

## Investigation of some Heavy Metals Concentration in Certain Vegetable Crops Grown in Industrially Polluted And Non-Polluted Areas in Misurata City

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### Abstract

This study was performed a complete scan the area of Kaser Ahmed (polluted), Sket and Zerak areas (non-Polluted ) in regarding some heavy metals concentrations such as Pb, Cd, Fe, Cu, Cr and Zn in certain vegetables (Tomato, Pepper, Eggplant, Corn, Bean and Garden pea). A total of 26 and 34 vegetable samples from Polluted and non-Polluted Areas respectively were chosen for analysis. Wet-dry digestion method using HNO<sub>3</sub>: HClO<sub>4</sub> (ratio 2:1) was employed in sample preparations for analysis. The concentrations of heavy metals in vegetable sample were determined using Differential Pulse Stripping Voltammetry (DPAdSV) and inductively coupled plasma optical emission spectrometry (ICP-OES). Statistical analysis were carried out using SPSS program. The results revealed , that the concentrations of studied heavy metals in vegetable, shown a from permissible limit. Fe concentration in all studied samples was relatively high compared with other elements. Zn concentration was within the allowed limit for samples in Kaser Ahmed region . Cu concentration exceeded permissible limit in Bean sample of Kaser Ahmed region and it was within allowed limit for other samples. The concentration of Pb was lower than permissible limit . Cd concentration was exceeded the allowed limit in Eggplant, Bean and Gardenpea samples in Kaser Ahmed region and Pepper sample in Sket region .For Cr, the concentration exceeded the permissible limet and allowable limits in vegetables , approaching the level of poisoning for all samples. Eventually, all elements studied except that of Cr not exceeded the level of poisoning . The results of analyses by( DPAdSV ) were in good agreement with the result of ( ICP-OES) technique.

*Keywords:* Trace elements, Differential Pulse Stripping Voltammetry ( DPAdSV ), (ICP-OES), Wet dry digestion, Industrially Polluted and non-Polluted Areas.

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### 1. Introduction

Consumption of vegetables is one of the most important pathways by which heavy metals enter the food chain. Both the farmland and urban environment often suffer from the metal contamination Therefore, human exposure to contaminations of vegetables is a matter of health concern.[1]. Vegetables are staple part of human meal taken as food in raw or cooked forms. Over the past few decades, there has been a change in the focus of nutritional, health concerns from malnutrition to wide spread chronic shortages of micronutrients. Their

deficiency may cause serious functional disorders [2]. Trace elements are inorganic compounds, which are essentially required for normal metabolism [3]. These minerals are required in minute quantities [4]. They have tendency to accumulate in human vital organs over prolonged period of time leading to unwanted side effects [5]. The excess and deficiency of micronutrients may produce undesirable effects. Excess of these nutrients in food are associated with number of diseases especially with cardiovascular, kidney, nervous as well as bone diseases [6]. The deficiency of trace metals also cause diseases like impaired immune functions, gastrointesti-

nal distress, muscular pains etc [7]. Therefore determination of metal content in vegetables is important from view point of crop yield, food nutrition and health impacts. The requirement of vegetables in our daily diet must be 300-350 gm per person as these contain large quantities of Vitamins, Carbohydrates, essential amino acids and dietary fibers, which are required for normal functioning of human[8]. Lead, copper, zinc and iron concentrate in the soil and water and ultimately leads to the vegetables [9]. Metallic uptake has been widely investigated throughout the world. Metals usually enter the food chain from water to soil and then to plant roots[10]. Zinc and cadmium were found in vegetables [11]. Heavy metals in edible green vegetables grown along the sites of rivers were estimated [12]. Keeping in view of the importance of the role of heavy metals play in defining the nutritional status of human body. Cultivated land in the vicinity of industrial areas, which is irrigated by run water, gets contaminated because the industrial effluents enter into run The toxic heavy metals entering the ecosystem may lead to geo accumulation bioaccumulation and biomagnifications [13]. Heavy metals like Fe, Cu Zn, Mn and other trace elements are important for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders[14]. Environmental pollution is now-a-days a cause of concern. Heavy metal pollution of agricultural vegetables is one of the most severe ecological problems on a world scale and also in Misurata. The food chain contamination is the major pathway of heavy metal exposure for humans[15]. Some trace elements are essential in plant nutrition, but plants growing in the nearby zone of industrial areas display increased concentration of heavy metals serving in many cases as biomonitors of pollution loads[16].Vegetables cultivated in soils polluted with toxic metals due to industrial activities take up heavy metals and accumulate them in their edible and nonedible parts in quantities high enough to cause clinical problems both to animals and human beings consuming these metal-rich plants because there is no good mechanism for their elimination from the human body[17,18]. Therefore, a better understanding of heavy metal sources, on risk assessment. Information regarding the accumulation of essential heavy metals in vegetables in industrially polluted areas in Misurata is scarce.

