Original Research Article

Assessment of Vegetables and Soils from Minjingu Village-Tanzania using WDXRF Technique

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ABSTRACT

Wavelength dispersive x-ray fluorescence (WDXRF) spectrometer analyzed heavy metal concentration in soils and vegetables of the field study. The soil and vegetable samples were randomly collected from Minjingu village of Manyara region in Tanzania. The results indicate that soils were contaminated with heavy metals having the mean concentrations of 53±0.4 For Mn, 40±0.2 for Sr, 2059±4.2 for Fe, 760±2.7 for Al, 12±0.3 for Cs and 4±0.04 for Ni in mg/kg which was above the MTLs. Except Cl was below MDL. While vegetables recorded the mean concentrations of 60±1.2 for Mn, 68±0.1 for Sr, 620±2.36 for Fe, 284±1,13 for Al, 56±0.5 for Cs, 13±0.1 for Ni and 714±0.7 for Cl in mg/kg. The reference and experimental results of soil and vegetables (Fig. 5&6) revealed that the optimized machine has given the best results, whereas experimental data was almost the same as the reference values The reference material of soil 7 and IAEA 395 for vegetables shows the deviation of 2%. Furthermore, MDL for vegetables and soil show that the WDXRF has very low back ground values which means matrix effect is reduced to the maximum (Fig. 7&8). This makes WDXRF machine the best equipment to be used for measurements of various types of samples for better results. Moreover, the correlation coefficient of heavy metals in soils was significantly correlated with those in vegetables at 99% level and with anthropogenic activities was at a level of 95%. Therefore, findings indicate that Minjingu soils and grown vegetables were highly contaminated with heavy metals mainly from soils and dirty air, at levels able to pose detrimental health effects to the consumers. Therefore regular monitoring of the grown vegetables around phosphate mines is recommended.

Keywords:, Heavy Metals, WDXRF, crystal, MDL and Detectors.

1. INTRODUCTION

Background of the study

In few decades there has been a remarkable growth of mining sector in many parts of Tanzania. This has increased the use of fertilizers to uplift crop production. The increased mining operations has raised public concern about human health due to pollution of arable soils by trace elements, of which the contamination is associated

with ongoing mining processes including the Minjingu phosphate factory activities [1].

The phosphate rock refers to any material containing high quality of phosphorus which can be used for economic interest as a raw material for phosphate fertilizer factory or is applied directly in farmland [2]. Although phosphates escalate crop yields, but the continual production of phosphate may be increasing the accumulation of toxic metals to the nearby soils and edible plants of Minjingu via air and other transportation channels such as water runoffs, smoke and wind.

Heavy metal contamination in soils

Various research reviews conducted around the world on land pollution reported that in few past years there has been a gradual increase of heavy metal deposition in soils caused by human activities which in turn has affected the ecosystem [3]. A significant instance is China, where all farm soils indicated that Cd had the highest pollution rate of 7.75%. Pb and Cr had the lowest pollution rates with values lower than 1%. Furthermore, it was observed that the total pollution rate in Chinese soil was 10.18%, mainly affected by Cd, Hg, Cu, and Ni. These observations were attributed to human activities that released heavy metals hence causing soil pollution [4].

Evidences from the literature reveals that the soils of Minjingu village in Tanzania being nearby the phosphate mine might have accumulated elevated heavy metals. Therefore were examined by WDXRF to determine the unknown levels of heavy metals; this led the current study to be carried out.

Heavy Metals in vegetables

The vegetables grown on polluted soils translocate higher levels of metals through their leaves [5]. Chibuike and Obiora [6] found that, when concentrations of heavy metal in soil increases, plants are seriously damaged by trace metals which are normally retained into plant leaves. Several studies around the world indicated high potential health risk in relation to the heavy metal exposure through consumption of vegetables by people living around the mining areas [7]. In Togo, around the phosphate exploitation area [8] found that soils and plants contained elevated levels of Zn, Cd and Pb while in Bangladesh, Nasser [9] reported high concentration of cadmium mostly in leafy vegetables in which more Cd content was observed in spinach followed by green amaranth and red amaranth.

The aim of this study was to analyze the heavy metal concentration in soils and vegetables which necessitated the use of Wavelength Dispersive X-ray Fluorescence (WDXRF) spectrometry for important parameters to optimize the spectrometer performance. In addition, the correlation coefficient was used for better understanding of the primary source(s) of the heavy metals in vegetables. The results obtained intended to provide some insights into contamination of heavy metals in vegetables and serve as a basis for comparison in Tanzania and the world at large.

