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RESEARCH ARTICLE

ATOMIC ABSORPTION SPECTROSCOPY DETECTION OF HEAVY METALS (COPPER AND LEAD) IN DIFFERENT VEGETABLES OF DISTRICT GORAKHPUR, U. P. INDIA

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Abstract

Vegetables are very important in the human diet because it provide many nutrients for our body. Different types of industrial effluents, chemical fertilizers, municipal waste, and pesticides have resulted in heavy metal accumulation in soil and ultimately in vegetables. Exposure to heavy metals by the consumption of contaminated vegetables and its toxicity is a serious concern for human/animal. This present study reveals the heavy metal accumulation in different vegetables. The bioaccumulation of lead was higher in mustard leaf (0.435 mg/kg) and spinach leaf (0.593 mg/kg) of Gida; and spinach leaf (0.605 mg/kg) of Nausad. The bioaccumulation of Copper in potato (1.743 mg/kg) was higher in Nausad, whereas in spinach leaf higher value was found in Taramandal (2.410) and Mohaddipur (2.214 mg/kg). These contaminated vegetables could be hazardous to human beings and their health. Furthermore, strategy and policy should be devised to control the heavy metals in vegetables and those vegetables that are hyper-accumulators of heavy metals should be identified for awareness purposes.

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Introduction:-

Heavy metals are hazardous contaminants in food and the environment and they are non-biodegradable having long biological half-lives; and their ability to accumulate in different body parts (Monu et al., 2008; Heidarieh et al., 2013). It can emanate from both natural and anthropogenic processes and end up in different environmental compartments (soil, water, air and their interface). The most common heavy metals are lead (Pb), nickel (Ni), chromium (Cr), cadmium (Cd), arsenic (As), mercury (Hg), zinc (Zn) and copper (Cu). Although the aforementioned heavy metals can be found in traces, they still cause serious health problems to human and other mammals (Herawati et al., 2000). They can enter into the food chain through crops and accumulate in the human body through biomagnification, thus posing a great threat to human health (Sarwar et al., 2010; Rehman et al., 2017). The contamination of soil and vegetables by heavy metals is also a global environmental issue. Analysis of vegetables grown in locations close to industry has reported elevated levels of heavy metals contamination (Vousta et al., 1996; Kachenko and Singh, 2006). These heavy metals are easily accumulated in the edible parts of leafy vegetables, as compared to grain, storage organs or fruit crops (Mapanda et al., 2005; Yusuf and Oluwale,

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2009; Haq et al., 2019). Vegetables take up heavy metals and accumulate them in their edible (Bahemuka and Mubofu, 1991) and inedible parts in quantities high enough to cause clinical problems both to animals and human beings when they consume these metal-rich plants (Alam et al., 2003). Intake of toxic metals in a chronic level through soil and vegetables has adverse impacts on human, plants and the associated harmful impacts become apparent only after several years of exposure (Bahemuka and Mubofu, 1991; Ikeda et al., 2000). Heavy metals can be the cause of many chronic diseases whose symptoms are different depending on the level of toxicity of an element, as well as the duration and level of exposure (International Agency for Research on Cancer, 2012; Kim et al., 2015). Metals, such as lead, chromium, cadmium and copper are cumulative poisons. Lead (Pb) is a neurotoxic element, in the general public, but specially in children, elevated levels of Pb in the blood may cause changes in the brain, manifested by: lowering of the IQ level, a problem with proper perception and concentration and a hyperactivity (Rehman et al., 2018; Fu and Xi, 2020). Chronic exposure to Pb can be associated with an increased risk of developing neurodegenerative diseases (Karri et al., 2018). High concentrations of heavy metals (Cu and Pb) in vegetables were related to high prevalence of upper gastrointestinal cancer (Turkdogan et al., 2002). The intake of copper salts in larger quantities may cause haemolysis, hepatotoxic, neurotoxic effects, gastrointestinal, hepatic, and renal effects with symptoms such as severe abdominal pain, vomiting, diarrhoea, hepatic necrosis, hematuria, proteinuria, hypotension, tachycardia, convulsions, coma, and death (Tchounwou et al., 2008). The aim of present study is to investigate the level of heavy metals (Cu, Pb) contamination in some vegetables and soil of Gorakhpur city. In addition, the aim is to verify which vegetable is the most contaminated and poses a significant health risk to its consumers.

