

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

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Authors' contributions

This work was carried out in collaboration between both authors. Authors YIK and ST designed together the study, performed the analysis, wrote the paper and managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

Wavelength dispersive x-ray fluorescence (WDXRF) spectrometer was used to analyze heavy metal concentration in soils and vegetables. The soil and vegetable samples were randomly collected from Minjingu village of Manyara region in Tanzania. The results indicate the soils to be contaminated with heavy metals with 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 Maximum Tolerable Limits (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 revealed that the optimized machine has given the best results, where the experimental data was very close to the reference values. The reference material of soil 7 and International Atomic Energy Agency (IAEA) 395 for vegetables shows the deviation of less than 2%. The Minimum Detection Limit (MDL) for vegetables and soil of the WDXRF spectrometer was obtained under low back ground for different matrix effects. There were high correlation coefficient of heavy metals in soils and vegetables at 99% level. The findings indicate that Minjingu soils and grown

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vegetables were highly contaminated with heavy metals mainly from soils and polluted air, at levels able to pose detrimental health effects to the consumers. Thus need of regular monitoring of the grown vegetables around phosphate mines is recommended.

Keywords: Heavy metals; WDXRF; crystal; MDL and detectors.

1. INTRODUCTION

1.1 Background of the Study

In recent years, a remarkable growth of mining sector in many parts of Tanzania has been observed. Fertilizers companies have grown to uplift crop production. The increased mining operations and their effects on pollution has raised public concern about human health. The pollution of arable soils from major and trace elements has resulted into the contamination 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.

1.2 Heavy Metal Contamination in Soils

Various research reviews conducted around the world on land pollution reported that in recent 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]. There are certainly many other countries facing similar problems including Tanzania and thus need of having pollution studies.

The soils of Minjingu village in Tanzania being nearby the phosphate mine might have

accumulated elevated heavy metals. The samples from Minjingu were analyzed by WDXRF to determine the unknown levels of heavy metals. This is the objective of the current study.

1.3 Heavy Metals in Vegetables

The vegetables grown on polluted soils accumulate the elemental concentrations to higher levels in their edible 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.

This study aimed at analyzing heavy metal concentration in soils and vegetables which necessitated the use of Wavelength Dispersive X-ray Fluorescence (WDXRF) spectrometry. The equipment parameters were optimized to improve the spectrometer performance. The correlation coefficient between different leaves were used to determine the sources of the heavy metals in vegetables. The results obtained are 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.

1.4 Principles of X-ray Fluorescence (XRF) Analysis

Electromagnetic rays of different energies are composed of different wavelength and frequencies. X-rays are generated when 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 or radioisotope sources. 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 incident x-ray beam from the tube strikes an atom in the sample, two types of interaction are common. These interactions include scattering and photoelectric absorption. The 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 an 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 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 move 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].

1.5 WDXRF Sequential Spectrometer

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.

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;

$$n\lambda = 2d \sin \theta \tag{1}$$

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].

In a WDXRF there is 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

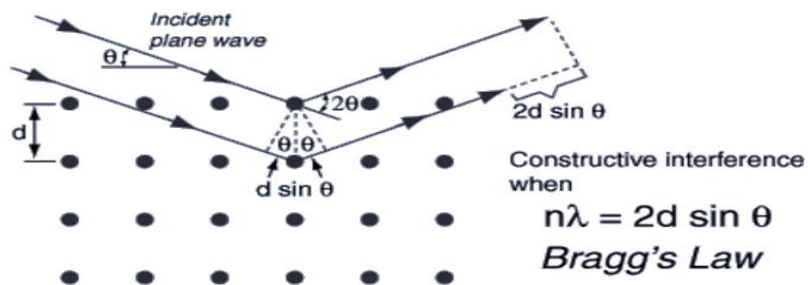


Fig. 1. Analyzing crystals diffracting radiation rays

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
				λ_{min}	λ_{max}	
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 ₄ H ₂ PO ₄ > /ADP (200)	7.5	Mg	0.654	7.16	High resolution Mg only.
7.	Pentaerythritol< C(CH ₂ OH) ₄ > (PET) (002)	8.742	AL-Ti and Rb-I	0.762	8.34	Has greatest expansion coefficients
8.	Thallium hydrogenphalete< TIHC ₈ H ₄ O 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 ₄ Cl)	200	B/Be	-	-	Measures B/Be

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)

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].

1.6 Detectors

The two types of detectors used in WDXRF spectrometer are, the gas proportional counter detector and scintillation counter detector. These detectors convert x-ray photons from the crystals into measurable voltage pulses. WDXRF consists of full wide-range of x-ray wavelengths from 0.012 to 12 nm (100 to 0.1 keV) [14,15] as shown in Table 2.

The strengths of WDXRF [10,13] is that;

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. It 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.

