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Determination of Some Heavy Metals in Soil and Vegetable Samples from Gonglung Agricultural Location of Jere Local Government Area of Borno State, Nigeria

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ABSTRACT

The vegetable samples of (Tomatoes, Onion, Spinach and lettuce) and the soil samples were all collected at Gonglung Agricultural Locations. The soil samples were collected at three different depths of 0-5 cm, 5-10 cm and 10-15 cm respectively. The concentrations of some of the heavy metals Cr, Mn, Co, Ni, Cu, Zn and Pb were found to be lower than the threshold limit of 100mg/kg, 0.3 mg/kg, 0.2 mg/kg, 10 mg/kg, 10 mg/kg, 1.5 mg/kg, and 2 mg/kg. However, Fe and Cd recorded a higher concentration value than the threshold limit of 0.3 mg/kg and 0.02 mg/kg in a soil samples collected at a depth of 0-5 cm, 5-10 cm and 10-15cm. The concentration of the heavy metals Fe, Co, Ni, Cu, Zn in vegetable samples (Tomatoes, Onion, Spinach and lettuce) exceeded the maximum threshold limits of 0.3 mg/kg, 0.02 mg/kg, 0.1 mg/kg, 10 mg/kg and 1.5 mg/kg set by FAO/WHO. Also, the concentrations of Cd both 0.06 mg/kg in (Tomato and Onion) and Mn 0.04 mg/kg (Onion) were found to be higher than the maximum limits of 0.02 mg/kg and 0.04 mg/kg set by FAO/WHO. However, Cr and Pb in all the four vegetable samples were found to be lower than the threshold limit of 0.2 mg/kg and 0.1 mg/kg.

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Introduction

The consumption of vegetables as food offer rapid and least means of providing adequate vitamins, supply minerals and fibers. Vegetables that are used as food include those used in making soups or served as integral parts of the main sources of a meal. Leafy vegetables occupy a very important place in the human diet [1], but unfortunately constitute a group of food which contributes maximally to nitrate and other anions as well as heavy metal consumption. Heavy metals deposition is associated with a wide range of sources such as small scale industries (including battery, metal smelting and cable coating industries); vehicular emissions, and diesel generator sets. Heavy metals such as cadmium, lead and zinc are important environmental pollutant, particularly in areas where vegetables are irrigated with waste water, consumption of vegetables such as Spinach, Tomato, lettuce, and Onion by humans and animals pose serious health hazards, although some heavy metals as Lead, Cadmium and Magnesium are important in plant nutrition, many of them do not play any significant role in the plant's physiology. The uptake of these heavy metals especially into the human food chain is done through these leafy vegetables and they have harmful effects on health [2].

Vegetables act as neutralizing agents for acidic substances formed during digestion, as human activities increases especially with the application of modern technology, pollution and contamination of human food chain has become inevitable. Heavy metals cannot be underestimated as these food stuffs are important components of human diet, they are very rich and comparatively cheaper sources of vitamins, Consumption of these items provides taste and palatability increases appetite and provides fiber for digestion and prevent constipate ion [2]. Heavy metal contamination of food item is one of the most important aspect of food quality assurance; International and national regulation on food qualities have lowered the maximum permissible levels of toxic metals in food items due to an increased awareness of the risk these metals pose to food chain contamination. Rapid and Unorganized industrialization and Urbanization has contributed to the elevated levels of metals in the environment in developing countries, Heavy metal are non bio- degradable and persistent environmental in the contaminants which may deposited on the surfaces and then absorbed into the tissues of the vegetables; Plants take up heavy metals by absorbing them from deposits on the parts of the plant exposed to the polluted water [3]. Waste water from industries of mining electroplating paints or chemical laboratories often contains high concentrations of heavy metals. These elements at concentration exceeding the physiological demand of vegetables, not only could administer toxic effects in them but also could enter food chain, get biomagnified and pose a potential threat to human health. Heavy metal contamination in agricultural soils from waste water irrigation is of serious concern due to its implications on human health.