Principles of X-ray Fluorescence Analysis

Electromagnetic rays behave as visible light colours such as rainbow which are interpreted as different wavelengths. The electromagnetic rays like light can also behave as particles which are termed as packets of energy called “photons” or x-rays or characteristic rays. Electromagnetic radiation is generated whenever electrically

charged particles, or electrons, lose energy due to deceleration or moving to a lower energy level in the atomic shell [10, 11]. In XRF system, incident radiation, known as primary x-rays are generated in an x-ray tube. The primary x-rays escape through a beryllium window and interacts with atoms in the analyzed sample resulting to emission of characteristic x-rays that are used to detect the elements present in the sample.

When the primary x-ray photon strikes an atom, two types of interaction may occur. These interactions are scattering and photoelectric absorption. These two basic interactions result to the attenuation of the primary x-rays which is known as the absorption effect. Since the energy of x-rays used in XRF ranges from 0 to 40 KeV, the photoelectric effect is more dominant than others [12]. Photoelectric Absorption is a type of interaction where the incident x-ray energy is absorbed by an atom upon interacting with the material. The absorption of this energy by the atom may result into three effects known as the Photoelectric effect, Fluorescence radiation and Auger effect [10].

An atom consists of various orbital shells such as K, L, and M in with different energies. These orbitals contain electrons. The electrons are named with respect to the orbit in which they are found. An electron within the orbit is bound to the atom with the binding energy that equals the energy of the respective orbit. If the energy of the primary x-ray is greater than the binding energy of a given electron, the particular electron is knocked out of its orbit as shown in and become a free electron [12]. The released characteristic x-ray photon may interact and be absorbed by the electrons in the outer shell of the atom as it is moving out manage to remove it out of the atom. This process is called the Auger effect and the ejected electron is known as the Auger electron. Auger effect predominates in low Z elements [12].

When the electron is knocked out of the atom, leaves the gap in the original shell. The vacancy left in K-shell results to an unstable state of the atom and the electron from a shell of lower binding energy migrates to the K-shell to fill the gap. The difference in binding energies between the two shells forms excess energy which is emitted in form of photons called fluorescence x-rays [11].

WDXRF sequential spectrometer

Diffraction

According to Schlotz and Uhlig[13] defines diffraction as the deviation of light from a straight line due to the absence of reflection or refraction is called diffraction. The prerequisite of WDXRF are diffraction effects resulting from Bragg's law separates different wavelengths by means of analyzing crystals in Fig. 1.

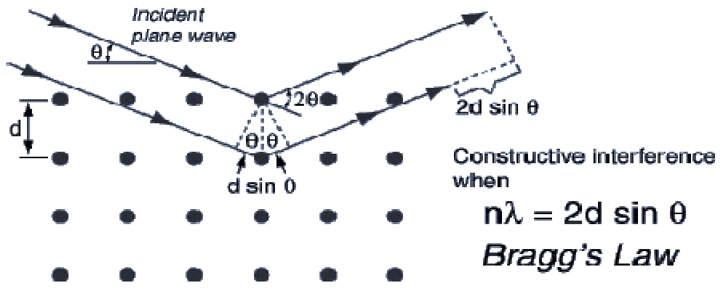

Fig. 1. Analyzing crystals diffracting radiation rays

If the d-value of the analyzer crystal is known Bragg's equation can be solved for the element characteristic wavelength (λ) which is given by equation 1;

$$n\lambda=2d\sin\theta$$

(1)

Where n is 1, 2, 3 ... represents reflection order, λ is the wavelength, d is the phase lattice distance and θ is the diffraction angle [13].

WDXRF simply refers to spatial separation of x-ray photons by means of diffracting crystals according to their wavelengths. The crystals are important components in WDXRF. These crystals basically distinguishes WDXRF from EDXRF, by playing a significant role of diffracting characteristic x-rays from the sample hence enables the measurement of wavelengths possible (Table1). The *d*-spacing is proportional to the reflectivity. What determines a good crystal is wavelength of elements. Crystals with longer *d*- spacing are proper for elements with low Z while heavier elements utilize shorter d-spacing crystals [14, 15].

Table 1. Crystals, diffracted elements, lattice distance and their wavelengths [10, 13, 16].

