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ASSESSMENT OF SOME HEAVY METALS IN FRUIT AND VEGETABLES GROWN IN SAMAWAH CITY, IRAQ

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Abstract: ***This research is conducted to evaluate the levels of some heavy metals (Pb, Cd, Cr, Hg, and As) in fruits and vegetables which are cultivated in farms in different areas of Al-Samawah city, Iraq. The estimation of heavy metals were determined using Atomic Absorption Spectroscopy (AAS). The collectedsamples were digested using tri-acid mixture of HNO_3, $HClO_4$ and H_2SO_4(5:1:1). The results showed that fruit samples were within the permissible levels according to (WHO/FAO), with concentrations of Pb (0.101 -0.405 mg/kg), Cd (0.007 - 0.032 mg/kg), Cr (0.013- 0.131mg/kg) Hg (0.002 - 0.003 mg/kg). For vegetables,results showed thatthe highest concentration of Pb was detected in olive and basil samples with values of 2.122 mg/kg and 2.538 mg/kg, respectively. Pb concentrationsfor the rest of vegetables were within the permissible levels with concentrations ranged at (0.109 -1.451mg/kg). On the other hand, tomatoes showed high levels of Cd with value of (0.211 mg/kg), the results of this metal for the rest of vegetables were at the permissible limitwith values ranged of (0.003- 0.095 mg/kg). The levels of Cr and Hg for vegetables were at the permissible limit with values ranged at (0.110 - 0.326mg/kg), (0.001 - 0.008 mg/kg) respectively.The results indicatesthat fruits and vegetables samples are not contaminated with arsenic,as this metal is not detected by AAS instrument.***

Keywords:Heavymetals, Fruit contamination, Vegetablescontamination,AAS, Accumulation.

Introduction:

Heavy metals contamination resulting from human industrial or agricultural activities is a serious form of environmental pollution[1].In recent years, scientists have been interested in studying heavy metals, their presence in the environment, their biological effects and their relationship to human health,and found that food is one of the main sources of human

exposure to these metals[2]. Food safety and quality has become a main public concern around the world. During the last decades, the increasing demand for food safety has prmote research regarding the risk related with the consuming of food stuffs contaminated by heavy metals[3]. Fruits and vegetables are an important part of the human diet becausethey are staple part of food, especially in the raw form,they contain carbohydrates, protein, vitamins, mineral salts, and they are rich with cellulosic fibers and pectin as well as antioxidants [4], [5]. Therefore, fruits and vegetables are very useful for health and for protecting against various diseases [6].Despite their importance for disease prevention and many other benefits, theycannot be guaranteed safety from pollution [7]. Therefore, fruits and vegetables may be contaminated with heavy metals, whether from the air, soil or irrigation water, and thus many vegetables may lose some vitamins when harvested,About half of them may be lost within a few days, unless they are cooled after harvesting[8]. Heavy metals, in general, are not biodegradable and have long biological half-lives, and also have the potential for accumulation in different body organs, leading to unwanted side effects[9], [10]. Accumulation of lead in edible aquatic plants and in animals has been reported in many literatures[11]. Lead has been found to be toxic to the red blood cells, kidneys, nervous and reproductive systems[12]. Excess of cadmium has been reported to cause renal tubular dysfunction accompanied by Osteomalacia (bone softening) and other complications that can lead to death [13]. Lead and cadmium are two of the most abundant heavy metals and are extremelytoxic. The excess amount of these metals in the diet is linked to a number of pathogens, especially diseases of the heart, blood vessels, kidneys, nervous system, as well as bones[14], [15].Most of the studies show that the use of waste water and well water contaminated with heavy metals for irrigation over long period of time may be increases the heavy metal contents of soils above the permissible limits. [16], [17]. Ultimately, increasing the heavy metal content in soil also increases the uptake of heavy metals by plants depending upon the soil type, plant growth stages and plant species [18], [19].This study aims to determine the potential contamination with heavy metals in several types of fruits and vegetables grown in different farms in Al-Samawah city in Al-Muthanna Governorate, and to determine whether these concentrations are at safe levels according to the international standards, and are safe for human consumption.