Results and Discussion

Heavy metals

Heavy metals are generally referred to as those metals which possess a specific density of more than 5 g/cm3 and adversely affect the environment and living organisms [2]. A heavy metal may be toxic when its concentration in the plant and animal exceeds a certain threshold ("it is the dose that makes the effect"). Some elements, called trace elements or micronutrients, have essential functions in plant and animal cells. This has been shown for Co, Cu, Fe, Mn, Mo, Ni and Zn. Only when the internal concentration exceeds a certain threshold do they demonstrate toxic effects, and then they are commonly termed "heavy metals' [4]. Heavy metals are significant environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons [5]. Heavy metals are one of the important types of contaminants that can be found on the surface and in the tissues of fresh vegetables. Heavy metals rank high amongst the major contaminants of leafy vegetables [6]. [7] found that the concentrations of heavy metals in vegetables per unit dry matter generally follow the order: leaves > fresh fruits > seeds. The prolonged human consumption of unsafe concentrations of heavy metals in foodstuffs may lead to the disruption of numerous biological and biochemical processes in the human body. Vegetables, especially leafy vegetables grown in heavy metal-contaminated soils, accumulate higher amounts of metals than do those grown in uncontaminated soils because they absorb these metals through their leaves [8].

Heavy metal concentrations

The concentrations (mg/kg) of Chromium (Cr), Manganese (Mn), Iron (Fe), Cobalt (Co), Nickel (Ni), Copper (Cu) Zinc (Zn), Arsenic (As), Cadmium (Cd) and Lead (Pb) of both soil and vegetable samples are shown in Figure 1 and Figure 2. A comparative bioavailability of the heavy metals among the soil samples obtained from three different depths, 0-5, 5-10 and 10-15 cm is displayed in Figure 1. In addition, comparative bioaccumulations of the heavy metals among the vegetable samples of Tomato, Onion, Spinach and lettuce are showed in figure 2.

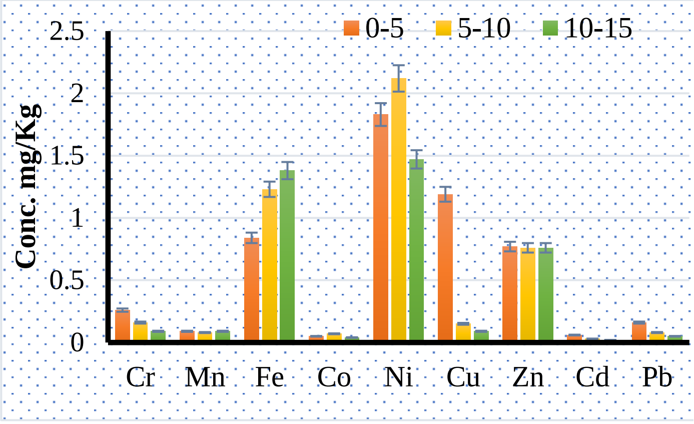

Figure 1. Mean Concentrations of Some Heavy Metals in Soil Samples From Gongulog Agricultural Location of Jere Local Government, Area, Borno State, Nigeria.

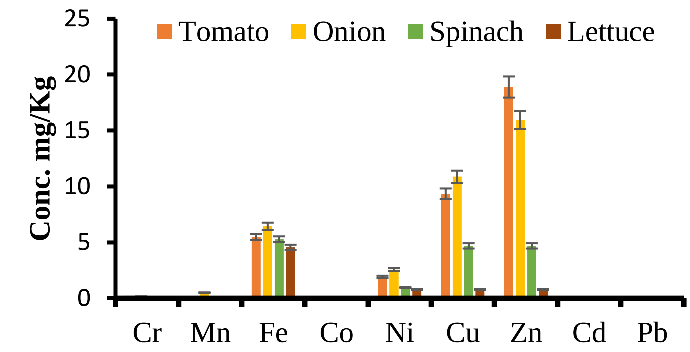

Figure 2. Mean Concentrations of Some Heavy Metals in Some Vegetables Samples from Gongulon Agricultural Location of Jere Local Government Area, Borno State, Nigeria.