Materials and Methods:-

Study Area

Different study sites (5 sites) were selected to study the level of heavy metals in vegetables. All these sites were situated in Gorakhpur (Latitude 26° 46' N, Longitude 83° 22' E) district of Uttar Pradesh, India on the left bank of river Rapti. Gorakhpur is an industrialized city, heavy a population of many lakh. Different types of industries effluent along with municipal waste are dumped in different Lakes of Gorakhpur city and the vegetables are growing in these areas. These 5-study areas are listed in Table 1, in which Gida and Nausad are the industrial dominant areas of Gorakhpur city.

Table 1:- List of sampling sites in Gorakhpur city.

Site number	Site Name
1	Gida
2	Nausad
3	Taramandal
4	Mohaddipur
5	Nanda nagar

Sampling procedure

Different types of vegetables and Soil (Table 2) were taken as sample from five different sites of Gorakhpur city. The factors were taken into account during site selection that the sites are residential site, industrial area and road sites. After drying at 90° Celsius and pulverizing, the vegetables were placed in polythene bags and stored in the refrigerator. 1-gram dry weights of each sample were taken for metal detection.

Table 2:- List of vegetables and soil collected from different sites of Gorakhpur city.

S. No.	Vegetables/soil
1	Brinjal
2	Cauliflower
3	Potato
4	Radish
5	Mustard leaf
6	Spinach leaf
7	Soil

Chemicals Used

Concentrated Nitric acid (HNO₃) (Merck, pro analysi), Millipore water and HCl. Standards of Pb and Cu were

purchased from Perkin Elmer, 710 Bridgeport Avenue (USA).

Apparatus

Perkin Elmer analyst 400 atomic absorption spectrophotometer, Hot plate, Oven, Porcelain Pestle and mortar, Glassware, Whattman type filter paper 60, Micropipette.

Analytical Methods:-

The wet digestion of organic matrix sample by the use of concentrated HNO_3 is the most common procedure. The digestion time was extended so as to achieve maximum recoveries of metal in the solution. About 1 gram dried wet of each sample was placed in an open tube. 10 ml of concentrated HNO_3 were added to each tube and place on hot plate till dryness. Residue were dissolved again with 10 ml concentrated HNO_3 followed by 10 ml 2M HCl and heated on hot plate till dryness. Left residues were warmed in 20 ml of 2M HCl to re-dissolve the metal salts and then filter by 60- whattman filter paper in borosilicate funnels into 150 ml borosilicate beakers. The final volumes of samples were made up to 25 ml with de-ionized double distilled water. Prepared solution then transfer to labelled test tube for Pb and Cu analysis on Atomic absorption spectroscopy (AAS).

Standard preparation

Standard solution was prepared by dissolving known concentration (1, 2, 5 and 10 ppm) of Pb and Cu in 25 ml double distilled water. All prepared solution was then transferred to labeled beakers for lead and copper analysis using Atomic Absorption Spectroscopy (Perkin Elmer analyst 400) by the method of Agrahari et al., (2017).

Schematic representation of various sampling sites of Gorakhpur city



Description of sites:

GIDA		Nausadh		Taramandal	
Nandanagar		Mohaddipur			

Result:-

The mean concentration of lead in vegetables and soil from each site are given in Table 3. The bioaccumulation of lead was not found in vegetables and soil but slightly lower value was observed in spinach and mustard leaf. In Site 1 (Gida) the lead concentration in mustard and spinach leaf was 0.435 and 0.593 mg/kg respectively. In the 2nd site (Nausad) the concentration of lead in spinach leaf was 0.605 mg/kg. In the 3rd site (Taramandal) the concentration of lead in spinach leaf and soil was 0.492 and 0.086 mg/kg respectively. In the 4th site (Mohaddipur), the concentration of lead in mustard and spinach leaf was 0.016 and 0.328 mg/kg respectively. In the 5th site (Nanda Nagar) the concentration of lead in mustard leaf was 0.024 mg/kg. The value indicates that the lead come from air to soil and soil to vegetables is due to increase level of pollution in the city.