No.	Analyzing crystal	Lattice distance 2d (Å)	Diffracted element(s)	Wavelength (Å)		Applications
				ʎmin	ʎmax	
1.	Lithium Fluoride‹ LiF › (420)	1.801	>Ni	0.157	1.72	Natural crystal
2.	Lithium Fluoride‹ LiF › (220)	2.848	>V	0.248	2.72	Like Topaz.
3.	Lithium Fluoride‹ LiF › (200)	4.027	>K	0.351	3.84	Universal general crystal
4.	Germanium‹ Ge › (220)/ XS-Ge-C	4.00	P, S, Cl	0.349	3.82	Flat/curved crystal
5.	Indiumantimonide‹ InSb › (111)	7.4806	Si	0.652	7.23	Stable temperature than PET
6.	Ammoniumdihydrogen phosphate‹ $NH_4H_2PO_4$› /ADP (200)	7.5	Mg	0.654	7.16	High resolution Mg only.
7.	Pentaerythritol‹ $C(CH_2OH)_4$› (PET) (002)	8.742	AL-Ti and Rb-I	0.762	8.34	Has greatest expansion coefficients
8.	Thallium hydrogenphalete‹ $TIHC_8H_4O_4$› (TIAP) (100)	25.9	F, Na	2.26	24.7	Artificial crystal
9.	XS-55 (Multilayer W/Si)	55	O-Si		-	Analyses O-Si
10.	XS-N (Multilayer Ni/BN)	110	N		-	Measures N
11.	XS-C (Multilayer TiO_2/C)	120	C		-	Measures C
12.	XS-B (Multilayer La/B_4Cl)	200	B/Be		-	Measures B/Be

Detectors

There are two types of detectors used in WDXRF spectrometer, the gas proportional counter detector and scintillation counter detector. These detectors convert x-ray photons coming from the crystals into measurable voltage pulses. WDXRF consists of full wide-range of x-ray wavelengths 0.012-12 nm (100-0.1 keV) [14, 15].

Table 2. Types of detectors in WDXRF [15]

Detector type	**Wavelength/energy coverage**	**Good for**
Sealed proportional counter	**0.08=12 nm/15-0.1 keV**	**Low Z elements (Be=Cr)**
Scintillation counter	**0.012=1.5 nm/100-8 keV**	**High Z elements (Mn-U)**

The strengths of WDXRF [10, 13, 17] is as listed:

- **It is fast and non-destructive when measuring elemental concentrations of various natural and synthetic materials such as minerals, metals, glasses, semi-conductors and ceramics; this makes it to be widely used in industries and in geological laboratories as compared to other methods.**
- **It has a higher spectral resolution which helps to distinguish one spectral line from the other, thus corrections are not required for accuracy is increased.**
- **It exhibits superior peak resolution 5 eV to 20 eV of elements and this makes it sensitive to trace elements as it reduces spectral overlaps.**
- **Separates x-rays according to the wavelengths, by the aid of crystals, which diffracts rays by means of Bragg's law.**
- **It has a wide range of analyzing elements in the periodic table from Be to U.**
- **It is independent of the chemical bonding of the elements, so samples can be analyzed directly without advanced sample preparation.**

- **The resolution does not depend on the detector (in EDXRF) rather on the crystal and arrangement of collimators.**
- **Unlike EDXRF, WDXRF does not measure all elements at once, but sequentially, this reduces matrix effect to the maximum.**

Drawbacks of WDXRF

- **It cannot analyze multiple isotope masses of an element but can be achieved by means of mass spectrometry.**
- **The WDXRF analyses cannot distinguish the valence states of an element unless by the use of Mossbauer spectroscopy.**
- **Cannot determine low Z elements below Be.**
- **Crystals and optical facilities (collimators) are very costly.**
- **Does not produce sample spectrum of all wavelengths/energies at a single analysis as compared to EDXRF.**

2. MATERIAL AND METHODS

Study Area

Minjingu village is situated along the rift valley escarpment on the Eastern part of Lake Manyara region. Within the village there is a phosphate pit near the Minjingu hill Fig. 2. where phosphate is mined. The village of Minjingu is found on the Northern part of Tanzania, along latitude 03°42' 30.9" S and longitude 035° 54' 56.3" E. It is estimated that this village consists of about 11,000 population occupying approximately 24,000 hectares of land according to URT report [18]. Major activities of theMinjingu people are pastoralism and farming. Main crops cultivated in Minjingu includes; Watermelon, mung beans, maize and vegetables such as Chinese cabbages and spinach. The area of Minjingu which is used for agriculture is found on the North-Eastern part of Babati-Arusha road, while on the North-West of the same road is for pastoralism where the Minjingu phosphate mine is situated Fig. 3.

