND	ND	ND
Cauliflower-A	ND	ND	ND	ND

The Potassium (K) concentration in Cucumber ranged from 529.00 ppm (Sonepat) to 977.30 ppm (Rohini supermarket). The onion sample K concentration was found ranging from 172.63 ppm (Sonepat) to 711.60 ppm (Rohini supermarket). Orange sample K concentration ranged from 350.77 ppm (Azadpur market) to 725.33 ppm (Sonepat). K concentration in Apple gourd was found to be ranging from 299.23 ppm (Azadpur market) to 387.00 ppm (Rohini supermarket). Watermelon sample K concentration ranged from 174.80 ppm (Sonepat) to 662.30 ppm (Rohini supermarket). K concentration in Cauliflower sample ranged from 686.33 ppm (Sonepat) to 1149.97 ppm (Rohini supermarket) (Graph 1).

The Calcium concentration in Cucumber ranged from 13.27 ppm (Sonepat) to 20.00 ppm (Rohini supermarket). The onion sample Ca concentration was found ranging from 8.67 ppm (Sonepat) to 17.33 ppm (Rohini supermarket). Orange sample Ca concentration ranged from 9.27 ppm (Sonepat) to 18.83 ppm (Azadpur market). Ca concentration in Apple gourd was found to be ranging from 4.67 ppm (Azadpur market) to 12.70 ppm (Sonepat). Watermelon sample Ca concentration ranged from 7.33 ppm (Sonepat) to 14.37 ppm (Azadpur market). Ca concentration in Cauliflower sample ranged from 9.77 ppm (Sonepat) to 17.57 ppm (Rohini supermarket).

The Iron (Fe) concentration in Cucumber ranged from 53.90 ppm (Sonepat) to 57.60 ppm (Rohini supermarket). The onion sample Fe concentration was found ranging from 23.20 ppm

The results of analysis of trace minerals showed that although there was variation in concentration of four trace metals namely: Sodium, Magnesium, Potassium and Calcium in fruit and vegetable samples of same species collected from different sources yet the concentration of the trace metals was below the toxicity dosage therefore the fruit and vegetables samples under study will not cause any harm to the consumer in relation to the trace minerals content upon ingestion.

CONCLUSION

Fruit and vegetables form important dietary components of people of India. They are important sources of nutrition and provide minerals to the consumers. But they may also be contaminated by heavy metals which are toxic to the health at elevated levels though some heavy metals may be beneficial (Cu, Zn, Fe, etc.) at lower concentrations. For the present study five vegetables and one fruit was taken namely: Cauliflower, Cucumber, Onion, Water melon, Tinda (Apple Guard) and Orange. The samples were then analyzed for the determination of concentration of nine metals namely: Iron, Sodium, Calcium, Magnesium, Potassium, Zinc, Lead, Cadmium and Mercury. Iron concentration was determined by thiocyanate colorimetry using UV-VIS Spectrophotometer whereas the concentration of rest eight metals of interest was determined by ICP-MS (Inductively Coupled Plasma Mass spectrometry). The analysis showed that the concentration of heavy metals and trace minerals was well within prescribed limits by Food safety and standards (contaminants, toxins and residues) regulation, 2011 therefore the fruit and vegetables samples under study will not cause any harm to the consumer in relation to the specified heavy metals and trace minerals content upon ingestion. The results for iron concentration determination by UV-VIS Spectrophotometer by thiocyanate colorimetry showed that the iron concentration in the fruit and vegetables was well below its toxic dosage which may cause any harm upon ingestion to the consumer.

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