The mean concentration of copper in vegetables and soil from each site are given in Table 4. The bioaccumulation of Copper in potato was higher (1.743 mg/kg) in site 2 (Nausad), whereas the bioaccumulation of Copper in spinach leaf was higher (2.410 and 2.214 mg/kg) in site 3 and 4 (Taramandal and Mohaddipur), respectively. The value indicates that the higher amount of copper present in vegetables and soil is due to higher level of pollution in the city.

Discussion:-

Heavy metals have a high atomic weight and a density at least 5 times greater than that of water. Their toxicity depends on several factors including the dose, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals. Vegetables absorb metals from contaminated soils, besides from deposits on the parts of the vegetables exposed to polluted air (Haiyan and Stuanes, 2003). The consumption of vegetables contaminated with heavy metals may pose a risk to the health of humans. It was found that heavy metals accumulated more in leafy vegetables than those in other parts because these leaves considered as entry points of heavy metals from air. Many studies have so far been published on heavy metal contamination because of their effects on human health and ecosystem (Caussy et al., 2003; Buschmann et al., 2008; Mousavi et al., 2013; Ametepey et al., 2018).

In our study, the observed value of Cu in vegetables was range from 0.093 mg/kg to 2.410 mg/kg (Table 2), which was less than the permissible limit (10.00 mg/kg) of WHO (1994). Demirezen and Ahmet (2006) reported that levels of Cu (22.19–76.50 mg/kg) were higher in the leafy species than the non-leafy vegetable species in Turkey. Sharma et al., (2006) also reported the concentration of Cu (2.25–5.42 mg/kg) in vegetables grown in wastewater areas of Varanasi, India to be within the safe limit. Ali and Al-Quhtani (2012) reported that leafy vegetable accumulated Cu higher in Jews mallow leaves (33.22 µg/g) which is higher than the permissible limit. Copper is essential for humans as a trace dietary mineral. However, excessive consumption of Cu can lead to adverse effects on human health (Rahman et al. 2014). The oral dose of copper is only 0.04 mg/kg/day (US EPA, 2017). When a person takes excess Cu, it causes acute intestine and stomachache, and liver damage (Rahman et al. 2014). Although the concentration of copper accumulation is very low in vegetables, which is less hazardous for human health, but their continuous accumulation creates a severe condition in future, because the impact of increasing urbanization, industrialization, number of vehicles in city and disposal of wastes is increasing day by day.

Lead has toxic effects on organs that include kidneys, liver, lung and spleen that cause different biochemical defects. It exhibits neuropathology when adults are exposed occupationally or accidentally to excessive levels. Lead is known to disrupt several enzymes. The major biochemical effect of Pb is its interference with heme- synthesis, which leads to hematological damage (Reddy, 2005). Pb inhibits several enzymes involved in heme synthesis. Lead interferes at several steps in heme (the pigment that combines with protein to form haemoglobin) synthesis in the bone marrow by inhibiting the activities of enzymes ferrochelatase, α - amino laevulinate dehydrogenase (ALAD) and with the uptake of iron into mitochondria (Piomelli, 1980). It is a cumulative general poison and associated with several health hazards like anaemia (Moore, 1988) which leads to deficiency of haemoglobin and reproductive effects (Wildt et al., 1983; Cullen et al., 1984). There is a relationship between Pb in the human body and the increase of blood pressure of adults (Maihara and Fávoro, 2006).

In the present study, the concentration of lead metal are only found in the spinach leaves of Gida (0.593), Nausad (0.605), Taramandal (0.492) and mohaddipur (0.328 mg/kg); Mustard leaf of Gida (0.435), Mohaddipur (0.016) and Nanda Nagar (0.024); and Soil of Taramandal (0.086 mg/kg). In rest vegetables, the lead concentrations were below the detectable level. The lead concentrations in Mustard leaf and Spinach leaf are greater than others, which

