DETERMINATION OF HEAVY METALS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROSCOPY IN VEGETABLES GROWN NEAR YAMUNA RIVER IN DELHI

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ABSTRACT

The concentrations of heavy metals such as Lead (Pb), Cadmium (Cd), Arsenic (As), Mercury (Hg) and Chromium (Cr) were determined in 5 different vegetables collected from the areas near Yamuna River of Delhi, India using Inductively Coupled Plasma Mass Spectroscopy(ICP-MS). Dietary exposure to several heavy metals has been recognized as a risk to human health through the consumption of vegetable crops. This study investigates the source and magnitude of heavy metal contamination in various kinds of vegetables including Okra, Tomato, Brinjal, Pumpkins and Beans. The concentration of Pb, Cd, As, Hg, Cr were ranged 0.842-5.032 mg/kg in Okra; 0.594-3.532 mg/kg in tomato; 0.228-4.213 mg/kg in brinjal; 0.459-3.302 mg/kg in beans; and0.501-2.142 mg/kg mg/kg in pumpkin.Tthe concentration of Pd, Cd, As were found above the Maximum limit approved by Food Safety and Standards Authority of India (FSSAI) and Cr not specified. Our study highlights that vegetables growing bank of Yamuna are containing higher amount of metals that could be transferred into edible parts of the plant. Hence, complete monitoring of Yamuna river bank vegetables should be done periodically to avoid health risk of human being due to exposure of toxic level.

Keywords: Heavy metals; inductively coupled plasma mass spectroscopy; human health; contaminate; vegetables.

INTRODUCTION

Trace metals refers to metals which are available in food items and can have some toxicological or nutritious significance as per their level in the food product while some inorganic elements like sodium, potassium, calcium are required for human growth. The metals such as lead, cadmium, mercury, arsenic are found to have health hazards even in low levels (in ppb). During the past decades, widespread of contamination of heavy metals in food has gained a lot of interest because of their essential and toxic nature [1]. The presence of essential metals like Copper, Iron and Zinc are extremely useful for the healthy growth of the body however high levels are intolerable. The concentration of metal in different types of food varies and it changes depending on the metals that are introduced during the developing, transport and processing of food. The other innovative procedures that are utilized to get the food to the buyer can fundamentally expand the metal concentration in the food [2].

Vegetables are vital components of the human diet, and in particular provide the well-known nutrients to maintain normal physiological functions. The prolonged application of large amount of fertilizers and pesticides effluent disposal from industries has resulted in heavy metal accumulation in the gardens where vegetables are grown. Exposure to heavy metals by the consumption of contaminated vegetables and its toxicity is a serious concern. This article reviews the presence of heavy metals in different vegetables, their mechanism of absorption, impact of heavy metals on physiology, and nutrient reduction [2].

Due to the use of 250-300 grams of vegetables daily, the consumers should know the toxic content of metals in it. The main purpose of this research is to estimate the level of heavy metals such as (Chromium, Arsenic, Lead, Mercury, and Cadmium) in different types of vegetables commonly used and collected from the nearby Yamuna River in Delhi. Also, the concentration of investigated heavy metals were compared with the standard level approved by FSSAI.

Some of the heavy metals and their side effects on human health are described below:

1. ARSENIC

Food and drinking water are major source of inorganic arsenic. Intake of arsenic may lead to gastrointestinal side effects, disturbances in nervous system and eventually death. The permissible limit approved by FSSAI for Arsenic is 1.1 mg/kg [3].

2. LEAD

Earlier, contamination of lead in food came from the utensils that were utilized for cooking and storage. The side effects of lead are migraine and stomach pain. Individuals with long term exposure of lead may experience the ill effects of memory weakening. The permissible limit approved by FSSAI for Lead is 1.0 mg/kg [4].

3. CADMIUM

Intake of cadmium may lead to kidney issues. The bones becomes fragile, lose bone mineral density and become weaker. This causes the pain in the joints and the back, and also increases the risk of fractures. The permissible limit approved by FSSAI for cadmium is 1.5 mg/kg [5].

4. MERCURY

Ingestion of mercury may lead to weakness in muscles, numbness in the feet and hands, uneasiness, memory loss, speech and hearing problems and vision related issues as well. The permissible limit approved by FSSAI for Mercury is 1.0 mg/kg [6].

5. CHROMIUM

Acute poisoning occurs through the oral route, whereas chronic poisoning is mainly from inhalation or skin contact. Intake of Chromium may lead to fever, diarrhea, liver damage and nausea. Though no permissible limit approved by FSSAI for Chromium is not but this element is considered as trace elements and require extremely small amount [7].

MATERIALS AND METHODS

Sample Collection

Samples were collected from following locations of Delhi located nearby Yamuna River.

Table 1. Locations in Delhi from where vegetable samples were collected

Sample Date	Sampling Point (Field)	Number of Farms	Number of samples
10-July-2019	Mayur Vihar in Delhi	3	1 kg each of Tomato, Okra and Brinjal
11-July-2019	Lakshmi Nagar in Delhi	2	1 kg of Beans and Pumpkin

Vegetables samples collected Near the Yamuna River in farms near Delhi. Collected 1 Kg of each vegetable sample in poly bags (Zipper Bag) and stored at 2-8ºC. Then the samples were ground by a grinder and homogenized by homogenizer.