Chromium (Cr)

Chromium (Cr) plays a vital role in the metabolism of cholesterol, fat, and glucose. Its deficiency causes hyperglycemia, elevated body fat, and decreased sperm count, while at high concentration it is toxic and carcinogenic [9]. Chromium (Cr) is more available in the soils than the vegetable samples. While an opportune is observed in the soil and vegetable samples obtained from Gongulog Agricultural Location of Jere Local Government Area, Borno State, Nigeria. These differences may be adduced to the varying abilities of plants to absorb minerals from the soils on which they grow. These varying abilities, according to [10] depend on: (i) root architecture induction of root-based transport systems; (ii) adaptation to changes in the climate and atmosphere; and (iii) enhanced absorption associated with beneficial soil microorganisms. The Cr concentrations vary from 0.26 to 0.09 mg/Kg among the soil samples (Figure 1) and from 0.05 to 0.15 mg/kg among the vegetable samples (Figure 2). This observation is a way to confirm that the same plant behaves differently on different soils and climatic conditions.

This study shows that the concentration of Cr in soil sample at a depth of 0-5cm recorded a significant value of 0.26 mg/kg as compared to the other depths, while Onion was observed to show the higher level of Cr 0.15 mg/kg in vegetables. In comparison the concentration of Cr in all the four vegetable samples were observed to be lower than the concentration in soil samples. Similarly, the concentrations of Cr both in soil and the vegetables samples were found to be much lower than the values of 17.2 mg/kg in soil and 4.63 mg/kg in vegetable reported in a separate studies carried out by [11] and [12] respectively and as well [13] in a similar study reported a higher value of Cr (43.54 mg/kg) in soil at a depth of 20-30cm. Also, in furtherance the results were further compared with standard threshold limits and observed that the concentrations of Cr in soil and the vegetable samples were found to be lower than the maximum permissible limit of 100 mg/kg (soil) and 0.2 mg/kg (vegetables) set by [14] and [15] respectively.

Manganese

Manganese is a very essential trace heavy metal for plants and animal's growth. Its deficiency produces severe skeletal and reproductive abnormalities in mammals. High concentration of manganese (Mn) causes hazardous effects on lungs and brains of humans [2]. The range of Manganese (Mn) concentrations in the soil samples is 0.08 to 0.09 mg/kg (Figure 1) while in the vegetable samples is between 0.01 to 0.5 mg/kg (Figure 4.2). Manganese toxicity is a relatively common problem compared to other micronutrient toxicity. It is normally associated with soils of pH 5.5 or lower, but can occur whenever the soil pH is below 6.0. Possible symptoms include chlorosis and necrotic lesions on old leaves.

The level of Mn in this study was observed to higher in a soil sample collected at a depth of 0-5 cm with a value of 0.09 mg/kg while Onion was observed with a higher level of 0.50 mg/kg. [16] in a similar study carried out in District Kasur, Pakistan reported a higher value of 33.98 mg/kg in soil and 129.32 mg/kg in vegetable than in the present study. Also, [17] in a similar study reported a moderate value of (80.00 mg/kg) Mn in soil sample but yet higher than the concentration in the present study. However, the levels of Mn in this study was observed to be lower than the threshold values of 0.3 mg/kg (Soil) while in vegetable only Onion recorded a higher value than the standard limit of 0.04 mg/kg (Vegetables) as specified by [15]and [14]respectively. According to [18] Higher proportions of Mn in the vegetable samples are another confirmation of high absorption of Mn by the tissues from the soils on which they grow and other non-anthropogenic sources. Hence the high absorption rate of Mn by the tissue is coupled with low mobility of Mn through phloem to other tissue after reaching the leaves which also resulted to inhibit synthesis of chlorophyll by blocking iron (Fe) process.

Zinc (Zn)

Zinc is one of the most essential metals for normal growth and development in humans (Divrikli *et al*., 2006). Zinc deficiency is of growing concern in developing countries. Zinc deficiencies have been attributed to the large consumption of vegetables. Excess Zinc can also be harmful, and cause Zinc toxicity. Such toxicity levels have been seen to occur at ingestion greater than 225 mg/kg of Zinc. The concentration of Zinc in all the samples analyzed ranging from 0.76 to 0.77 mg/kg in the soil sample (Figure 1) and 0.78 to18.89 mg/kg in vegetables samples (Figure 2). Zinc (Zn) accumulation in high amounts can cause eminent health problems, such as stomach cramp, skin irritation, vomiting, nausea and anemia.

