

Studying the Concentration of Mn and Zn Elements in Some Vegetables and Soils in Khartoum State - Sudan Using XRF & AAS Techniques

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Abstract

The elemental contents in vegetables are very important for human health. That was a motivation to do this work. XRF(X-Ray Fluorescence) and AAS(Atomic Absorption Spectroscopy) techniques were used to determine Zn and Mn concentrations in different soils and some vegetables (Onion, Mallow, Watercress, Marrow and Cucumber).The mean values of concentrations of zinc in these vegetables by XRF technique, were found as follow: Onion (13.33 μ g/g), Mallow (7.61 μ g/g), Watercress (13.58 μ g/g), Marrow (13.58 μ g/g) and Cucumber (15.67 μ g/g), while the mean values of concentrations of zinc in soil corresponding vegetables 26.63 μ g/g, 22.34 μ g/g, 23.71 μ g/g, 22.93 μ g/g and 24.40 μ g/g respectively.

The mean value of concentrations of zinc in these vegetables by AAS technique, were found; Onion (13.33 μ g/g), Mallow (23.92 μ g/g), Watercress (22.63 μ g/g), Marrow (30.56 μ g/g) and Cucumber (28.80 μ g/g), while the mean value of concentrations of Zinc in soil corresponding vegetables 49.18 μ g/g, 76.01 μ g/g, 72.12 μ g/g, 62.02 μ g/g and 57.96 μ g/g respectively. The mean value of concentrations of manganese in this vegetables by XRF technique, were found; onion (41.67 μ g/g), Mallow (41.72 μ g/g), Watercress (51.06 μ g/g), Marrow (17.70 μ g/g) and Cucumber (ND), while the mean value of concentrations of manganese in soils corresponding vegetables 350.59 μ g/g, 432.14 μ g/g, 423.75 μ g/g, 421.50 μ g/g and 396.62 μ g/g respectively. The mean value of concentrations of manganese in this vegetables by AAS technique, were found; onion (37.36 μ g/g), Mallow (88.25 μ g/g), Watercress (89.84 μ g/g), Marrow (12.74 μ g/g) and Cucumber (10.98 μ g/g), while the mean value of concentrations of manganese in soils corresponding vegetable 780.01 μ g/g, 106.09 μ g/g, 1012.90 μ g/g, 854.94 μ g/g and 788.49 μ g/g respectively. This work it is very interesting to note that the concentrations of zinc and manganese found by AAS technique is higher than that of XRF technique. This is due to the fact that light element emits more visible photons than x-ray photons.

Key words: XRF technique, AAS technique, Vegetables, Soils, Onion, Jew Mallow, Watercress, Marrow, Cucumber, Zn, Mn.

1. Introduction:

Environmental pollution whether in solid, liquid or gaseous form is causing adverse effects on the behavior and life of mankind and considerably damaging the animal and plant life. The

primary sources of these pollutants are garbage's, trash, raw sewage, chemical effluents of the industries and emission of irritant and harmful gases from various sources. Chemicals contamination in human diet has been an international issue that needs more sophisticated strategies to face it. Before industrial revolution, there has been a dramatic increasing in population numbers over the world, which counters parting with a decrease in food production. This situation require more production techniques in order to face the existing demands, consequently it leads to use chemicals such as pesticides or may grow plants in a contaminated areas such as heavy metals to ensure a sustainable supply for their demands and therefore it causes food pollution [1]. Contamination of vegetables with heavy metal may be due to irrigation with contaminated water, the addition of fertilizers and metal-based pesticides, industrial emissions, transportation, the harvesting process, storage or at the point of sale. It is well known that plants take up metals by absorbing them from contaminated soil as well as from deposits on parts of the plants exposed to the air from polluted environments [2,3]. Soil pollution is caused by misuse of the soil, such as poor agricultural practices, disposal of industrial and urban wastes, etc [4].

Soil is also polluted through application of chemical fertilizers (like phosphate and Zn fertilizers), and herbicides [5].

Zinc: is an essential for the human nutrient, a cofactor for over more than 300 enzymes, and is found in all tissues, a list of key enzymes containing zinc or affected by zinc status are provided [6].