## 2. Materials and methods

**Selection of sampling sites and vegetables:** Samples of vegetables were chosen from three agricultural areas exposed to different degrees of environmental pollution. Area 1 : Direct pollution due to The vegetable samples in this area were taken from the side of iron and steel complex, where the samples were collected from a distance of 400 m. Area 2: Indirect pollution by rain water and submerged the adjacent cultivable land where the farmers grew their vegetables in winter a distance of 4.5 km. As control. Area 3 : The same vegetables samples were collected from I considered as check area. a distance of 35 km. As control as well. For comparison samples were taken from a distance of 35 km to ensure that the sample be accurately represents the source it has been compiled following types of vegetables: tomatoes, corn, eggplant, peppers, beans and peas. **method of sample collection:** The samples were collected from the study area by standard methods and by the way the world Estienne [19]. according to the presence nearby of iron and steel complex agricultural areas. Took samples from the target of the study sites randomly and by three replicates for each sample. Samples are placed in paper bags impermeable to air with the writing of the initial data on each bag.- Samples are transported to the laboratory. Sample is washed and placed in plastic bags labeled preliminary data developed at a temperature of about (20 °C) to when transferred to drying, and the number of pooled samples arrived from the study area and the comparison during the summer to (22). a sample of vegetable crops, with three replicates. The samples were taken from mature and ready for human use vegetables **Reagents and solutions:** All reagents are of analytical grade. A solution of 0.01M of each Cu (II), Cd (II), Fe (III), Pb (II) and Zn (II) were prepared respectively by dissolving the required amounts  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (BDH),  $\text{Pb}(\text{NO}_3)_2$  (Sigma),  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (BDH),  $\text{Fe}(\text{NO}_3)_3$  (BDH) and  $\text{Zn}(\text{NO}_3)_2$  (BDH) in deionized water. **Preparation and preservation:** The vegetables were washed in fresh running water to eliminate dust, dirt, possible parasites or their eggs and then were again washed with deionized water. The clean vegetable samples were cut into 2-cm pieces and air-dried and placed in an electric oven at 65°C for 72–96 h depending on the sample size. The dried vegetables samples were homogenized by grinding using a ceramic coated grinder and used for metal analysis. **Digestion and determination:** One gram of dry matter was weighed into 50-ml beakers, fol-