Materials and Methods

Sample collection:

More than 75 samples of harvested fresh fruits and vegetables were collected during 2020 grown in different farms in Al-Samawah City, Al-Muthanna Governorate. Three subsamples were collected from different farms for the same fruit and vegetable. All collected samples were stored in clean polyethylene bags and were classified according to their types and prepared for analysis.

Chemicals and Instruments

All the reagents and chemicals used in the study were of analytical grade. HNO_3 (70%, CDH), HCl (36%, Sigma-Aldrich), H_2SO_4 (98%, BDH), $HClO_4$ (65%, Himedia) and deionized water, were used for digestion and dilution of samples. The Samples were analyzed by Flame Atomic absorption spectroscopy (FAAS, Shimadzu Company, AA-7000, Japan) background hollow cathode lamps of Pb, Cd, Cr, Hg and As have been used in specific wavelengths.

Washing and drying:

Fruit and vegetable samples were washed with tap water several times, then with distilled water to remove dust,then they cut to small pieces using clean knife. The samples were dried in an oven at 100 °C for several hours until they were completely dry from the water. After that, each sample was taken separately and milled to fine powder. Later, the dried powdered samples were stored in polyethylene bags and prepared for acid digestion.

Digestion:

The samples were digested using dry digestion method, where 1 gram of each sample was weighed and placed in a 250 mL conical flask, then two drops of perchloric acid were added and vigorously shaken, then the conical flaskwas covered with a layer of aluminum foil and left for a whole day.After that, 15 ml of tri-acid mixture of (70% HNO_3, 65% $HClO_4$ and 98% H_2SO_4; 5:1:1) was added to the conical flask[20].The mixture was then digested on a hot plateat 80 °C, conical flaskwas covered with a watch glassand stirred with magnetic stirrer and left until dense white fumes was evaporated, then the samples left to cool. After cooling, the digested samples were filtered using Whatman filter paper No. 42 and the filtrates were diluted with deionized water to 50 ml in a volumetric flask and stored in fridge at 4 °C.

Statistical Analysis

All the samples analyses in this study were carried out in triplicate and the results were reported as mean ± standard deviation. Statistical analysis were carried out using SPSS software, version 22.

Results and discussion:

The analytical results of the present study indicate the heavy metal content of Pb, Cd, Cr, Hg and As determined in selected fruit and vegetables collected from Different areas of the city of Samawah in Al-Muthanna Governorate. The observed concentrations of Pb, Cd, Cr, Hg and As in the fruit and vegetables were compared with the recommended limits as established by literature[21] to assess the levels of food contamination. The mean concentrations are summarized in Tables 1 and 2 and Figures 1 and 2. Results are expressed as mean ± SD of the three replicate analyses.

Table 1: Concentrations of heavy metals in different Fruit samples in mg/kg. (Mean ± standard deviation).

Fruits	pb	Cd	Cr	Hg	As
Watermelon	0.199 ±0.018	0.012±0.002	0.105±0.004	ND[a]	ND
Melon	0.235 ±0.015	0.009 ±0.000	0.119 ±0.005	0.002 ±0.000	ND
Banana	0.103 ±0.004	0.007 ±0.000	0.013±0.002	ND	ND
Orange	0.101 ±0.004	0.011 ±0.002	0.114±0.005	0.003 ±0.000	ND
Apple	0.176 ±0.011	0.024 ±0.003	0.131±0.012	ND	ND
Grape	0.123 ±0.008	0.014 ±0.002	0.109 ±0.004	ND	ND
Pear	0.129 ±0.008	0.011±0.002	0.127 ±0.006	ND	ND
Pomegranate	0.341 ±0.029	0.013 ±0.002	0.118 ±0.005	ND	ND