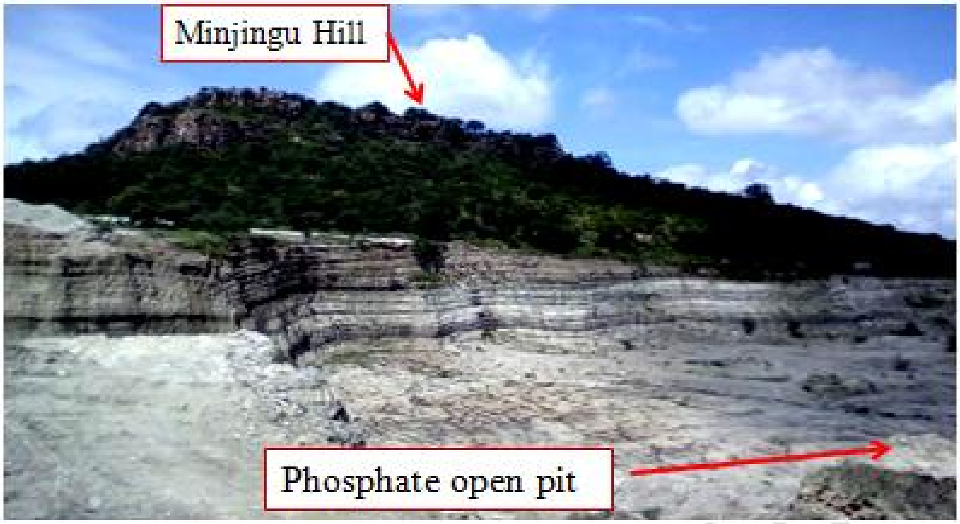

Figure 2. Minjingu pit picture (Photo taken by the researcher on March, 2018).

Figure 3. The Minjingu village in Manyara region-Tanzania.

Preparation of samples and Analysis

Samples of vegetables collected for analysis in Minjingu village were Cowpea leaves scientifically are known as Vigna unguiculata. Spinach scientifically is called Oleracea Spinacea. Sweet potato leaves is scientifically called Ipomoea batatas, Ethiopian mustard, scientifically is Brassica Carinata. L and Chinese cabbages is scientifically called Brassica Rapa.

The vegetables were washed in fresh running water to eliminate debris. Then samples were dried at a temperature of 65^0C for 48 hours, homogenized and grinded to the size of reference materials. The WDXRF machine schematically represented in Fig. 4 was used in this study. The instrument was based on end window Rh-anode equipped with 4 kW high intensity x-ray generator at a maximum voltage of 60 kV and a maximum tube current of 170 mA. The set of crystals covered the entire range of elements from Beryllium to Uranium whereby up to 8 automatic crystal changers were used.

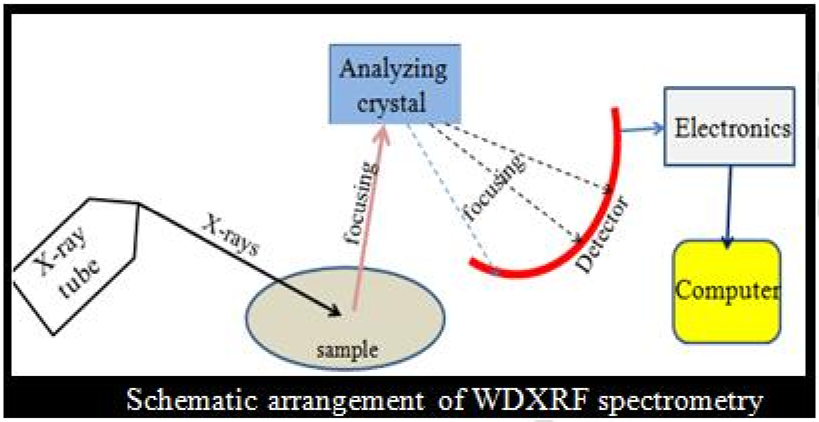

Fig. 4. Schematic arrangement of WDXRF spectrometer.

3. RESULTS AND DISCUSSION

Quality assurance, Precision and Accuracy of an Instrument

Quality control was carried out by using two reference materials for elements. The first one was for soil; IAEA SOIL 7 [19] in Fig. 5, standard material was used, and for cabbage IAEA 359 [20] for vegetables Fig. 6. The analytical acceptance test was performed for the precision and accuracy of S8 TIGER WDXRF prior to sample measurements. The certified material Geo*PT* was taken as a control sample, and STG 2 as experimental material. The S8 TIGER WDXRF spectrometer system passed the Analytical Acceptance for quality control.

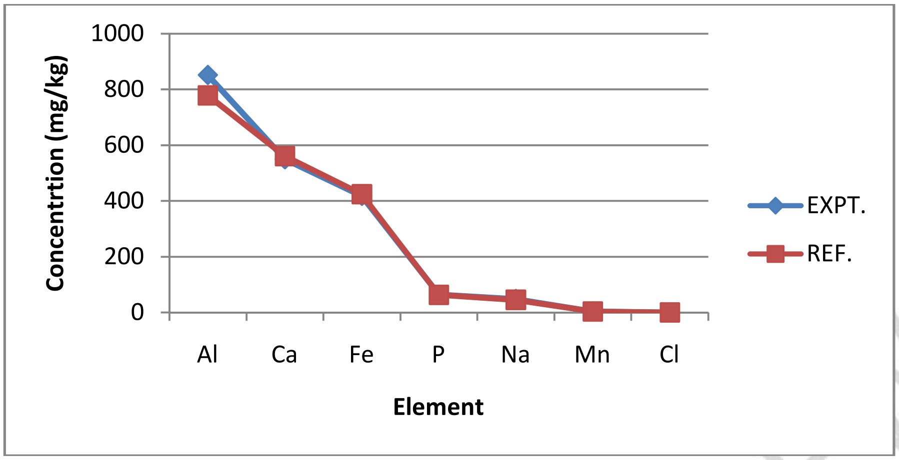

Fig. 5. Experimental and reference (Soil 7) samples results of AMGC LAB.