lowed by the addition of 10 ml mixture of analytical grade acids  $\text{HNO}_3$ :  $\text{HClO}_4$  in the (ratio 2:1). The digestion was performed at a temperature of about  $190^\circ\text{C}$  for 1.5 h. After cooling, the solution was made up to a final volume (25 ml) with deionized water in 25ml a volumetric flask. The metal concentrations were determined by Differential Pulse Stripping Voltammetry (DPAdSV) and inductively coupled plasma optical emission spectrometry (ICP-OES). Analysis of each sample was carried out three times to obtain representative results. The mean data reported in  $\mu\text{g}/\text{ml}$  (on a dry matter basis). Statistical analyses Statistical analyses were carried out using the SPSS® statistical software package (SPSS for Windows version 13.0, SPSS Inc., Chicago, Illinois, USA), A “p” value  $<0.05$  was considered statistically significant. Student-t test was used to determine the difference between two techniques. All results are expressed as mean and standard deviation (mean  $\pm$  SD). Experimental: Instrumentation: All glassware was soaked in 10% (v/v)  $\text{HNO}_3$  for 24 h and rinsed three times with distilled water and then in deionized water before use. Anodic differential pulse stripping voltammograms were recorded by polarographic Analyzer stripping voltammeter Model 264 A (EG&G, Princeton Applied Research; Princeton, NJ, USA), coupled with a PAR 303 A Static Mercury Drop Electrode (SMDE; drop size: medium, area of the drop:  $0.014\text{ cm}^2$ ). The polarographic cell bottom (PAR Model K 0060) was fitted with Ag/AgCl saturated KCl, reference electrode, and platinum wire used as a counter electrode. A PAR 305 stirrer was connected to the 303 SMDE. A PAR Model RE 0089 X-Y recorder was used for recording the voltammograms. Before measurements the sample solution was deaerated by bubbling for 16 minutes with nitrogen. During measurements, an inert atmosphere over the solution was maintained by flushing with nitrogen. During the deposition step, the solution was stirred automatically, followed by a quiescent period of 15 sec before scanning. All the determinations were carried out by inductively coupled plasma optical emission spectrometry (ICP-OES). Thermo Fisher Scientific Announces Enhanced iCAP 6200 Optical Emission Spectrometer was used with the following operating conditions: Nebulizer Gas flow rates: 0.6 l/min; Auxiliary Gas Flow: 0.5 l/min; Coolant Gas Flow: 12 l/min; Nebulizer Argon Flow: 0.6 l/min; Pump Speed: 45 rpm; RF Forward Power: 1150 Prior to analysis. pH was measured with Hanna microprocessor pH model 211. Analytical proce-

dure: the following parameters were used to perform Differential Pulse Anodic Stripping Voltammetry (DPASV). Scan rate  $10\text{ mVs}^{-1}$  with duration for 1 sec and pulse amplitude ( $\Delta E$ ) 25 mV. For determination of Cu(II), Pb(II), Cd(II) and Zn in vegetables samples in the same cell. 5 mL of each sample solution and 1 mL of 0.1 M  $\text{HNO}_3$  solution as supporting electrolyte were transferred into the electrolysis cell and completed to 10 mL using bidistilled water (pH  $\sim 2$ ). The solution was deaerated by passing pure nitrogen for 16 min. The deposition potential were controlled at -1.2, -0.25, -0.6 and -0.75 V vs. Ag/AgCl sat'd KCl respectively and applied to a fresh mercury drop while the solution was stirred. After the deposition step and further 15 sec. (equilibrium time) the voltammogram was recorded. Different concentration from the standard metal ion (individually) were added to the cell using an automatic pipette, while keeping the deposition time constant. The solution was stirred and purged with nitrogen for 30 sec. after each spike. The concentration of each Cu (II) and Pb (II), Cd (II), Fe (III), Cr (III) and Zn (II) in the electrolytic cell was calculated in the sample solutions by using standard addition method, Then the concentration in  $\mu\text{g}/\text{ml}$  of each the vegetable crops were calculated and compared. 1. Determination of Zn (II), Cd (II), Pb (II) and Cu (II) in vegetable samples by Differential Pulse Anodic Stripping Voltammetric (DPASV) technique: 5 ml of each sample solution and 1ml of 0.1M  $\text{HNO}_3$  solution as supporting electrolyte were transferred into the electrolysis cell and completed to 10 mL using bidistilled water. The final pH of solution is  $\sim 2$  and deaerate by passing pure nitrogen through 16 minutes. Use deposition potential of -1.2 , -0.75 , -0.55 and -0.25 V vs. Ag/AgCl sat'd KCl for Zn (II), Cd (II), Pb (II) and Cu (II) respectively. The solution was stirred-following the suitable deposition time. Then the stirring was stopped. After the deposition step and a further 15 sec. (equilibrium time), the voltammogram (quiescent solution) for a positive going potential scan was recorded. Different concentrations from the standard zinc, cadmium, lead or copper ion solution were spiked to the cell while keeping the deposition time constant. The solution was stirred while purging with nitrogen for 30 sec. after each addition and then proceed through the deposition and stripping step as before. The voltammograms were recorded following the deposition periods.