Reagents

The sample preparation were done by using supra-pure concentrated Nitric Acid (HNO_3) (69-70%, Merck, and Fisher) and 30% Hydrogen peroxide (H_2O_2) (Merck.BDH). Milli-Q water was used for all dilutions. The element standards solutions used for calibration curve were prepared diluting stock solution 1000 mg/l (As, Cd, Pb, Hg, Cr).

Apparatus

Inductively Coupled Plasma Mass Spectroscopy (Agilent Technology 7800) was used for the analyses of As, Cd, Pb, Hg, Cr.

Sample preparation

0.25-1.0 grams of sample (based on sample nature) into digestion vessel were added with 5-6 ml of Nitric Acid and add 0.5-1 ml H_2O_2 (Hydrogen peroxide). The vessels left for 10-15 minutes for /pre-digestion. Close the caps of vessels by hand tight properly and loaded the vessel into a microwave digestor and run the digestion in Multiwave 3000 (Anton Par). After digestion, vessel were cooled and volume made up to 50ml with Milli Q water in volumetric flask [8].

Digestion Using Microwave Digestion System (Anton Par)

Microwave digestion is common technique used by elemental scientists to dissolve heavy metals. This technique exposes the samples to a strong acid in a closed vessel and raise the pressure and temperature through microwave irradiation. This increase in temperature and pressure of the low pH sample medium increase both the speed of thermal decomposition of the sample and the solubility of heavy metals in the solution [9].

Analysis of Metal Using Diode Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

There are various diverse ICP-MS models accessible today, which share numerous comparable segments, for example, nebulizer, spray chamber, plasma torch, and detector, however can contrast in the outline of the interface, system of ion focussing, vacuum chamber and mass separation device. The Digested sample is injected by the auto sampler injector at 1 ml/min, into a nebulizer, further it is changed over into a aerosol with argon gas at around 1 L/min. The aerosol droplets are isolated from large droplets with the help of spray chamber. The aerosol at that point rises up out of the spray chamber tube and is transported into the plasma torch by means of a sample injector [10]. When the particles are created in the plasma, they are coordinated into the mass spectrometer through the interface region. It comprises of two cones that are known as the sampler and a skimmer cone, each with a little opening to enable the particles to go through the particle optics and are later transferred into mass separation device.

The interface area helps in transporting the particles from the plasma to the mass spectrometer analyser area. There is a coupling of plasma and RF coil, creating a potential contrast of hundred volts. Once the particles have been separated from the interface area, they are transferred to the vacuum region by ion optics. The ion beam that contains analyte particles leaves the ion optics and goes into the mass separation device. There are a wide range of mass separation device, all with their qualities and shortcomings. The most common are quadrupole and collision cell. However they fundamentally work on the same function, which is to permit analyte particles of a specific mass to charge proportion through the detector and filters the analyte particles [11]. The last procedure is to convert ions into an electrical signal which is done by the ion detector. The calibration curve was obtained by using the standard stock solution 1000 ppb and further serial dilution for the linearity points 0.5 ppb, 1 ppb, 2 ppb, 5 ppb, 10 ppb, 20 ppb, 50 ppb, 100 ppb, and 200 ppb in ICP-MS for the detection of heavy metals in different vegetables.

Operating Parameters Mass Spectrometer ICP-MS

The instrument ICP-MS used for analysis of heavy metals in the vegetable samples is based on the working parameters including mass range, Detector mode, Carrier gas, Plasma gas, etc with optimal values for proper working and analysis.

Table 2. Parameters used in operation of ICP-MS

Parameter	Value*
Mass Range	5 to 260 amu
ICP Octp RF	200 V
Plasma Mode	Low Matrix
Detector Mode	Pulse and Analog Counting
Nebulizer pump	0.30 rps
Carrier gas	1.0 L/min
Auxiliary gas	1.0 L/Min
Plasma gas	15 L/min

RESULTS

The concentrations of various heavy metals recorded in selected vegetables were as follows:

Lead (Pb)

The maximum concentration of lead was found 1.626 mg/kg in okra, 2.001 mg/kg in tomato, 2.132 mg/kg in brinjal, 1.231 mg/kg in beans and 1.330 mg/kg in pumpkins (Fig. 1).

Cadmium (Cd)

The concentration of cadmium were found as 2.520 mg/kg in okra, 1.932 mg/kg in tomato, 2.002 mg/kg in brinjal, 1.735 mg/kg in beans and 2.142 mg/kg in pumpkins.

Arsenic (As)

The concentration of arsenic were found as 2.240 mg/kg in okhra, 1.353 mg/kg in tomato, 1.628 mg/kg in brinjal, 1.553 (mg/kg) in beans and 1.226 (mg/kg) in pumpkins.