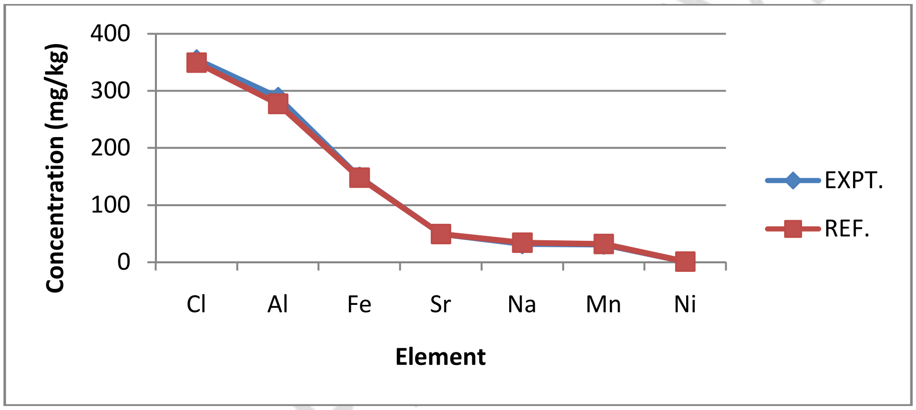

Fig. 6. Experimental and reference values for cabbages IAEA 359.

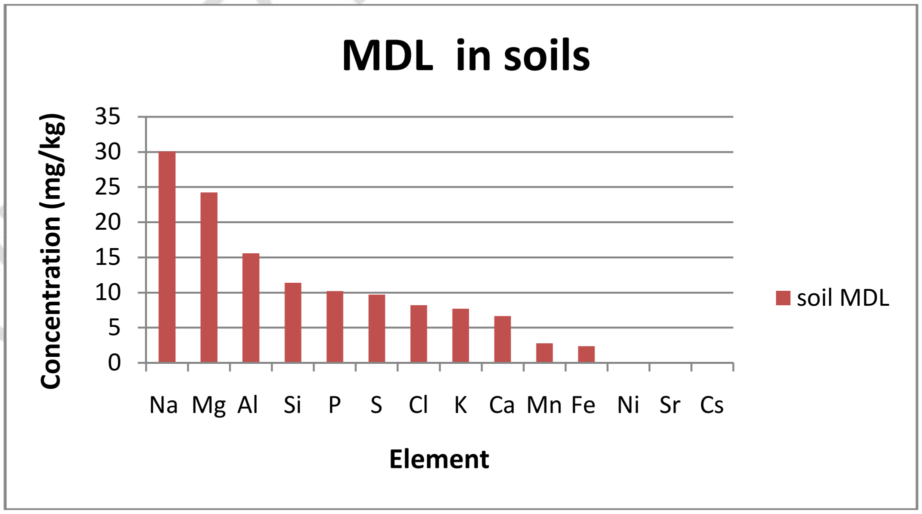

Fig. 7. The Minimum Detection Limits (MDL) for elements in soil analyzed by WDXRF.

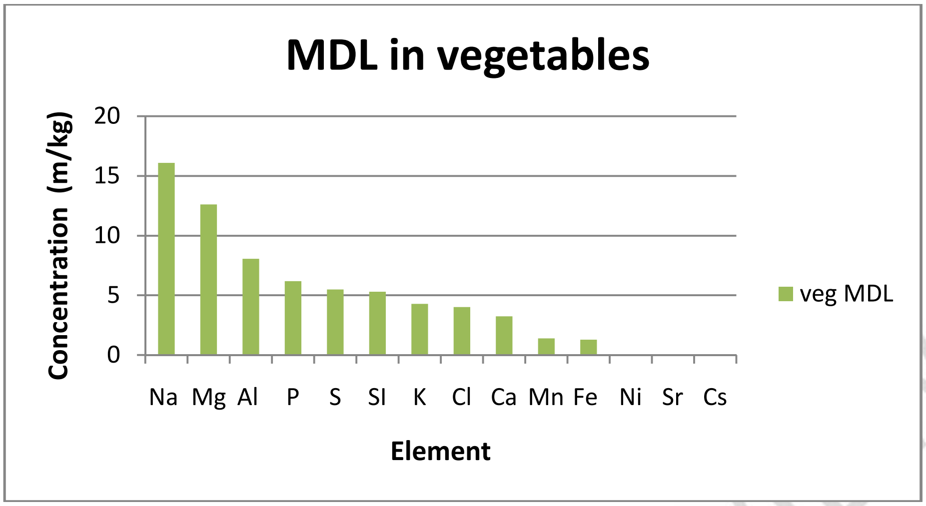

Fig. 8. The Minimum Detection Limits (MDL) for elements in vegetables by WDXRF.