Zinc has three functions in these metal enzymes:

1. Participation in catalytic functions.
2. Maintenance of structural stability.
3. Regulatory functions Zinc is also involved in DNA and ribonucleic acid (RNA) synthesis.

The body contains 1.5 - 2.5grams of Zinc Deficiency of this level affects reproduction adversely in both males and females since all the hormones and a wide range of enzymes involved in reproduction are sensitive to zinc stress, Zinc fingers exercise significant controls on the biological effects of estrogens and androgens elements of the DNA that turn on the genes active in protein synthesis during early pregnancy, Anemia a Night blindness excess of this level is toxic and effect Acute gastrointestinal distress , Nausea and Cramping - Large amount of zinc intake reduces copper and iron utilization and vitamin A [7].

Manganese: is a component of the antioxidant enzyme superoxide dismutase (SOD), which is present in all aerobic cells, where it is required for the detoxification of oxygen metabolites. It is required for the action of vitamin B1 (thiamine) and for normal brain function (due to its role as an activator of brain enzymes), manganese deficiency can be associated with epilepsy [8, 9]. Mn is also required for bone and cartilage formation; low levels are often associated with joint surface diseases, e.g. arthritis [10, 11]. Until 1920 it was believed that the total nutrient requirement of plants were fully satisfied by ten essential element : the seven inorganic elements (N, S, P, k, Ca, Na, and Fe) supplied by the cultural solution as salts plus carbon (C) from carbon dioxide and hydrogen (H) and oxygen (O) from water. Recent knowledge has revealed that plants require at least seven other elements in trace amounts (B, Cu, Cl, Mn, Mo, Na, and Zn). The ultimate source of trace elements in the soil [12]. This work aim is to estimate the level of (Manganese and Zinc) in some vegetables and soils agriculture in the area of study by two techniques (XRF and AAS) and Compare the of the concentrations with the two spectroscopic measurement techniques and interpretation of the differences. Section two is concerned with

materials and methods, while section three is devoted for results, while discussions and conclusion are exhibited in section four and five respectively.

2. Materials and Methods:

2.1. Study area:

The study area lies entirely in Khartoum State (Khartoum, Omdurman and Khartoum North).

Climate of area is hot in summer and the temperature in season varies between (17-45°C) in the year.

In the study area there are many food factories they use vegetables and soils agriculture.

A map showing the area from which plants samples have been collected is presented in Fig. (2.1)