Peach	0.405 ±0.038	0.032 ±0.004	0.107 ±0.004	ND	ND

[a]ND= Not Detectable

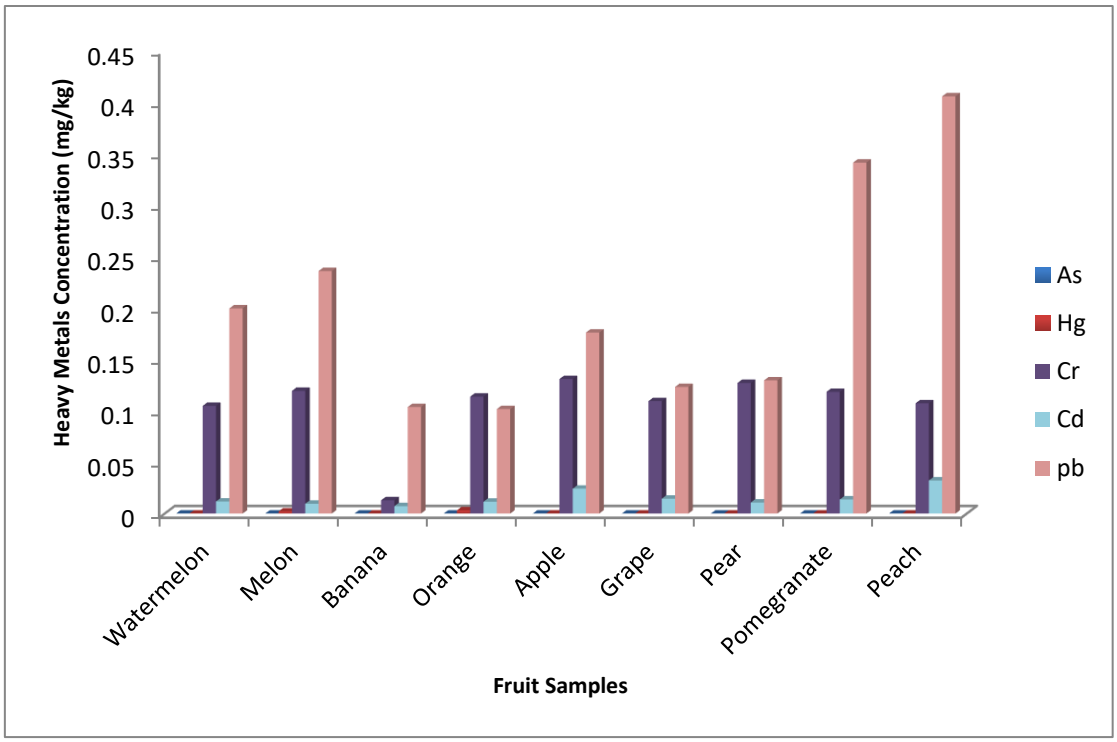

Figure 1: Heavy metals concentrations (mg/kg) in Fruit Samples

The obtained results of the present study showed that the concentration ofPbin peach recorded the highest concentration among the fruit samples withconcentration of 0.405 mg/kg.However, the lowest concentration of Pb in orange which was 0.101 mg/kg.Which is considered at the permissible limits at the WHO and FAO(World Health Organization,Food and Agricultural Organization) for lead concentrations which is 2 mg/kg[22].The results also showed thatthe highest concentration of cadmium metal recorded in peach also, with concentration of 0.032 mg/kg, and the lowest concentrationwas in banana and melonwhich was 0.007 and 0.009 mg/kg, respectively.Which is considered at the permissible limits at the WHO and FAO for Cd concentrations, which is0.2 mg/kg[22]. For chromium concentrations, the results showedapples and pears have the highest levels, with concentration of 0.131 and 0.127 mg/kg,respectively, and the lowest concentration was in banana which was 0.013 mg/kg.It is also considered at the permissible limits at the WHO and FAO for Cr concentrations, which is 1 mg/kg [21].The results showed that no concentrations of mercury appeared in fruit samples, except for watermelon and oranges,

and the concentrations were very low, with values of 0.002 and 0.003, respectively. thus did not exceed the permissible limit according to the WHO and FAO for Hg, which is 0.5 mg/kg[21]. On the other hand,the results did not show any concentrations ofarsenic in all fruit samples.In this work, the results of heavy metals in fruit samples were lower than the report of literature[23] but agreed withliterature[24].The reason for the lack of contamination of fruit samples with these metals (pb, Cd, Cr, Hg and As)may be due to that they were not transferred to the markets, but were directly collected from farms and various orchards in Samawah and took for analysis.