Minimum Detection Limits (MDL) for soils (Fig. 7) and vegetables (Fig. 8) were calculated from the formula given by Koleleni, Mbike and Mosha[21, 22].The WDXRF machine in this study has shown very low detection limits especially for vegetables. This has been contributed by optimized curved crystals, good arrangement of collimators and sequential measurement aided by two detectors which reduce background intensity of the machine.

Comparison of heavy metal concentrations in soil of this study and other studies

From Table 3, India and Namibia studies shows high content of iron than the current study except Poland. Fe concentration values in these countries are high though the Fe recommended limits are unknown; this may harm the population surrounding these areas. The Mn and Ni concentration values were found to be lower in this study compared to other studies. This may be ascribed to differences in natural formation of soils.

Table 3. Comparison of soil heavy metal concentrations (mg/kg) in this study and other studies

Element	Tanzania (Minjingu)[a]	India (East Singhbum)[b]	Namibia (Kombat)[c]	Poland (Miedzianka)[d]
Fe	2059	38,215	13,873	-
Mn	53	520.8	760	1334
Ni	4	94.2	9.4	14.9
Al	760	-	-	-
Cs	12	-	-	-
Sr	40	-	-	-
Pb	-	47.0	119	46
Cd	-	0.34	-	1.4

[a]Present study, [b][23], [c][24], [d][25].

The Al, Sr and Cs metals are missing in other studies [23]-[25] but are observed in Minjingu soils. The source of these metals in Minjingu may be attributed to Minjingu phosphate which is different from other places. Aluminum and strontium are among the radioactive elements which may be originating from the Minjingu mine and

enriching the nearby soils. The presence of these metals in soils might be exposing the dwelling community into deleterious health problems. Cd and Pb went missing in Minjingu soils. But these toxic metals were present in India, Namibia and Poland. These countries might be having the same geological backgrounds, hence similar content of elements [26].

Elemental concentrations in vegetables

Elements such as Ni, Mn, Sr, Cl, Al, Cs and Fe were found in Minjingu. Comparing field and control mean results reveals that, field vegetables were embedded with Ni toxic metal with values of 13±0.1 mg/kg in Table 4 This amount is about 130 times the allowable limits of 0.1 mg/kg [27].

Table 4. Comparison of heavy metal concentration (mg/kg) in vegetables in this study and other studies

Element	Tanzania (Minjingu)[1]	Iran (Shiraz)b	Nigeria(Benue)3	China(Chongqing)4
Fe	620	-	54.7	-
Mn	50	-	-	-
Ni	13	-	278	-
Al	284	-	-	-
Cs	56	-	-	-
Sr	68	-	-	-
Pb	-	3.21	0.76	0.03
Cd	-	0.28	44,075	0.11
Cl	714	-	-	-

[1]Current study, [2][28], [3][29], [4][4].

Table (4) shows that Minjingu vegetables contain higher concentration values of Fe than those reported in Iran, Nigeria and China. The matured Minjingu vegetables has much iron content because iron increases with plant age [30].The amount of iron in Minjingu (620 mg/kg) is above MTLs of 425 mg/kg [31] and also the intake of Fe beyond 3.0 g is toxic to the body which is usually accompanied with symptoms such as inter-intestinal bleeding and restlessness [32].

Further Table 4 indicates that Cd and Pb are missing in Minjingu vegetables but present in China, Nigeria and Iran vegetables with highest concentration values beyond MTLs. The absence of Mn, Al, Cs, Sr, and Cl in other studies but showing up in this study might be associated with the differences in the origin of contaminating source. Minjingu vegetables are thought to be contaminated with chemicals from the phosphate mine as a major polluting source which is lying in the vicinity of the vegetable gardens.