3. Determination of Fe (III) in vegetable samples

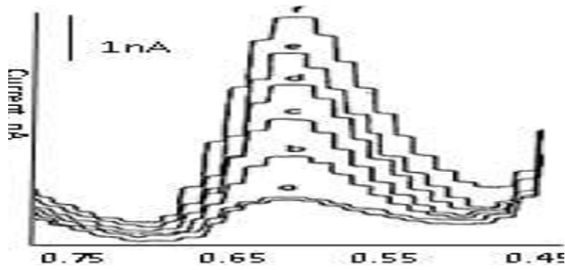


Fig. (1): DPAS voltammetry for determination of Cd (II) in vegetable crops with different concentration of Cd (II) ions [0.1M HCl+2M NaCl], pH=1.0 at initial potential -0.75 V and deposition time 150 sec:  
 (a) Sample, (b)  $S_6 + 1.5 \times 10^{-8}$  (c)  $S_6 + 3 \times 10^{-8}$   
 (d)  $S_6 + 4.5 \times 10^{-8}$  (e)  $S_6 + 6 \times 10^{-8}$  and (f)  $S_6 + 7 \times 10^{-8}$  M Cd(II)

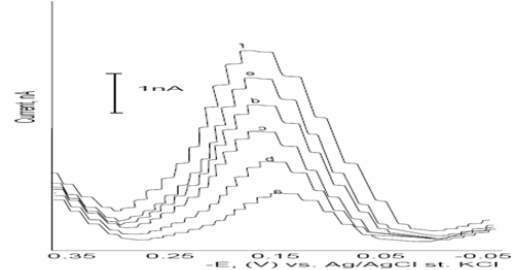


Fig. (2): DPAS voltammetry for determination of Cu (II) in vegetable crops with different concentration of Cu (II) ions [0.1M HCl+2M NaCl], pH=1.0 at initial potential -0.35 V and deposition time 120 sec:  
 (a) Sample, (b)  $S_6 + 1.5 \times 10^{-6}$  (d)  $S_6 + 4.5 \times 10^{-6}$   
 (c)  $S_6 + 3 \times 10^{-6}$  (e)  $S_6 + 6 \times 10^{-6}$  and (f)  $S_6 + 7 \times 10^{-6}$  M Cu(II)

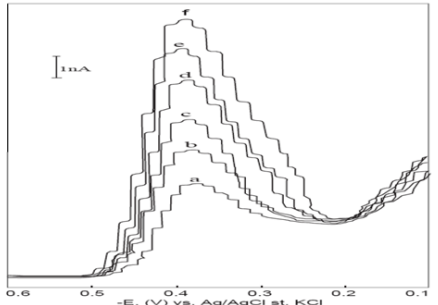


Fig. (3): DPAS voltammetry for determination of Pb (II) in vegetable crops with different concentration of Pb (II) ions [0.1M HCl+2M NaCl], pH=1.0 at initial potential -0.6 V and deposition time 10 sec:  
 (a) Sample, (b)  $S_{18} + 1 \times 10^{-8}$  (d)  $S_{18} + 3 \times 10^{-8}$   
 (c)  $S_{18} + 2 \times 10^{-8}$  (e)  $S_{18} + 4 \times 10^{-8}$  and (f)  $S_{18} + 5 \times 10^{-8}$  M Pb(II)

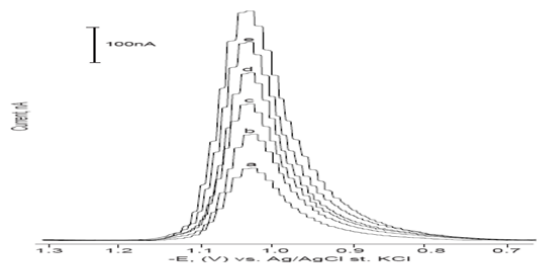


Fig. (3): DPAS voltammetry for determination of Zn (II) in vegetable crops with different concentration of Zn (II) ions [0.1M HCl+2M NaCl], pH=4.0 at initial potential -1.3 V and deposition time 15 sec:  
 (a) Sample, (b)  $S_5 + 5 \times 10^{-7}$  (d)  $S_5 + 15 \times 10^{-7}$   
 (c)  $S_5 + 10 \times 10^{-7}$  (e)  $S_5 + 20 \times 10^{-7}$  and (f)  $S_5 + 25 \times 10^{-7}$  M Zn(II)