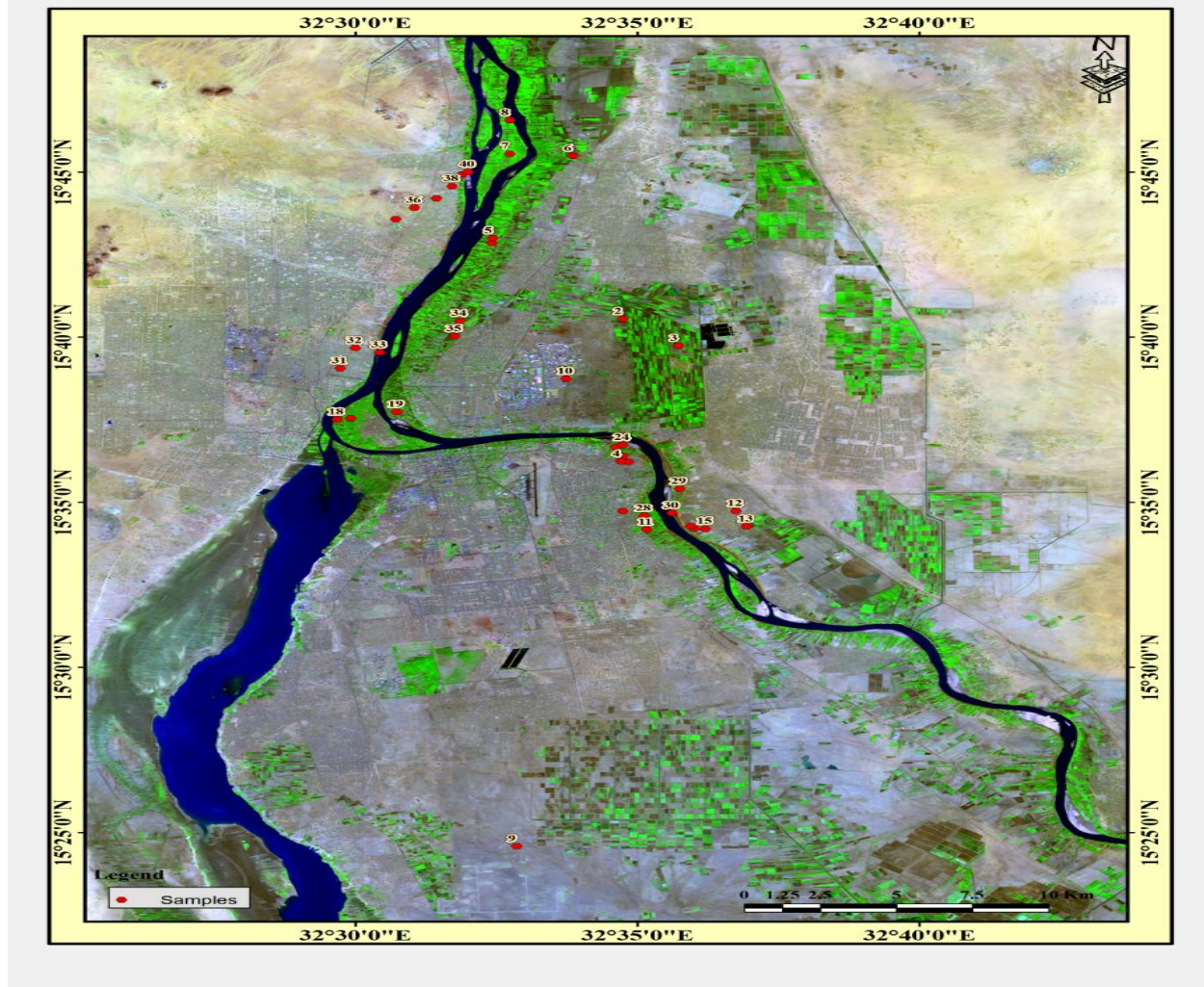


Fig. (2.1): The locations of collection samples from farmland at Khartoum state

2.2. Collection and preparation samples:

All plants and soil samples were collected in allotment gardens located in Khartoum state, according to the procedure recommended by International Atomic Energy Agency (IAEA). Plant samples consist of vegetables (onion, mallow, cress, cucumber, morrow) the parts used (fruit, leaf and tuber) were collected from investigated sites on the period between October 2015 and March 2016. For the first stage all plant samples were washed carefully to remove soil. The

leaves were air dried and ground in a mortar, Fruits and tuber were cut using stainless steel knife and dried at 105°C combusted in the furnace. Composite surface soil (0-20cm) samples (from a bulk soil made up of 20 different soil samples per farm) of the farms were collected separately and properly labeled.

Soil samples were dried at room temperature, then in a drier at 105°C. After that the soil sample was grounded in mortar and sieved by 1 mm sieve, to remove stones and organic parts. The samples were dried to convert to soft powder by mechanical grinder then reset the samples in the form of pellet by pressing machine. The pressing machine type space consists of a die system comprising, it consists of the base cylinder, and plunger, two steel pellets, extractor ring, and a cursor reading atone. In the normally uses special paper previous shall be known sample weight of 1 g. The machine was cleaned up from the remnants of the previous samples by using the alcohol or one of its compounds. The samples were put in the sample holder. Forty samples soils and forty samples of five vegetables (cucumber, marrow, mallow, Watercress and onion) were collected from different three locations (Omdurman, Khartoum and Khartoum North) in Khartoum state. All soil and vegetable samples were packed into polyethylene bags and taken to the laboratory for analysis. Each sample was divided into two parts, stored in plastic container and used in the analysis by XRF technique and AAS techniques.

2.3. Experimental Methods:

2.3.1. Energy dispersive X-ray fluorescence

2.3.1.1. Sample preparation:

Two grams of each sample ($n = 8$ for each species collected vegetables and soil at various distances from farmlands in Khartoum state County, Sudan) were pressed manually, without any chemical treatment, in a plastic vial with Mylar in the bottom and then analyzed.