At 0-5 cm depth the highest level of Zn (0.77 mg/kg) was observed while Tomato also among the vegetable samples was observed with the higher level of Zn (18.89 mg/kg). The concentrations of Zn both in soil and vegetables revealed in this study were found to be lower than the reported values of 331.89 mg/kg in soil and116.25 mg/kg in vegetable by [19]. Similarly, [11] reported a higher range value of Zn (62.3 – 181.7mg/kg) in vegetables as compared with the present study. Likewise, the levels of Zn determine in the soil samples were observed to be below the acceptable limit of 1.50 mg/kg as specified by [14] while in vegetable samples are observed to be above the acceptable limit of 0.60 mg/kg as specified by [15].

Copper (Cu)

Copper is the third most used metal in the world. Copper is an essential micronutrient required in the growth of both plants and animals. The concentration of Cu in the soil samples is between 0.09 to 1.19 mg/kg (Figure 1) and the vegetables samples from 0.78 to 10.87 mg/kg (Figure 2). The highest levels of Cu were observed in vegetable samples. Long- term exposure to copper dust can irritate nose, mouth, eyes, and cause headaches, dizziness, nausea, and diarrhea.

The highest level of Cu (1.19 mg/kg) in this study was found in a soil sample collected at a depth 0-5 cm while Onion was also observed to show the higher levels of Cu (10.87 mg/kg). previous study by [12] reported a higher value of Cu (25.96 mg/kg) in soil and (16.27 mg/kg) in vegetable respectively while [20] in a similar study reported a lower value of Cu 1.09 mg/kg in vegetable and higher (27.35 mg/kg) in soil than the present study. In addition, the concentrations levels in both soil and vegetable samples were found to be lower than the maximum permissible limit of 10 mg/kg in soil but higher than 0.1 mg/kg in vegetable as specified by [14] and [15] respectively.

Cadmium (Cd)

Cadmium is a non-essential element in foods and natural waters and primarily it accumulates in the kidneys and liver [21]. In all the samples analysed the concentration of Cd in the soil sample is between 0.02 to 0.06 mg/kg (Figure 1) and the vegetable sample from 0.01 to 0.03 mg/kg (Figure 2).

The concentration of Cd was significantly higher with a value of 0.06 mg/kg in a soil sample collected at a depth of 0-5 cm, while in vegetable samples of Tomato and Onion recorded a significant value of 0.03 mg/kg. [20] in a similar study also reported a higher values of Cd 14.35 mg/kg in soil samples and 0.62 mg/kg in vegetable samples as both compared with the present study. Also, [22] in a similar study carried out in Agricultural Areas of Kota Bharu and Bachok Districts of Kelantan, Malaysia reported a higher value of Cd 0.93 mg/kg in vegetable samples. However, in this study the concentration of Cd in vegetable samples (Tomato and Onion) and soil samples collected at a depth of 0-5 and 5-10 cm were found to be higher than the maximum permissible limit of 0.02mg/kg for both soil and vegetables as specified by [15] and [14] respectively.

Nickel (Ni)

Nickel is a mineral found in several food, the body needs nickel but in very small amounts. Nickel is a common trace element in multiple vitamins. Nickel is used for preventing nickel levels in the blood from getting too low (nickel deficiency). It is also used for low levels of healthy red blood cells (anemia) due to iron deficiency and treating weak and brittle bones (osteoporosis). The concentration of Ni in soil sample ranged from 1.47 to 2.12 mg/kg (Figure 1) and in vegetable sample from 0.77 to 2.56 mg/kg (Figure 2).

The highest level of Ni (2.12 mg/kg) was observed in a soil sample collected at a depth of (5-10 cm) when compared to other depths. Similarly, in vegetable samples Onion was observed to show the highest levels of Ni (2.56 mg/kg). The concentrations of Ni in this study were found to be lower than the reported value of 53.57 mg/kg in soil and 2.97 mg/kg in vegetable by [21] and also a reported value of Ni (3.54 mg/kg) in vegetable by [23]. Notwithstanding, the levels of Ni determine in both the soils and Vegetable samples were observed to be lower the acceptable limit of 10 mg/kg (soil) and higher than 0.1 mg/kg (Vegetable) as specified by [14] and [15] respectively.

Iron (Fe)

It is the most abundant and an essential constituent for all plants and animals. On the other hand, at high concentration, it causes tissues damage and some other diseases in humans. It is also responsible for anemia and neurodegenerative conditions in human being [24]. The results show that iron (Fe) is the most abundant nutritionally essential metal in both soil and vegetable samples, ranging from 0.84 to 1.38 mg/kg in the soil samples and 4.56 to 6.44 mg/kg (Figure 1) in the vegetable samples (Figure 2). The variations in the absorption of Fe from the soil by the plant's tissues are evident in the high Fe contents in the vegetable samples.