by cathodic linear sweep Stripping Voltammetric (CLSSV) technique: 5 ml of each sample solution, 1ml of 0.1M NaClO<sub>4</sub> solution as supporting electrolyte and 1ml of 0.4x10<sup>-4</sup>M catechol as a complexing agent were transferred into the electrolysis cell and completed to 10 mL using bidistilled water. The final pH of solution is ~ 7.15 and deaerate by passing pure nitrogen through 16 minutes. Use deposition potential of -0.2V vs. Ag/AgCl sat'd KCl. The solution was stirred-following the deposition time 5, 10 or 15 sec. Then the stirring was stopped. After the deposition step and a further 15 sec. (equilibrium time), the voltammogram (quiescent solution) for a negative-going potential scan was recorded. Different concentrations from the standard metal ion solution were spiked to the cell while keeping the deposition time constant. The solution was stirred while purging with nitrogen for 30 sec. after each addition and then proceed through the deposition and stripping step as before. The

voltammograms were recorded following the deposition periods. Determination of Cr (VI) in vegetable crops samples by cathodic linear sweep stripping voltammetry (CLSSV): (7.5 mL of each sample + 1 mL of the 0.1M KNO<sub>3</sub> and 1 mL of the 0.01M (H<sub>2</sub>A<sup>-</sup>, HA<sup>2-</sup>) sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>) = (H<sub>2</sub>A<sup>-</sup>), disodium monohydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) = (HA<sup>2-</sup>) was transferred and diluted to 10 mL using bidistilled water into the voltammetric cell; pH~7.0. The solution was deaerated by passing pure nitrogen for about 15 min. the preconcentration potential (+0.05 V vs Ag/AgCl 3.5M electrode) was applied to a fresh mercury drop while the solution was stirred and the final potential is -0.4V. Cathodic Linear Sweep Stripping Voltammogram (CLSSV) was recorded using 100 mV s<sup>-1</sup> scan rate. After the accumulation step, and further 15 sec. equilibrium time the background voltammogram was recorded. Different concentrations of the

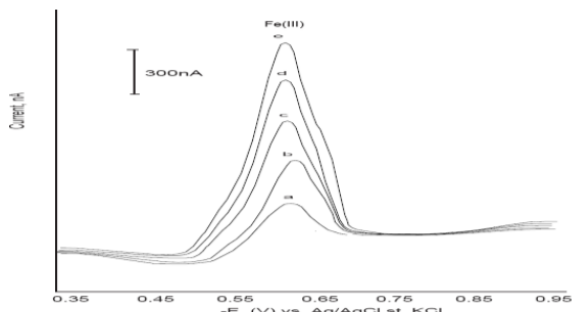


Fig. (5): DPA<sub>2</sub>SV voltammetry for determination of Fe(III) in vegetable crops in presence of 0.11M (NH<sub>4</sub>OH, NH<sub>4</sub>Cl), and 10<sup>-5</sup> M 5-Br-PADAP, pH=8.5 at accumulation potential -0.35V and different accumulation time 20 sec (a) sample, (b) S<sub>1</sub> + 2x10<sup>-4</sup> (c) S<sub>2</sub> + 4 x10<sup>-4</sup> (d) S<sub>3</sub> + 6 x10<sup>-4</sup> and (e) S<sub>4</sub> + 8 x10<sup>-4</sup> M Fe(III)