2.3.1.2. Experimental set-up:

The sample was grinded firstly up to become soft, then pressed by the pressing machine and placed on the sample holder. The XRF spectrometer system was used which composed of a radioisotope excitation source cd-109, together with (ORTEC) Si(Li) detector and associated electronics, Canberra multi channel analyzer and computer. The amplifier settings were adjusted for optimum values. Then analyzed samples, respectively (Onion, Cucumber, Jew Mellow, Water cress and Marrow) each sample was separate over lapping, fitting the spectra by the (win QXAS), and appointed the elements within each sample by the (QXAS) software in addition to the peak area and concentration of each element. The bias supply was used 600V for Si (Li) detector. The machine was cleaned before you start pressing to avoid inaccuracies in the experiment and the surface area of the sample holder was matched with a surface area of samples in the development of the sample holder specimens. MCA and the QXAS software were calibrated before the start of analysis X-Ray Fluorescence spectrometers use high energy X-rays or gamma rays to excite fluorescent radiation (or photons) from a sample for chemical or elemental analysis. In an energy dispersive X-ray fluorescence spectrometer, the fluorescent photons from the irradiated sample are detected without being separated first (as they are in wavelength dispersive XRF spectrometers).

The accuracy of the results as evaluated by measuring a certified reference sample (IAEA). Limits of detection for EDXRF spectrometers is typically in the parts per million (ppm) ranges.

2.3.2. Atomic absorption spectrometry:

2.3.2.1. Samples Treatment:

Approximately one 1g of finally powdered sample was weighed accurately and placed into 250 ml beaker. 5ml of conc. Nitric acid was added and the mixture evaporated slowly on hot plate to near dryness, other 5ml of conc. nitric acid was added and evaporated until the production of brown NO₂ fume ceased. 10ml equal crgia (1HNO₃: 3HCl) prepared recently were added and evaporated to near dryness or semi-dryness. Finally, 5 ml of per chloric acid HClO₄ was added and evaporated until complete digestion was achieved, which was indicated by a non-turbid and/or a white solution. The residue was diluted with de ionized water into 100ml volumetric flask. The 36 prepared solutions was placed into 100ml of glass bottle and stored at room temperature.

2.3.2.2. Experimental set-up:

Determination of elemental concentrations in samples of vegetables and soils were performed using the method of calibration curve according to the absorber concentration. Several standard solutions of different known concentrations have been prepared and the elemental concentration in unknown sample was determined by extrapolation from the calibration curve. All samples concentrations were reported as mg/kg dry weight of material. The amounts of manganese, and zinc were determined by Atomic Absorption Spectrometer (AAS), model: A6800, Shimadzu, Japan. Firstly standard solutions of each element were prepared as fallow:

250 µl was taken from the stock standard solution (1000µg/ml) in a plastic volumetric flask (25ml) and made up to the mark with 0.5 normality of hydrochloric acid solution, thus made the intermediate standard solution (10µg/ml) secondly, working standard solutions were prepared to be suitable to the concentration of each elements in the sample solution by the following:

Zn: a series of 10,20,400 and 1000µL were taken from the intermediate standard solution (10mg/l) in a plastic volumetric flask 10 ml with a micro pipette and were made up to the marks with HCL 0.5N solution to be smaller to the solvent of the sample (to avoid the physical interference) corresponding to 0.02,0.1,0.4,0.7 and 1ppm of zinc respectively.

Mn: a series of 5,500,1000 and 2000µL were taken from the intermediate standard solution (10mg/l) in a plastic volumetric flask 10 ml with a micro pipette and were made up to the marks with HCL 0.5N solution to be smaller to the solvent of the sample (to avoid the physical interference) corresponding to 0.005,0.5,1, and 2ppm of manganese respectively.

2.4. Accuracy of the result:

International Atomic Energy Agency (IAEA) certified reference material (hay V-10) and (soil-7) was used as quality control sample throughout the measurement period in order to confirm the consistency of the comparison between the measured and the certified values.

3. Results:

In this study the concentrations of Mn and Zn as have been measured in the selected vegetables and soils the results are presented in table (3.1), (3.2), (3.3), (3.4) and (3.5) also in figures (3.1), (3.2), (3.3) and (3.4).