Table 2: Average concentrations of heavy metals in different vegetable samples in mg/kg. (Mean ± standard deviation).

vegetables	pb	Cd	Cr	Hg	As
Olive	2.122±0.123	0.020±0.002	0.124 ±0.008	ND	ND
Basil	1.451 ±0.065	0.007 ±0.000	0.220 ±0.002	0.002 ±0.000	ND
Aubergine	0.109±0.005	0.015 ±0.001	0.121±0.008	ND	ND
Okra	0.254±0.017	0.003±0.000	0.118 ±0.006	0.003 ±0.000	ND
Mint	0.308 ±0.028	0.008 ±0.000	0.208±0.002	0.001 ±0.000	ND
Cucumber	0.127±0.008	0.019 ±0.001	0.135±0.007	0.001±0.000	ND
Celery	1.083±0.043	0.095 ±0.006	0.292 ±0.019	0.008 ±0.000	ND
Tomato	1.243 ±0.061	0.211±0.014	0.170 ±0.011	0.003±0.000	ND
Green pepper	0.328±0.029	0.075 ±0.004	0.190 ±0.012	0.005 ±0.000	ND
Cress	0.223 ±0.015	0.033±0.003	0.238 ±0.015	ND	ND
Onions	0.139	0.025	0.178±0.011	ND	ND

	±0.007	±0.002			
Radish	2.538 ±0.136	0.128±0.008	0.326±0.028	0.002±0.000	ND
Lemon	0.294 ±0.019	0.018 ±0.001	0.114±0.006	ND	ND
Zucchini	0.114 ±0.006	0.008 ±0.000	0.110 ±0.006	ND	ND

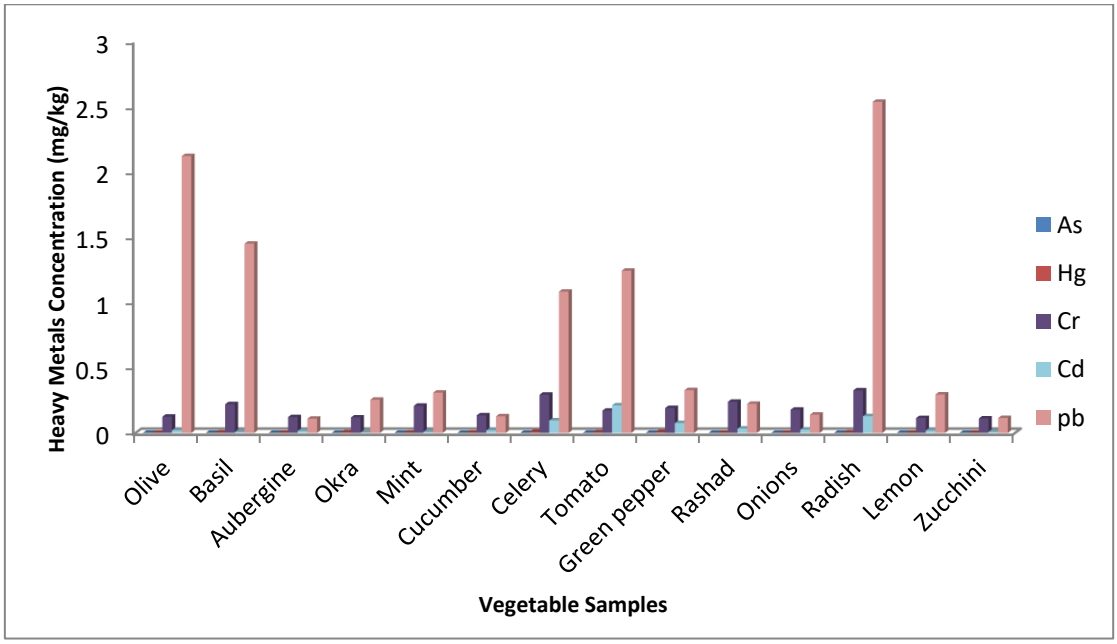

Figure 2: Heavy metals concentrations (mg/kg) in Vegetable Samples

Table 2 demonstrates that some vegetable samples contain lead concentrations above the limit permitted which mention in the literature[22].These are olive and radish samples, where the concentrations were 2,122 mg/kg and 2,538 mg/kg, respectively, and this is agreed with the range reported by[25], While lead concentrations in the rest of the vegetable samples were within the permissible limits, as they range of 0.109 to 1.451 mg/kg for eggplant and basil, respectively. The range is slightly lower than the report [26]but agreed with the results reported by[27].The reason for the high leadconcentrations can be attributed to car exhaust, organic fertilizers, mines and sludge[28], as well as air pollutants and industrial progress that had a great impact on the spread of industrial pollutants containing heavy metals, which leads to an increase of these metals in the soil and the environment, and thus their transferto plants by absorbing them from contaminated