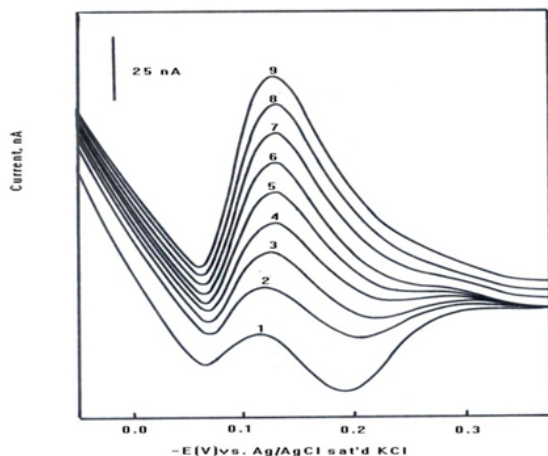


Fig. (6): CLSS Voltammograms for determination of Cr(VI) ions in vegetable crops sample spiked with different concentrations of Cr(VI), and accumulation time 30 sec.  
 1) sample, S 2) S + 10x10<sup>-5</sup> 3) S + 20x10<sup>-5</sup> 4) S + 30x10<sup>-5</sup> 5) S + 40x10<sup>-5</sup>  
 6) S + 50x10<sup>-5</sup> 7) S + 60x10<sup>-5</sup> 8) S + 70x10<sup>-5</sup> 9) S + 80x10<sup>-5</sup> M Cr(VI).

analyte were added to the same voltammetric cell and purge for 2 min. and complete the procedure as above.

### Blank measurements:

The ultra trace amounts of the elements under investigation probably found as impurities (if any) in the supporting electrolytes were determined using the optimal conditions. This is more precise rather than the subtraction of the residual current directly from the experimental readings of the samples a construction of standard calibration plots in the supporting electrolyte Calculation of the concen-

tration: After each determination, the plot of peak current against concentration was drawn for each spike. The standard addition method was used to determine each analyte in the sample. The experiments were done in 5 replicates for each metal ion in each sample. The interception of the line with the concentration axis at zero current signals gives the concentration of the analyte in the voltammetric cell for each sample, these values multiplied by the factor 2 since the original volume of the sample is 5 ml.

### 3. Results and Discussion

The concentrations of Fe, Cu, Cr, Pb, Zn and Cd were observed in vegetables samples collected from three different locations. are given in Table 1 ,2. The data have been presented at 99 % (± 2S) confidence. level for triplicate measurements in each of the case. The magnitude of trace elements content in vegetables in respect of two locations was directly polluted and non-polluted. The concentrations of trace elements (µg/ml) in vegetables were quite variable such as and Fe (136.42–151.35), Zn (40.22–43.44) ,20.86 – Cu (18.57 A statistically significant difference (P<0.01) was found between the polluted and non-polluted areas in vegetables Similar result was observed by Ambirika (2008)[20] .There were significant differences in the average Cr, Fe, Cu, and Zn concentrations (µg/ml) in different vegetable species (Tomato, Pepper, Eggplant, Bean , and Gardenpea ) in different locations. In directly polluted area, Pb (µg/ml) was highest in Tomato with a mean of 1.26 followed by , Pepper with a mean of 1.26 and minimum in Corn with 0.009 (µg/ml). Iron (µg/ml) was highest in Tomato with a range of 151.35 to 136.42 followed by Pepper with a range of 91.77 to 88.004 . This group of vegetable appears to be rich in iron content, especially in Tomato, Pepper, Eggplant, Garden pea. whereas minimum concentration of Fe ranged from 30 to 31.87 in Bean . Iron concentration waslower than the reported values of Haliru (2009) [21] but more than those obtain by Ghafoor and Manzoor. (2004) [22]. Copper (µg/ml)was found highest in Tomato with a range of 20.86to 18.41 followed by Pepper with a range of 9.86 to 14.1 and garden Bean was 9.14 to 12.6. Lowest content was found in Eggplant (8.01-10.9). The extent of Cu content can be arranged in the order of Tomato > Coriander > Eggplant > Pepper. Zinc concentrations (µg/ml) with a range of 43.44to 1.11 ( followed the trend Tomato