indicate, that the accumulation of lead become started in the leafy vegetables that is not good for all living system. However, all of vegetables sample were below to WHO standard permissible limit i.e. 2mg/kg, but these trace level of lead will be very hazardous for living system by the continuous exposure due to continuous bioaccumulation and biomagnifications inside the organism. Al Jassir et al. (2005) studied six washed and unwashed green leafy vegetables from Saudi Arabia and noted the highest concentrations of Pb in coriander and purslane. Muchuweti et al. (2006) reported the level of Pb (6.77 mg kg^{-1}) in vegetables irrigated with mixtures of wastewater and sewage from Zimbabwe to be higher than WHO safe limit (2 mg/kg). Sharma et al. (2006) also reported the Pb concentration in vegetables grown in industrial areas was range from $17.54\text{--}25.00 \text{ mg/kg}$. Odai et al. (2008) reported that the Pb concentration was range from 2.42 to 13.50 mg/kg . Recently, Ametepey et al. (2018) also reported the lead concentration in cabbage, carrot, green pepper and onion ranged from BDL to 0.03 mg kg^{-1} , BDL to 0.02 mg kg^{-1} , BDL to 0.04 mg kg^{-1} , and BDL to 0.05 mg kg^{-1} , respectively. They found that the concentration of heavy metals in the various vegetables were below the World Health Organization (WHO) standard. The maximum value of Pb was found in spinach leaves of Nausad (0.605 mg/kg), because of heavily traffic in this area, which lead to the accumulation of Pb emitted from cars exhaustions in leaves. The reason behind this in car engines lead is burn, so that lead salts (chlorines, bromines, and oxides) will originate. These lead salts enter the environment through the exhausts of cars. The larger particles will drop to the ground immediately and pollute soils or surface waters, the smaller particles will travel long distances through air and remain in the atmosphere. Part of this lead will fall back on earth when it is raining. This lead-cycle caused by human production is much more extended than the natural lead-cycle. It has caused lead pollution to be a worldwide issue.

Table 3:- The mean lead concentration in vegetables and soil in each sampling site 1-5 (mean value in mg/kg).

SR.NO	SITES	VEGETABLES NAME	CONCENTRATION OF Pb (lead) METAL (mg/Kg)
1	GIDA	BRINJAL	ND
		CAULIFLOWER	ND
		POTATO	ND
		RADISH	ND
		MUSTARD LEAF	0.435
		SPINACH LEAF	0.593
		SOIL	ND
2	NAUSAD	BRINJAL	ND
		CAULIFLOWER	ND
		POTATO	ND
		RADISH	ND
		MUSTARD LEAF	ND
		SPINACH LEAF	0.605
		SOIL	ND
3	TARAMANDAL	BRINJAL	ND
		CAULIFLOWER	ND
		POTATO	ND
		RADISH	ND
		MUSTARD LEAF	ND
		SPINACH LEAF	0.492
		SOIL	0.086
4	MOHADDIPUR	BRINJAL	ND
		CAULIFLOWER	ND
		POTATO	ND
		RADISH	ND
		MUSTARD LEAF	0.016
		SPINACH LEAF	0.328
		SOIL	ND
		BRINJAL	ND
		CAULIFLOWER	ND
		POTATO	ND

5	NANDA NAGAR	RADISH	ND
		MUSTARD LEAF	0.024
		SPINACH LEAF	ND
		SOIL	ND

Abbreviation: ND -not detected.

Table 4:- The mean Copper concentration in vegetables and soil from each sampling site 1-5 (mean value in mg/kg).

SR.NO	SITES	VEGETABLES NAME	CONCENTRATION OF Cu (copper) METAL (mg/kg)
1.	GIDA	BRINJAL	0.203
		CAULIFLOWER	0.120
		POTATO	0.113
		RADISH	0.127
		MUSTARD LEAF	0.166
		SPINACH LEAF	0.306
		SOIL	0.136
2.	NAUSAD	BRINJAL	0.266
		CAULIFLOWER	0.120
		POTATO	1.743
		RADISH	0.100
		MUSTARD LEAF	0.156
		SPINACH LEAF	0.407
		SOIL	0.138
3.	TARAMANDAL	BRINJAL	0.257
		CAULIFLOWER	0.319
		POTATO	0.125
		RADISH	0.089
		MUSTARD LEAF	0.135
		SPINACH LEAF	2.410
		SOIL	0.465
4.	MOHADDIPUR	BRINJAL	0.149
		CAULIFLOWER	0.099
		POTATO	0.196
		RADISH	0.105
		MUSTARD LEAF	0.146
		SPINACH LEAF	2.214
		SOIL	0.235
5.	NANDA NAGAR	BRINJAL	0.264
		CAULIFLOWER	0.097
		POTATO	0.093
		RADISH	0.150
		MUSTARD LEAF	0.150
		SPINACH LEAF	0.287
		SOIL	0.103

Abbreviation: ND -not detected.

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