Soil sample collected at a depth of (10-15 cm) was observed to show the highest level of Fe (0.06 mg/kg) when compared to other depths. Similarly, Onion was observed to show the highest level of Fe (6.44 mg/kg). This result is not in synch with the higher values of 959.39 mg/kg in soil and 537.75 mg/kg in vegetable reported by [22]. But higher than the maximum standard limit of 0.3 mg/kg for vegetables and lower in soil as specified by [14] and [15] respectively. Thus, the intensity of extent of the uptake therefore influences the actual contents of an element in the plant. Presence of Fe in high concentration in plant poses serious pollution and health problem [17]. Toxicity of Fe in human leads to vomiting, cardiovascular collapse and diarrhea [17, 25].

Lead (Pb)

Lead is a soft metal that has known many applications over the years. It has been used widely since 5000 BC for application in metal products, cables and pipelines, but also in paints and pesticides. Lead is one out of four metals that have the most damaging effects on human health. It can enter the human body through uptake of food (65%), water (20%) and air (15%). Foods such as fruit, vegetables, meats, grains, seafood, soft drinks and wine may contain significant amounts of lead. Cigarette smoke also contains small amounts of lead. The concentration of lead in soil sample ranges from 0.05 to 0.16 mg/kg (Figure 1) and in vegetable samples from 0.03 to 0.08 mg/kg (Figure 2).

The significant level of Co in soil sample collected at a depth of 5-10 cm was revealed to be 0.07 mg/kg while Tomato and Onion were also observed to show the higher levels of Co to be 0.06 mg/kg. Comparably [16] reported a higher value of Co 7.56 mg/kg in soil and lower value of 0.036 mg/kg than the values in Tomato and Onion in this study. Similarly, the concentrations of Cd in the vegetable sample was found to be higher than the standard limit of 0.02 mg/kg but lower than 0.2 mg/kg in soil samples as specified by [15] and [14] respectively.

Cobalt (Co)

Cobalt is beneficial for humans because it is a part of vitamin B12, which is essential for human health. Cobalt is used to treat anemia with pregnant women, because it stimulates the total daily intake of cobalt is variable and may be as much as 1mg, but almost all will pass through the body un adsorbed, except that in vitamin B12. When plants grow on contaminated soil they will accumulate very small particles of cobalt, especially in the parts of the plant we eat, such as fruits and seeds. Health effects that area result of the uptake of high concentrations of cobalt are; Vomiting, nausea, Vision problems, Heart problems Thyroid damage etc. The concentration of cobalt in the soil sample ranges from 0.04 to 0.07 mg/kg (Figure 1) and in vegetable samples from 0.02 to 0.06 mg/kg (Figure 2).

The significant level of Co in soil sample collected at a depth of 5-10 cm was revealed to be 0.07 mg/kg while Tomato and Onion were also observed to show the higher levels of Co to be 0.06 mg/kg. Comparably [16] reported a higher value of Co 7.56 mg/kg in soil and lower value of 0.036 mg/kg than the values in Tomato and Onion in this study. Similarly, the concentrations of Cd in the vegetable sample was found to be higher than the standard limit of 0.02 mg/kg but lower than 0.2 mg/kg in soil samples as specified by [15] and [14] respectively.

Experimental

Sample and sampling

Soil and some commonly consumed vegetable (Tomato, onion, Spinach, and Lettuce) were used as samples for the analysis of the heavy metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd and Pb).

Sample collection

Vegetable sample collection

Three samples of each of the 4 vegetable (Tomato, Onion, Spinach, Lettuce) were collected randomly from 3 different farms in the outskirts of Gongulog Agricultural Location Borno State. Sample of the same vegetables were mixed together to get a representative sample of the vegetable. Precautionary measures were taken to avoid any form of contamination. Vegetables samples were identified by an expert from the department of Biological Science University of Maiduguri, the sample were collected in a container, labeled with unique identification number and transported to the research laboratory, Department of Pure and Applied Chemistry, University of Maiduguri for further analysis.