The more elevated concentrations were found in onion, mallow, watercress, marrow, cucumber and soils.

Table (3.1): Concentration (µg/g) of Mn and Zn in Onion plant and soil measured by two techniques:

Code of sample	Onion plant				Code of sample	Onion soil			
	XRF technique		AAS technique			XRF technique		AAS technique	
	Mn	Zn	Mn	Zn		Mn	Zn	Mn	Zn
P1	72.40	20.00	59.92	14.27	S1	ND	28.90	750.80	47.50
P6	ND	15.50	55.90	17.50	S6	400.00	20.90	760.19	50.82
P11	36.60	13.70	25.32	9.66	S11	347.00	31.80	776.22	49.90
P16	ND	14.90	21.77	11.29	S16	236.00	24.90	671.92	47.34
P21	NA	NA	NA	NA	S21	NA	NA	NA	NA
P26	16.00	2.53	23.87	13.95	S26	419.00	ND	680.91	50.34
P31	NA	NA	NA	NA	S31	NA	NA	NA	NA
P36	NA	NA	NA	NA	S36	NA	NA	NA	NA
Mean	41.67	13.33	37.36	13.33	Mean	350.50	26.63	780.01	49.18

ND refers to non-detectable, NA refers to non-analysis

Table (3.2): Concentration ($\mu\text{g/g}$) of Mn and Zn in Watercress plant and soil measured by two techniques:

Code of sample	Water Cress plant				Code of sample	Water Cress soil			
	XRF technique		AAS technique			XRF technique		AAS technique	
	Mn	Zn	Mn	Zn		Mn	Zn	Mn	Zn
P3	98.40	15.70	115.20	23.30	S3	465.00	23.70	980.10	72.20
P8	116.00	26.80	69.80	23.00	S8	465.00	17.70	1021.20	76.22
P13	27.20	1.11	80.15	20.70	S13	315.00	19.00	1075.20	75.32
P18	38.20	1.24	82.43	20.53	S18	460.00	27.10	1020.10	75.60
P23	30.80	2.69	83.32	23.65	S23	296.00	26.20	1020.13	57.26
P28	36.20	2.34	84.40	23.25	S28	479.00	29.00	1012.04	70.75
P33	28.40	2.47	121.28	20.62	S33	507.00	22.60	912.50	70.62
P38	33.30	ND	82.11	25.95	S38	403.00	24.40	1061.72	78.95
Mean	51.06	7.48	89.84	22.63	Mean	423.75	23.71	1012.90	72.12

Table (3.2): Concentration ($\mu\text{g/g}$) of Mn and Zn in Jew Mallow plant and soil measured by two techniques:

Code of sample	Jew Mallow plant				Code of sample	Jew Mallow soil			
	XRF technique		AAS technique			XRF technique		AAS technique	
	Mn	Zn	Mn	Zn		Mn	Zn	Mn	Zn
P2	NA	NA	NA	NA	S2	NA	NA	NA	NA
P7	58.50	25.20	70.47	24.11	S7	428.00	15.30	1050.10	78.72
P12	53.20	15.10	82.65	21.80	S12	395.00	24.90	1100.15	78.92
P17	ND	3.13	84.32	21.14	S17	589.00	19.50	1050.20	80.50
P22	25.20	3.21	85.42	25.62	S22	221.00	ND	1035.03	60.50
P27	26.80	1.70	86.39	25.92	S27	482.00	24.40	1018.06	72.72
P32	59.90	2.41	125.35	21.72	S32	428.00	ND	1091.18	79.99
P37	26.70	2.52	83.18	27.13	S37	482.00	27.60	1081.92	80.72
Mean	41.72	7.61	88.25	23.92	Mean	432.14	22.34	106.09	76.01

ND refers to non-detectable, NA refers to non-analysis

ND refers to non-detectable

Table (3.4): Concentration ($\mu\text{g/g}$) of Mn and Zn in Marrow plant and soil measured by two techniques:

Code of sample	Marrow plant				Code of sample	Marrow soil			
	XRF technique		AAS technique			XRF technique		AAS technique	
	Mn	Zn	Mn	Zn		Mn	Zn	Mn	Zn
P4	ND	43.60	14.29	30.13	S4	361.00	ND	1038.14	68.28
P9	ND	22.40	15.20	31.10	S9	428.00	21.30	905.20	56.00
P14	ND	21.50	8.58	23.38	S14	413.00	24.00	843.98	52.32
P19	ND	3.77	11.90	38.29	S19	302.00	29.90	670.35	54.30
P24	ND	4.53	13.45	39.42	S24	516.00	ND	680.33	60.67
P29	ND	4.34	13.51	29.16	S29	318.00	16.70	665.48	55.36
P34	17.70	4.48	13.66	32.27	S34	536.00	26.20	1020.82	70.30
P39	ND	4.03	11.32	20.72	S39	498.00	19.50	1015.20	79.02
Mean	17.70	13.58	12.74	30.56	Mean	421.50	22.93	854.94	62.03

ND refers to non-detectable

Table (3.5): Concentration ($\mu\text{g/g}$) of Mn and Zn in Cucumber plant measured by two techniques:

Code of sample	Cucumber plant				Code of sample	Cucumber soil			
	XRF technique		AAS technique			XRF technique		AAS technique	
	Mn	Zn	Mn	Zn		Mn	Zn	Mn	Zn
P5	ND	32.20	12.24	27.43	S5	358.00	21.30	796.08	59.28
P10	ND	36.00	12.15	28.35	S10	361.00	26.50	892.22	54.22
P15	ND	33.00	7.90	22.25	S15	517.00	17.60	640.80	42.25
P20	ND	5.91	9.44	36.86	S20	419.00	26.20	655.25	52.20
P25	ND	5.34	12.65	37.32	S25	277.00	21.30	665.27	59.01
P30	ND	4.85	12.32	28.15	S30	416.00	29.90	650.15	52.25
P35	ND	5.66	12.88	31.72	S35	293.00	27.10	1005.82	69.00
P40	ND	2.38	8.23	18.34	S40	532.00	25.30	1002.30	75.43
Mean	ND	15.67	10.98	28.80	Mean	396.62	24.40	788.49	57.96

ND refers to non-detectable

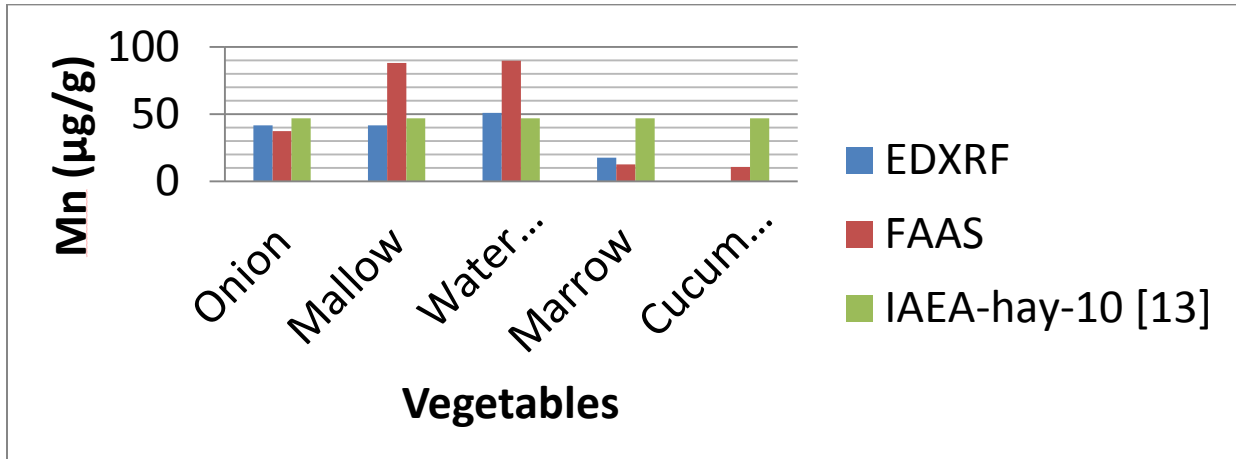


Figure (3.1): Comparison between measured Mn concentration ($\mu\text{g/g}$) of vegetables by two techniques and certified