Mercury (Hg)

The maximum permissible limit is 1.0 (mg/kg) and in all vegetable samples have 0.842 (mg/kg) in okra, 0.594 (mg\kg) in tomato, 0.228 in brinjal, 0.459 in beans and0.501 in pumpkins.

Chromium (Cr)

The chromium concentration in different vegetables samples are shown in table. The concentration of chromium were found as 5.032 mg/kg in okra, 3.532 mg/kg in tomato, 4.213 mg/kg in brinjal, 3.302 mg/kg in beans and 2.735 mg/kg in pumpkins. For chromium the maximum permissible limit as per FSSAI (2011) not specified but as experimentally found, its concentration is for health risk, So all the vegetables samples under study show source of Cr accumulation in body and are thus health hazards.

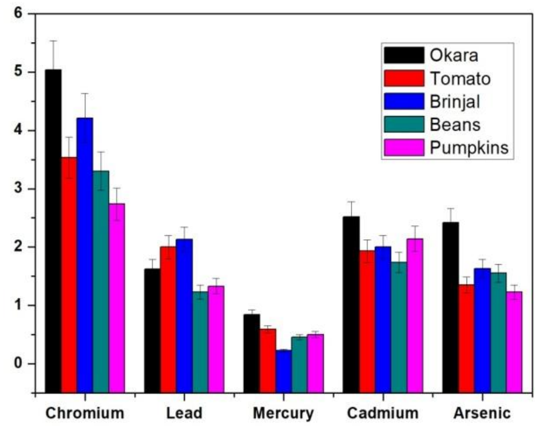

Fig. 1. The heavy metal concentration in some selected vegetables collected from nearby area of Yamuna River (Average of 25 samples of each vegetables; significance p<<0.5)

DISCUSSION

The concentration of metals in different vegetables from different location of Yamuna river in Delhi is shown in Fig. 1. The high level of heavy metals in vegetables indicates that the water of Yamuna is highly polluted. The previous studies obtained from Yamuna banks in Delhi were for spices, fishes etc. Out of the five metals tested, the concentration of four metals (Cadmium, Arsenic, Chromium and Lead) was exceeding the FSSAI limits for metals in these selected edibles as compared to Mercury. The concentration of Cadmium ranged between 1.5 mg/kg to 2.5 mg/kg, Chromium ranged between 2.0 mg/kg to 5.5 mg/kg, Lead ranged between 1.0 mg/kg to 2.5 mg/kg, Arsenic ranged between 1.0 mg/kg to 2.5 mg/kg in all the 5 vegetables tested were found much higher than the acceptable limits. Whereas, Mercury was the only metal that falls within the range of FSSAI limits i.e., below 1.0 mg/kg. This might be because the nearby industries don’t have lather industries, which are the root cause of Mercury pollution in the said area. The high content of Cadmium, Arsenic, Chromium and Lead may be due to the soil contamination from soil and effluent from industries in the river. The limit for chromium was not signified by FSSAI but for other three it was set 1.0 mg/kg. These pollutants accumulated in Yamuna river due to the Industries nearby the river or from drainage which are connected with the river.

The calibration curve prepared using the pure standards of Chromium, Lead, Cadmium, Mercury and Arsenic were found to be linear with correlation coefficient (r) of more than 0.999. The recovery studies were carried out at different concentration and results were given in the Fig. 1. The percent recovery for 4 metals out of 5 was exceeding the limit as per the regulatory guidelines. The ranges of metals were found to be various rivers in China 0.44 to 250.73 mg/kg for As, 0.02 to 8.67 mg/kg for Hg, 0.06 to 40 mg/kg for Cd, 0.81 to 251.58 mg/kg for Co, 4.69 to 460 mg/kg for Cr, 2.13 to 520.42 mg/kg for Cu, 39.76 to 1884 mg/kg for Mn, 1.91 to 203.11 mg/kg for Ni, 1.44 to 1434.25 mg/kg for Pb and 12.76 to 1737.35 mg/kg for Zn, respectively. The median values of these metals were descending in the order: Mn > Zn > Cr > Cu > Pb > Ni > Co > As > Cd > Hg [12]. In this study we also found the minimum concentration of mercury in Yamuna river water.

CONCLUSION

It can be concluded on the basis of these results that of the vegetables marketed in the local markets of Delhi were contaminated with heavy metals except a few cases as shown in table. As uptake of vegetables is very few grams per day, there are harmful effects on the body if consumed on regular basis. However, among excessive use of these could pose a health hazard to consumers. It is also recommended to monitor vegetables samples regular basis. The result clearly indicate that some heavy metals like Cr, As, Cd, Sn, Hg and Pb have been build up in bank of Yamuna river and thereby in plants mainly vegetables are responsible for contamination and risking the life of human population. Furthermore, it is recommended that the study of heavy metals in environmental components in the proposed area of Bank of Yamuna site of Delhi should be repeated at least two times in every year to ensure the contamination levels are occurring. The remediation of the contamination of water, soil and vegetables is absolutely necessary not only to preserve soil and vegetables but also to safeguard ecosystem.

It is suggested that the heavy metal bioremediation process of Yamuna water can be expedite with the Algal Bioreactor technology using nanoparticles [13].

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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