Soil sample collection

Three soil samples were collected randomly from 3 different farms in the outskirts of Gongulog Agricultural Location Borno state. The soil samples were mixed together to get a representative sample of the soil. Precautionary measures were taken to avoid any form of contamination. The sample were collected in a container, labeled with unique identification number and transported to the research laboratory, Department of Pure and Applied Chemistry, University of Maiduguri for further analysis.

Sample preparation

Vegetable sample preparation

The samples were properly washed with de-ionized water; the samples were then dried at room temperature until it was ready for grinding. The dried samples were then pounded with the crucible to fine powder the different leaf samples were then labeled into different small crucibles for identification.

Soil sample preparation

The soil samples were air dried for 48 hours, ground and sieved using 0.5 mm mesh size sieve to have uniform particle size. Each sample was labelled and stored in a dry plastic container that had been pre-cleaned with concentrated nitric acid prior to analysis with Atomic Absorption Spectrophotometer.

Digestion procedure

One gram of sample was placed in a 250 ml digestion tube and 10 ml of Concentrated HNO_3 was added. The sample was heated for 45minutes at $90^{O}C$ and the temperature is increased to $150^{O}C$ at which the sample was boiled for at least 8 hours until a clear solution was obtained. Conc. HNO_3 was added to the sample (5 ml was added at least 3 times) and digestion occur until the volume was reduced to about 1ml. The interior walls of the tube were washed down with a little distilled water and the tube was swirled through out the digestion to keep the wall clean and prevent the loss of the sample. After cooling, 5 ml of 1% HNO_3 was added to the sample. The solution was filtered with a wattman No. 42 filter paper. It was then transferred quantitatively to a 25 ml volumetric flask by adding distilled water.

Heavy metals analysis

Materials and methods

The equipments and instruments used in this study were all calibrated to check their status before and in the middle of the experiments. Apparatus such as volumetric flasks, measuring cylinder and digestion flasks were thoroughly washed with detergents and tap water and then rinsed with deionized water. All Glass wares were cleaned with 10% concentrated Nitric acid (HNO_3) in order to clear out any heavy metal on their surfaces and then rinsed with distilled-deionised water. The digestion tubes were soaked with 1% (w/v) potassium dichromate in 98% (v/v) H_2SO_4 and the volumetric flasks in 10% (v/v) HNO_3 for 24 hours followed by rinsing with deionized water and then dried in oven and kept in dust free place until analysis began. Prior to each use, the apparatus was soaked and rinsed in deionized water.

Quality control and quality assurance

The quality assurance and quality control were performed to confirm the accuracy of the methods used for analysis using spike recovery method. The spike recovery was done by adding a known amount of analyte concentration and analyzing it again. 90.90 to 95.50 recovery was achieved in the present study. Black was analyzed after the analysis of three samples of soil and four samples of vegetables. The LOD in mg/kg for Cr, Mn, Fe, Co, Ni, Zn, Cd, and Pb were 0.002, 0.001, 0.001, 0.001, 0.004, 0.0003, 0.0003 and 0.004 respectively, while LOQ in mg/kg for Cr, Mn, Fe, Cu, Ni, Hg, Cd, As and Pb were 0.01, 0.004, 0.004, 0.004, 0.01, 0.001, 0.001 and 0.01.

Conclusion

The heavy metal (Cr, Mn, Zn, Cu, Cd, Ni, Fe and Pb) in this study were all detected in both soil and vegetable samples. The concentrations of some of the heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Pb) were found to be lower than the threshold limit. However, Fe and Cd recorded a higher concentration value than the threshold limit in a soil samples collected at a depth of 0-5 cm, 5-10 cm and 10-15cm. The concentration of the heavy metals (Fe, Co, Ni, Cu, Zn) in vegetable samples (Tomatoes, Onion, Spinach and lettuce) exceeded the maximum threshold limits set by FAO/WHO. Also, the concentrations of Cd in (Tomato and Onion) and Mn (Onion) were found to be higher than the maximum limits. However, Cr and Pb in all the four vegetable samples were found to be lower than the threshold limit. In conclusion the vegetable samples (Tomatoes, Onion, Spinach and Lettuce) as at the time of sample collection are not considered safe for consumption with respect of issues related to Fe, Co, Ni, Cu and Zn. So also, Mn in Onion and Cd in Tomato and Onion sample.

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