Figure (3.2): Comparison between measured Mn concentration ($\mu\text{g/g}$) in soils by two techniques and certified



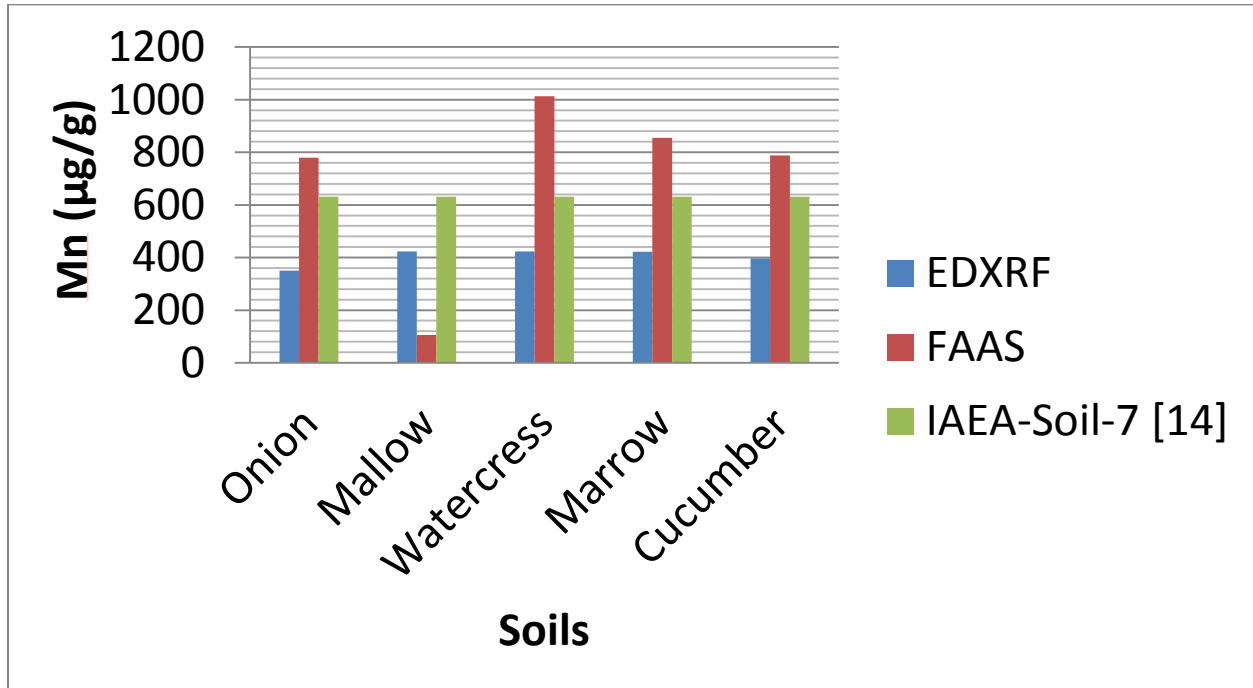


Figure (3.3): Comparison between measured Zn concentration (µg/g) in vegetables by two techniques and certified