2. MATERIALS AND METHODS

2.1 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 area is composed of Sedimentary rock formed by biogenic activities such as remains of bones of living birds which form layers containing phosphates. 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 with the grid map of

Minjingu shown elsewhere [17]. It is estimated that this village consists of about 11,000 population occupying approximately 24,000 hectares of land according to URT report [18]. The main activities of the Minjingu people are pastoralism and farming. The cultivation in Minjingu includes; Watermelon, mug 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.



Fig. 2. Minjingu pit picture (Photo taken by the researcher on march, 2018)



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

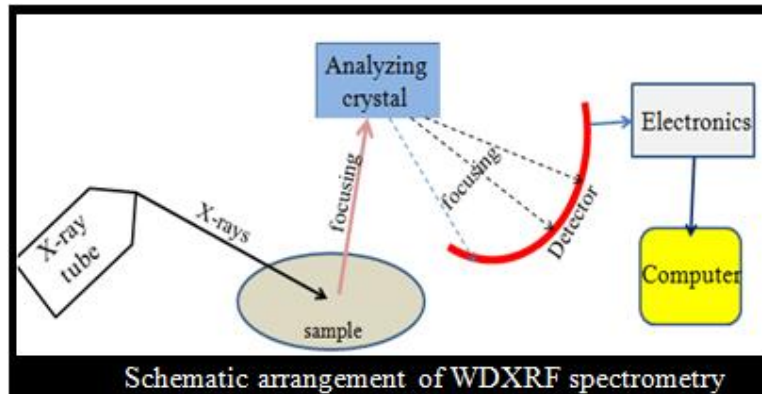


Fig. 4. Schematic arrangement of WDXRF spectrometer

2.2 Preparation of Samples and Analysis

The leaf samples from vegetable were collected from Minjingu village. These include; Cowpea leaves (*Vigna unguiculata*), Spinach (*Oleracea Spinacea*), Sweet potato (*Ipomoea batatas*), Ethiopian mustard (*Brassica Carinata*) and Chinese cabbages (*Brassica Rapa*).

The vegetables were washed by a distilled water to eliminate debris. Then samples were dried at a temperature of 65°C for 48 hours, homogenized and grinded to the size of reference materials. The WDXRF machine schematically represented in Fig. 4 was used to analyse the samples. The instrument include; end window Rh-anode operates at with 4 kW, x-ray generator which can operate 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. Up to 8 automatic crystal changers were used.

3. RESULTS AND DISCUSSION

3.1 Quality Assurance, Precision and Accuracy of an Instrument

Quality control was carried out by using two reference materials for some elements. The soil, IAEA SOIL 7 [19] in Fig. 5, standard material was used, and for cabbage IAEA 359 [20] for vegetables in Fig. 6. The analytical acceptance test was performed for the precision and accuracy of S8 TIGER WDXRF prior to sample measurements. The certified material GeoPT 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.