Table 5. Vegetable range concentration (mg/kg) of metals from four sites of Minjingu

Element	Idara maji	Mkwajuni	Mbulungu	Nkaiti	Control site
Fe	97-415	215-302	101-571	146-835	70-581
Cs	0-34	00-45	00-45	00-43	2-18
Mn	0-80	15-67	32-142	0-75	20-46
Sr	36-93	40-77	31-213	0-114	37-117
Ni	0-4	0-3	BDL	0-13	BDL
Al	26-72	51-76	23-120	27-286	64-254
Cl	273-1079	84-687	142-872	204-1067	151-459

Table 5 shows the highest range of Cl, Fe and Al contained in Nkaiti and Mbulungu. These places are 7 and 5 km, respectively away from the phosphate mine. The highest range of concentration observed in these places might be influenced by the heavy metal transferring by means of contaminated atmospheric particulates from the factory, and phosphate ore being deposited in high amount in vegetable leaves [33, 34]. Considering Idara ya maji which is only 1km from the polluting source, contains elevated amount of Cl. Apart from Nkaiti, Idara ya maji contain greater range values of Ni (0-4 mg/kg). The Cl and Ni metals contained in vegetables of this place might be reaching via various means such as air transportation, water runoffs, smoke and dust chemicals all the way from the Minjingu industry

Mbulungu indicates high concentration range of Mn, Sr and Cs. Table 5 shows the highest range of Mn from 32-142mg/kg in this study. Amin in Pakistan reported the range of Mn between 90 to 128.70 mg/kg [35]. The amount of Mn reported by Amin is lower than that of this study. The highest range of Ni was found in Nkaiti (0-13 mg/kg) while Okorosaye-Orubite and Igwe[36] recorded the highest range of Ni (5.37±0.4-12.5±0.16 mg/kg), this amount is lower than that found in this study. Therefore phosphate mine may be considered as the main contributing factor to the elevated range levels of Ni.

Generally the field area contained the higher concentration range levels as compared to the control site. The nearby place to the mine like Idara ya maji, which is1km from the mine, was thought to be contaminated with heavy metal by means of water run offs and air. But for the distant places 5 and 7 km from the mine, suggests that vegetables were contaminated by means of aerosol.

Table 6. Comparison of metal concentration in Minjingu vegetable species and other studies

(a) Spinach

Element	Minjingu[a] (mg/kg)	India –Naini, Arhabad[b]	Bangladesh Parkish[c]	Tanzania DSM[d]
Fe	329±3.0	69.98 mg/kg	58.094±1.3	0.10-0.11%
Ni	-	66.55mg/kg	-	-
Sr	50±1.1	-	0.54±0.02	6.63-9.83mg/kg
Mn	63±0.2	-	5.28±0.063	0.01-0.11%
Cl	415±4.4	-	-	2.95-3.37%
Al	111±4.0	-	-	-
Cs	42±1.2	-	-	-

[a]This study, [b][37], [c][38], [d][39]

(b) Sweet potato leaves

Element	Minjingu[a] (mg/kg)	Bangladesh Parkish[b]	Tanzania DSM[c] (mg/kg)	India Gujirat[d] (mg/kg)	Tanzania DSM (mg/kg)[e]
Fe	359±1.5	68.671±4.53	0.01-0.02	6.559 mg/kg	105 (170-180)
Ni	-	<0.1	-	0.334 (0.125-4.493)	-
Sr	43±0.2	-	41.00-110	-	141.8 (98.06-100)
Mn	39±0.1	1.22±0.016	39.96	-	38.238
Cl	272±2.3	-	2.23-2.93%	-	2.20% (2.23-2.93)
Al	92±1.3	-	-	-	-

Cs	**14±0.5**	**-**	**-**	**-**	**-**

^{a}This study, ^{b}[38], ^{c}[39], ^{d}[40], ^{e}[41].

In the study conducted in many parts of Africa [31], spinach vegetables were found to contain 17 mg/kg of iron. In this study spinach contained high amount of 329 mg/kg. This amount is greater than that found in most of African vegetables, but also it is above other studies of India and Bangladesh in Table 6 (a). Unlike Bangladesh (Parkish), Tanzania (Dar es Salaam) and in the present study: India (Naini-Arhabad) contain high concentration values of Ni (66.55 mg/kg), while other places contained none. Sr, Mn and Cl were present in Bangladesh and in Dar es Salaam vegetables but in low concentrations as compared with Minjingu. Al and Cs went missing in other studies however Minjingu vegetables showed elevated contents. Therefore spinach in this study contains high accumulation of Sr, Mn, Cl, Fe, Al and Cs compared with other studies. This can be associated with nearby phosphate source.

Al and Cs were absent in sweet potato leaves of India, Bangladesh and Dar es Salaam as it were in spinach of these places, but present in the current study. As compared to spinach, sweet potato leaves contain lowest levels of heavy metals generally in all studies listed on Table 6 (b). This may be ascribed to roots and nature of vegetable specie forming a barrier to absorption of heavy metals leading to poor uptake of these metals in sweet potato leaves. So the consumption of sweet potato leaves in Minjingu is encouraged rather than spinach.