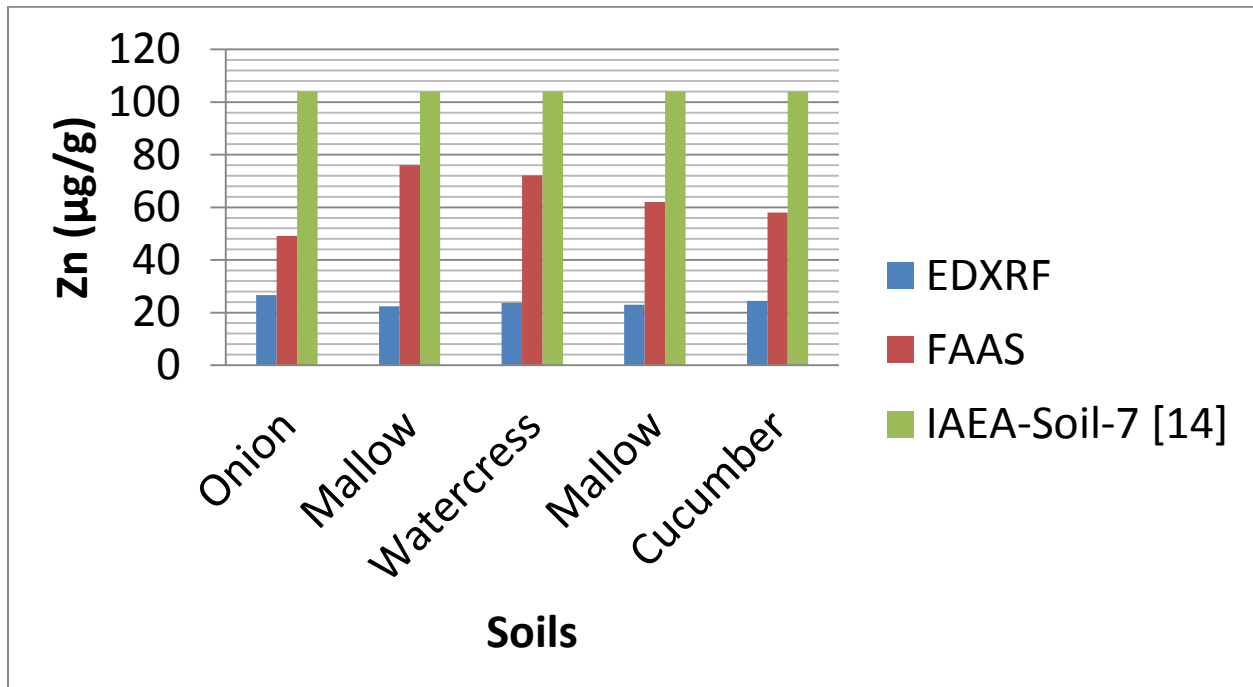


Figure (3.4): Comparison between measured Zn concentration (µg/g) in soils by two techniques and certified

4. Discussion:

The problem of environmental pollution by heavy metals has attracted much attention in recent years. Industrialization has resulted in increased mobilization and deposition of heavy metal pollutants in natural habitats. Automobiles using leaded gasoline as fuel are a major source of heavy metals in the atmosphere. Heavy metals being non-degradable become an integral part of the habitats after release into the environment. There are various methods used for obtaining plant extracts from plant samples, e.g. acid digestion methods adopted for preparing plant extracts. The digested plant samples were analyzed by atomic absorption spectrophotometer and x-ray Fluorescence spectrometry. The reliability of this method was ascertained by carrying out several direct measurements on extract Hay standard reference material (IAEA). The differences of soil and plant heavy metal contents in the studied two regions were not significantly different. The comparison of concentration of heavy metals by XRF and AAS techniques show interesting results. In view of tables (3.1), (3.3), (3.4) and (3.5) and figures (3.1), (3.2), (3.3) and (3.4) for Onion, Watercress, Marrow, Cucumber and corresponding soils shows that for light elements like Mn and Zn the concentration obtained by AAS spectrometer is larger than that obtained by XRF spectrometer. This may be attributed to the fact that these elements have more electrons in the outer most shell than the inner ones according to the relation:

$$\text{no of electrons} = 2n^2$$

$n \equiv$ principal quantum number

thus these elements emit more visible photons from the outer most shells compared to less x-ray photons emitted from the inner most shells.

Since AAS account for visible photon, and XRF take care of X-ray photons, thus for AAS, which receive more photons, the concentrations appear higher.

However for XRF it receives less photon, thus the concentrations appear lower.

4. Conclusion:

The Energy Dispersive X-Ray Fluorescence (XRF) spectrometry and the Atomic Absorption (AAS) spectrometry are two analytical methods which can be successfully used in complementary mode to determine the heavy metal concentration of vegetables and soils. The combination of two different techniques, XRF and AAS, was well suited to this analysis. XRF technique enables simultaneous determination of all the elements present in the sample ($Z > 13$), don't require a chemical sample preparation but, is limited by the detection limit. For this reason the elements which are a concentration less than 10 mg/kg had to be studied by the AAS technique. This work shows that the concentration of Mn and Zn obtained by AAS is larger than obtained by XRF.

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