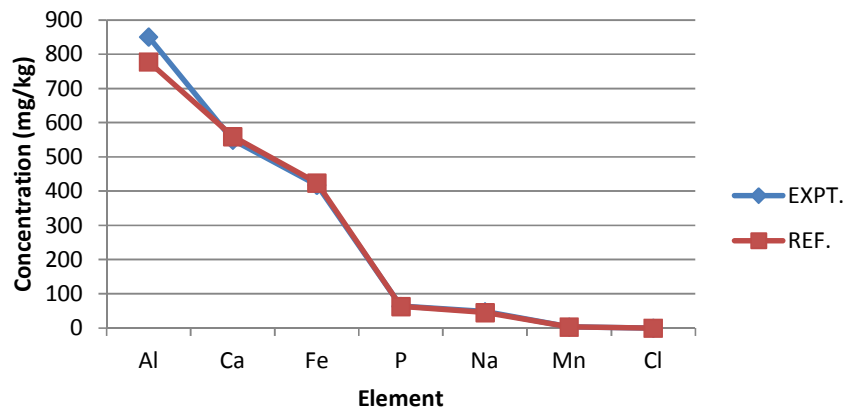


Fig. 5. Experimental and reference (Soil 7) samples results of AMGC LAB

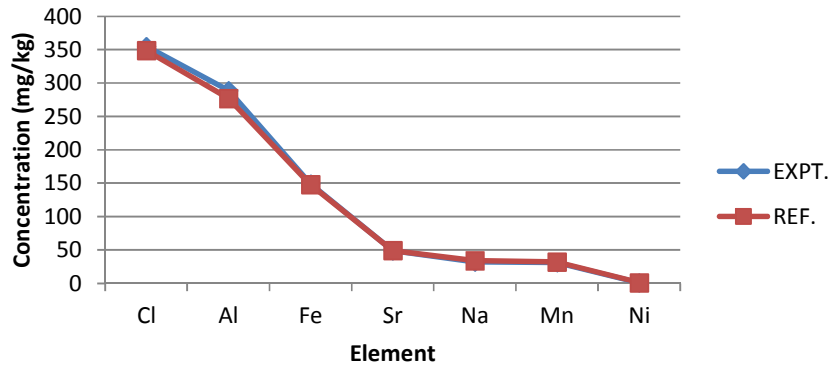


Fig. 6. Experimental and reference values for cabbages IAEA 359

MDL in soils

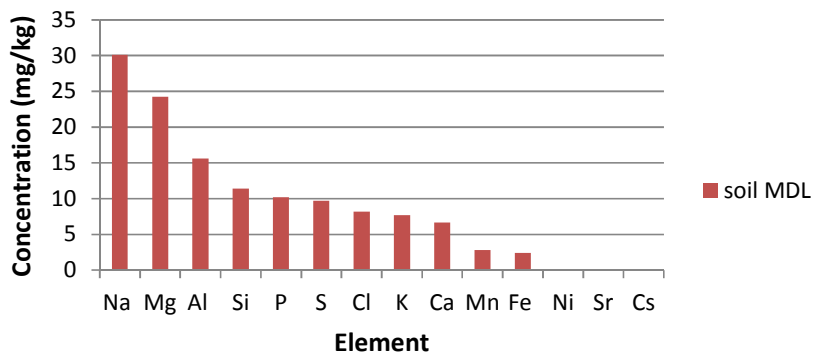


Fig. 7. The Minimum Detection Limits (MDL) for elements in soil analyzed by WDXRF

MDL in vegetables

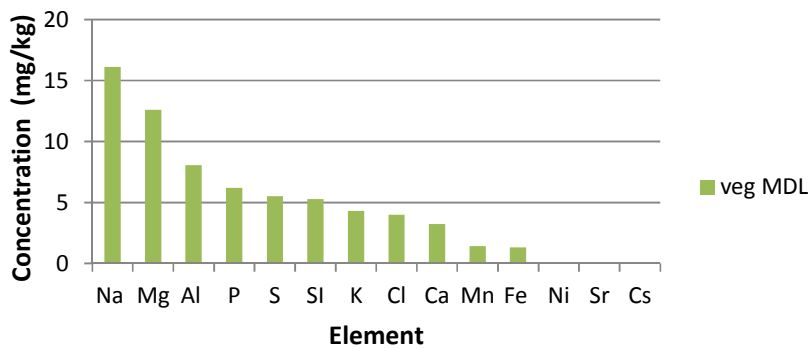


Fig. 8. The Minimum Detection Limits (MDL) for elements in vegetables by WDXRF

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

^aPresent study, ^b[23], ^c[24], ^d[25]

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

Element	Tanzania (Minjingu) ¹	Iran (Shiraz) ²	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	-	-	-

¹Current study, ²[28], ³[29], ⁴[4]

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

3.2 Comparison of Heavy Metal Concentrations in Soil of this Study and Other Studies

In Table 3, India [23] and Namibia [24] studies shows high content of iron than the current study except Poland [25]. 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 due to differences in natural formation of soils.

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 mine which is different from other places. Aluminum and strontium are among the radionuclide which may be originating from the Minjingu mine and enriching the nearby soils. The presence of these elements in soils might be exposing the dwelling community into deleterious health problems. Cd and Pb went missing in Minjingu soils. However, 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].

3.3 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 5. Vegetable range of 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

BDL-Below Detection Limit

Table 6. Comparison of metal concentration in Minjingu vegetable species and other studies**(a) Spinach**

Element	Minjingu ^a (mg/kg)	India –Naini, Arhabad ^b (mg/kg)	Bangladesh Parkish ^c (mg/kg)	Tanzania DSM ^d (mg/kg)
Fe	329±3.0	69.98 mg/kg	58.094±1.3	0.10-0.11%
Ni	-	66.55 mg/kg	-	-
Sr	50±1.1	-	0.54±0.02	6.63-9.83
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	-	-	-

^aThis study, ^b[37], ^c[38], ^d[39]

(b) Sweet potato leaves

Element	Minjingu ^a (mg/kg)	Bangladesh Parkish ^b (mg/kg)	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	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	-	-	-	-

^aThis study, ^b[38], ^c[39], ^d[40], ^e[41]

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 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 resulting from of contaminated atmospheric particulates from the factory, and phosphate ore. They are being deposited in high amount in vegetable leaves [33, 34]. Considering Idara ya maji which is only 1km from the polluting source, contains

significant 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 32-142 mg/kg. Amin reported in Pakistan the range of Mn between 90 to 128.70 mg/kg [35]. The amount of Mn reported by Amin is lower than that obtained in 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 ($5.37 \pm 0.4 - 12.5 \pm 0.16$ 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 increasing 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 is 1km 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 movement.

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 elsewhere in the literature.

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 $r=0.73$ (Table 7). This good correlation of Fe and Al may indicate that contamination of these metals

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

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

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 deteriorating 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, $284 \pm 1,13$ 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 have revealed that the optimized machine has given the best results, whereas experimental data very close to the reference values. Furthermore, MDL for vegetables and soil show that the WDXRF has very good,

accurate 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.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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