The elements Fe, Ni, Sr, Mn, Cl, Al and Cs contained in Chinese cabbages, Ethiopian mustard and cowpea leaves of Minjingu were not found in literature. Therefore, since the literature was limited Chinese cabbages, cowpea leaves and Ethiopia mustard could not be compared.

3.4 Correlation coefficient Analysis

Correlation coefficient “r” is any number that falls between -1 to +1 to determine if two paired sets of data are related. The correlation coefficient r provides the magnitude and direction of a linear association between two variables. The correlation coefficient r of -1 or +1 shows a perfect linear relationship, while r=0 shows no evidence for correlation [42]. Dependent and independent variables are perfectly correlated at +1 and -1, strong relationship is exhibited at 0.75 and 1 (-0.75 and -1), moderate relationship at 0.5 and 0.75 (-0.5 and -0.75), while 0.25 and 0.5 (-0.25 and -0.5) shows a weak relationship. At 0.25< (-0.25<) there is hardly or no relationship at all [43]. The correlation coefficient was used in this study to identify a probable common source of heavy metals in vegetables.

The *p-value* lies between 0 and 1. When $p<0.05$ means there is an evidence (1-20 chance or 5% or alpha). At $p<0.01$ means a strong evidence exists, 1 in 100 and when p< 0.001, 1 in 1000 more significant. It can be said that as p approaches 0 the significance or evidence increases, alternatively, the lower the p-value the higher the significance level or the evidence. For $p>0.05$ shows no significance level or very weak evidence [44,45].

At the significance level of $p\leq 0.05$ the r shown the weak correlation between Mn and Cl (r=0.30), Cs and Al (r=-0.29), Fe and Mn (r= -0.28), Cs and Cl (r=-0.27), Al and Cl (r=0.24), Fe and Ni (r=-0.20) and a very weak correlation was observed between Fe and Sr (r=0.15), Ni and Cl (r=0.13). Comparing these results with Basha and Rajaganesh [46] in Andhra Pradesh-India, there was a very strong correlation between Fe and Al

(r=0.71) while in this study it was r=0.73. This good correlation of Fe and Al may indicate that contamination of these metals originates from the natural sources as Fe and Al are among the most abundant elements on the earth's surface [26] and from the accumulated heavy metal deposited in soils

Table 7. Pearson Correlation Coefficient of Heavy metals in soil and Vegetables.

	Fe	Cs	Mn	Sr	Ni	Al	Cl
Fe	1						
Cs	-0.31	1					
Mn	-0.28	0.96	1				
Sr	0.15	0.33	0.46	1			
Ni	-0.20	0.58	0.74	0.88	1		
Al	0.73	-0.29	-0.45	-0.44	-0.73	1	
Cl	0.50	-0.27	-0.30	0.58	0.13	0.24	1

Note: Unbolded: Correlation is significant at the 0.01 level.
Bolded: Correlation is significant at the 0.05 level.

Therefore in this study the main anthropogenic source of heavy metals might be associated with the mining activities at the phosphate mine, going on close to the grown vegetables. Consequently, the Minjingu residents are under a constant and prolonged exposure to these metals which may lead to deleterious health effects [47].

4. CONCLUSIONS

The main objective of this study was to investigate the heavy metal concentration values in both soils and vegetables samples of Minjingu village. The Wavelength Dispersive X-ray Fluorescence (WDXRF) recorded the concentration of 7 heavy metals (Ni, Fe, Al, Cl, Cs and Mn). The concentration values of heavy metals in field study were higher than the control site. The results indicate that soils were contaminated with heavy metals having the mean concentration of 53±0.4 For Mn, 40±0.2 for Sr, 2059±4.2 for Fe, 760±2.7 for Al, 12±0.3 for Cs and 4±0.04 for Ni in mg/kg which were above the MTLs, except for C. Elements detected in vegetables shown the mean concentrations of 60±1.2 for Mn, 68±0.1 for Sr, 620±2.36 for Fe, 284±1,13 for Al, 56±0.5 for Cs, 13±0.1 for Ni and 714±0.7 for Cl in mg/kg beyond Minimum limits set by FAO and WHO.

The reference and experimental results for soil and vegetables (Fig. 5&6) have revealed that the optimized machine has given the best results, whereas experimental data was almost the same as the reference values. Furthermore, MDL for vegetables and soil show that the WDXRF has very low back ground values which means the results are more accurate. Therefore, this shows that WDXRF is the best equipment to be used for better results.

The correlation coefficient results shows the heavy metals in vegetables were significantly correlated with those in soils at a level of 99% and 95% level with anthropogenic activities. This indicates that heavy metal in field vegetables were greatly influenced by heavy metal accumulated in soil and from the contaminated atmospheric air.

COMPETING INTERESTS

Authors declare that, there is no any competing interest

COMPETING INTERESTS

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