**Table 2.1:** Level(mean±SD) µg/m l of ( Pb, Cd, Fe, Cu, Cr & Zn) in vegetables sample using (DPAdSV) techniques and Distances of each sample from the iron and steel complex

vegetable crops	Tomato			Pepper			Eggplant			Corn			Garden pea			Bean			p
Dist ances (Km)	0.4	4.5	35	0.4	4.5	35	0.4	4.5	35	0.4	4.5	35	0.4	4.5	35	0.4	4.5	35	
Cr	16.43±0.01	11.38±0.0	11.00±0.0	14.16±0.02	12.29±0.01	10.15±0.01	14.11±0.03	10.43±0.01	9.11±0.00	11.21±0.01	5.61±0.0	4.32±0.0	15.49±0.03	11.65±0.0	10.49±0.0	14.05±0.01	10.68±0.02	9.11±0.6	0.07
Cu	19.66±2.5	12.15±1.8	11.25±1.5	16.46±1.6	12.56±1.5	10.05±1.4	13.34±1.7	10.04±0.99	9.46±1.0	10.46±1.0	3.04±0.30	2.22±0.22	21.03±1.2	12.04±1.2	11.45±1.1	12.14±1.02	6.24±0.55	5.02±0.35	0.04
Cd	0.07±0.0	**	**	0.10±0.01	0.094±0.072	**	0.09±0.0	**	**	**	**	**	**	**	**	**	**	**	0.05
Pb	1.18±0.034	0.17±0.044	0.015±0.023	0.19±0.0113	0.094±0.072	0.05±0.0212	0.046±0.013	**	**	0.17±0.0318	**	**	0.25±0.0212	0.12±0.0034	0.02±0.0034	0.36±0.0027	0.12±0.044	**	0.081
Fe	150.35±0.02	77.08±0.2	70.21±0.05	91.37±0.09	68.32±0.09	65.14±0.04	85.48±0.09	70.12±0.01	68.21±0.08	57.09±0.02	50.15±0.03	39.47±0.03	90.09±0.03	66.42±0.04	58.22±0.08	84.44±0.04	78.43±0.04	66.16±0.07	0.03
Zn	43.04±0.0	29.15±0.27	20.54±0.55	40.31±0.11	27.45±0.75	10.21±0.1	35.32±1.0	19.16±0.11	17.16±0.6	22.63±0.33	18.17±0.02	7.12±0.09	33.11±1.0	23.57±0.89	4.55±0.01	13.24±0.55	3.01±0.35	1.28±0.0	0.05

(\*) represent the reading less than detection limit

**Table 2.2:** Level(mean±SD) µg/m l of ( Pb, Cd, Fe, Cu, Cr & Zn) in vegetables sample using (ICP-OES) techniques and Distances of each sample from the iron and steel complex