soil[29].Lead is concentrated in leafy vegetables due to the large surface area of their leaves as well as due to its direct precipitation on the aerial parts of the plant[30]. High lead levels cause many diseases such as pallor of the skin, kidney damage, congenital deformities, miscarriage of pregnancy, nausea, vomiting, abdominal pain, and joint paralysis [28].The results showed that cadmium levelsare in the range of 0.003 mg/kg and 0.095 mg/kg, these values are for okra and celery respectively.These values at the permissible limits and this is agreed withliteratures [26], [31].It was noticed that the highest concentration of cadmium was in tomatoes, where it was 0.211 mg / kg, which exceeded the permissible limit in a small amount, which is higher than the report in literature [26].

The high levels of cadmium in vegetables is due to the soil containing high levels of cadmium, which is transferred to the vegetables when planted in contaminated soil, and also due to the addition of fertilizers and the ability of plants to absorb high amounts of cadmium. Some metals such as cadmium [32]and others can be transferred to the soil from factory wastes, organic and chemical fertilizers and wastewater that are dumped in rivers without treatment and using contaminated river water for irrigation, which leads to the transmission of metals to the soil [29].High cadmium in the human body leads to osteoporosis, lung cancer, and liver disease, as well as kidney damage [33], deformities in the skeleton, disturbances in the digestive system, affects the heart and blood vessels, and high blood pressure[34].The results showed that chromium content in all vegetables ranges from 0.110 mg/kg to 0.326 mg/kg, (these values are for zucchini and radish respectively) and these values are at the permissible limit as described in the literature [18]. The range of chromium in vegetables is lower compared to the results reported by [25].Chromium (III) occurs naturally in fruits and vegetables, meat, yeast and grains and is an essential nutrient for humans, shortages of which may cause heart conditions disruptions of metabolisms and diabetes. However, excessive absorption of chromium may cause skin rashes, ulcers, liver and kidney damage, breathing and stomach problems, weak immunity, and a change in genetic material**,** as well as lung disease, cancer and death [28].

The mercury content in this study was generally lower than the permissible levels as described in [18], as the mercury content in vegetables resulting from this study presented in Table 2 ranges from 0.001 mg / kg to 0.008 mg / kg for cucumber and celery respectively. It is higher compared to the literature[29], but lower compared to the literature[35].Mercury is a major non-essential trace metal in food,its presence in food indicates the presence of contamination [36].This heavy metal targets the liver, immune

system and pituitary gland, causing untold damage that may sometimes lead to death. [37][38]. Table 2 also showed that arsenic did not record any significant percentage in any sample of the studied vegetables,This is what literature[39] found when analyzing some vegetable samples.All the fruits and vegetable had not detectedany arsenic levels.The permissible limit of 0.05 mg/kg for arsenic set by literature[21].Plants absorb arsenic from the soil as they grow, which means that thismetal works its way into our food with this method. Arsenic is extremely dangerous to human health,long term exposure to low doses of arsenic may change the way cells communicate, and reduce their ability to function. It could, in fact, play a role in the development of diabetes, cancer, vascular and lung diseases[9].

Conclusion

From the results obtained in this study, the following can be concluded:

- Very low concentrations were recorded for chromium, mercury and arsenic in samples of fruits and vegetables grown in different farms in the city of Samawah in the province of Muthanna/ Iraq.
- Olive and radish samples contained highlead concentrations of 2.122 and 2.538 mg/kg respectively, which are higher than the maximum permissible limits for the World Health Organization and the Food and Agriculture Organization, while we find thatlead concentrations in the rest of the vegetables and all the studied fruits did not exceed the permissible limits.
- For fruit and vegetable samples, all cadmium values are less than the permissible limits for WHO and FAO, with the exception of tomato samples, which recorded a concentration of 0.211 mg/kg, whichexceed the permissible limits.
- Vegetables and fruits studied in this research can be consumed safely due to acceptable levels of heavy metals contained in these plants.

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