vegetable crops	Tomato			Pepper			Eggplant			Corn			Garden pea			Bean			p	
Dist ances (Km)	0.4	4.5	35	0.4	4.5	35	0.4	4.5	35	0.4	4.5	35	0.4	4.5	35	0.4	4.5	35		
Cr	43.04±0.0	150.35±0.02	1.18±0.034	0.07±0.0	**	**	0.07±0.0	**	**	**	**	**	0.07±0.0	**	**	**	0.07±0.0	**	**	0.07
Cu	29.15±0.27	77.08±0.2	0.17±0.044	19.66±2.5	12.15±1.8	11.38±0.0	19.66±2.5	12.15±1.8	11.38±0.0	10.46±1.0	3.04±0.30	5.61±0.0	10.46±1.0	3.04±0.30	5.61±0.0	2.22±0.22	4.32±0.0	21.03±1.2	15.49±0.03	0.04
Cd	20.54±0.55	70.21±0.05	0.015±0.023	0.10±0.01	12.56±1.5	12.29±0.01	0.10±0.01	12.56±1.5	12.29±0.01	0.09±0.0	0.09±0.0	0.09±0.0	0.09±0.0	0.09±0.0	0.09±0.0	0.09±0.0	0.09±0.0	0.09±0.0	0.09±0.0	0.05
Pb	40.31±0.11	91.37±0.09	0.19±0.0113	0.094±0.072	0.094±0.072	**	0.094±0.072	**	**	0.046±0.013	0.046±0.013	0.046±0.013	0.046±0.013	0.046±0.013	0.046±0.013	0.046±0.013	0.046±0.013	0.046±0.013	0.046±0.013	0.081
Fe	27.45±0.75	68.32±0.09	0.094±0.072	0.094±0.072	0.094±0.072	**	0.094±0.072	**	**	0.05±0.0212	0.05±0.0212	**	0.05±0.0212	**	**	0.17±0.0318	0.17±0.0318	0.17±0.0318	0.17±0.0318	0.03
Zn	10.21±0.1	65.14±0.04	0.05±0.0212	0.05±0.0212	0.05±0.0212	**	0.05±0.0212	**	**	85.48±0.09	70.12±0.01	**	85.48±0.09	**	**	57.09±0.02	57.09±0.02	57.09±0.02	57.09±0.02	0.05
	17.16±0.6	68.21±0.08	**	17.16±0.6	68.21±0.08	**	17.16±0.6	68.21±0.08	**	18.17±0.02	50.15±0.03	**	18.17±0.02	50.15±0.03	**	7.12±0.09	39.47±0.03	7.12±0.09	39.47±0.03	
	22.63±0.33	57.09±0.02	0.17±0.0318	22.63±0.33	57.09±0.02	**	22.63±0.33	57.09±0.02	**	33.11±1.0	90.09±0.03	0.25±0.0212	33.11±1.0	90.09±0.03	0.25±0.0212	23.57±0.89	66.42±0.04	23.57±0.89	66.42±0.04	
	18.17±0.02	50.15±0.03	**	18.17±0.02	50.15±0.03	**	18.17±0.02	50.15±0.03	**	4.55±0.01	58.22±0.08	0.02±0.0034	4.55±0.01	58.22±0.08	0.02±0.0034	13.24±0.55	84.44±0.04	4.55±0.01	84.44±0.04	
	7.12±0.09	39.47±0.03	**	7.12±0.09	39.47±0.03	**	7.12±0.09	39.47±0.03	**	3.01±0.35	78.43±0.04	0.12±0.044	3.01±0.35	78.43±0.04	0.12±0.044	1.28±0.0	66.16±0.07	3.01±0.35	66.16±0.07	
	3.01±0.35	78.43±0.04	0.12±0.044	3.01±0.35	78.43±0.04	**	3.01±0.35	78.43±0.04	**	0.05	0.03	0.081	0.05	0.03	0.081	0.05	0.03	0.081	0.05	

(\*) represent the reading less than detection limit

> Eggplant > Pepper > Bean Cd ( $\mu\text{g/ml}$ ) was highest in Eggplant with a mean of 0.59 followed by Bean with a mean of 0.42. Cr ( $\mu\text{g/ml}$ ) was highest in Tomato with a mean of 16.93 followed by Garand bean with a mean of 15.69 whereas minimum concentration 0.10 ( $\mu\text{g/ml}$ ) was noted in Pepper Similar result was observed by Ambirika (2008) (20) . Comparison of the analytical methods: A comparative study was carried out between the results of Pb, Cd, Fe, Cu, Cr and Zn in certain vegetables obtained using differential pulse adsorptive stripping voltammetry(DPAdSV) and inductively coupled plasma optical emission spectrometry (ICP-OES). A comparison of the results is shown in (Tables 1,2). It was proved that the results obtained using stripping voltammetry for Pb, Cd, Fe, Cu, Cr and Zn in certain vegetables respectively) nearly in agreement with those obtained using inductively coupled plasma optical emission spectrometry of the same elements. certain vegetables. Generally, the data obtained by inductively coupled plasma optical emission spectrometry are in close agreement with those obtained by stripping voltammetry for some metals and slight differences for the others. However, the slight differences that may be found sometimes between both techniques are mainly due to the manipulation of the analyst and metal interferences in cases of inductively coupled plasma optical emission spectrometry while the standard addition method is used to perform the stripping voltammetry technique. The standard addition method is more accurate than the calibration curves, since additions of the standard analyt to the sample give precise results and minimize or even avoid the interferences usually inherent with the matrix analysis [23].

#### 4. Conclusion

Based on the Results Obtained from the study, the concentrations of studied heavy metals (Pb, Cd, Fe, Cu, Cr and Zn) in vegetable were within permissible limit for non -polluted area, while concentrations of these elements above permissible limit as compared with polluted area. The results of analyses by( DPAdSV ) were in good agreement with the result of ( ICP-OES) technique.The data obtained in this study could be provide important resource for further studies.

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