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

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12 **ABSTRACT**
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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 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.

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16 *Keywords: Heavy Metals, WDXRF, crystal, MDL and Detectors.*
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23 **1. INTRODUCTION**

24 **1.1 Background of the study**

25 In recent years, a remarkable growth of mining sector in many parts of Tanzania has
26 been observed. Fertilizers companies have grown to uplift crop production. The
27 increased mining operations and their effects on pollution has raised public concern
28 about human health. The pollution of arable soils from major and trace elements has
29 resulted into the contamination processes including the Minjingu phosphate factory
30 activities [1].
31

32 The phosphate rock refers to any material containing high quality of phosphorus
33 which can be used for economic interest as a raw material for phosphate fertilizer
34 factory or is applied directly in farmland [2]. Although phosphates escalate crop
35 yields, but the continual production of phosphate may be increasing the accumulation
36 of toxic metals to the nearby soils and edible plants of Minjingu via air and other
37 transportation channels such as water runoffs, smoke and wind.
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39 1.2 Heavy metal contamination in soils

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41 Various research reviews conducted around the world on land pollution reported that
42 in recent years there has been a gradual increase of heavy metal deposition in soils
43 caused by human activities which in turn has affected the ecosystem [3]. A significant
44 instance is China, where all farm soils indicated that Cd had the highest pollution rate
45 of 7.75%. Pb and Cr had the lowest pollution rates with values lower than 1%.
46 Furthermore, it was observed that the total pollution rate in Chinese soil was 10.18%,
47 mainly affected by Cd, Hg, Cu, and Ni. These observations were attributed to human
48 activities that released heavy metals hence causing soil pollution [4]. There are
49 certainly many other countries facing similar problems including Tanzania and thus
50 need of having pollution studies.
51

52 The soils of Minjingu village in Tanzania being nearby the phosphate mine might have
53 accumulated elevated heavy metals. The samples from Minjingu were analyzed by
54 WDXRF to determine the unknown levels of heavy metals. Thus the objective of the
55 current study.
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57 1.3 Heavy Metals in vegetables

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

69 This study aimed at analyzing heavy metal concentration in soils and vegetables
70 which necessitated the use of Wavelength Dispersive X-ray Fluorescence (WDXRF)
71 spectrometry. The equipment parameters were optimized to improve the
72 spectrometer performance. The correlation coefficient between different leaves were
73 used to determine the sources of the heavy metals in vegetables. The results obtained
74 are intended to provide some insights into contamination of heavy metals in
75 vegetables and serve as a basis for comparison in Tanzania and the world at large.
76

77 **1.4 Principles of X-ray Fluorescence (XRF) Analysis**

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79 Electromagnetic rays of different energies are composed of different wavelength and
80 frequencies. X-rays are generated when charged particles, or electrons, lose energy
81 due to deceleration or moving to a lower energy level in the atomic shell [10, 11]. In
82 XRF system, incident radiation, known as primary x-rays are generated in an x-ray
83 tube or radioisotope sources. The primary x-rays escape through a beryllium window
84 and interacts with atoms in the analyzed sample resulting to emission of
85 characteristic x-rays that are used to detect the elements present in the sample.
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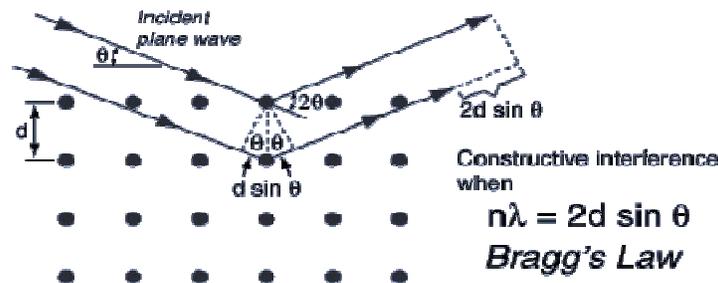
87 When incident x-ray beam from the tube strikes an atom in the sample, two types of
88 interaction are common. These interactions include scattering and photoelectric
89 absorption. The two basic interactions result to the attenuation of the primary x-rays
90 which is known as the absorption effect. Since the energy of x-rays used in XRF
91 ranges from 0 to 40 KeV, the photoelectric effect is more dominant than others [12].
92 Photoelectric Absorption is an interaction where the incident x-ray energy is
93 absorbed by an atom upon interacting with the material. The absorption of this energy
94 by the atom may result into three effects known as the Photoelectric effect,
95 Fluorescence radiation and Auger effect [10].
96

97 An atom consists of various orbital shells such as K, L, and M in with different
98 energies. These orbitals contain electrons. The electrons are named with respect to
99 the orbit in which they are found. An electron within the orbit is bound to the atom
100 with the binding energy that equals the energy of the respective orbit. If the energy of
101 the primary x-ray is greater than the binding energy of a given electron, the particular
102 electron is knocked out of its orbit and become a free electron [12]. The released
103 characteristic x-ray photon may interact and be absorbed by the electrons in the outer
104 shell of the atom as it is moving out manage to remove it out of the atom. This
105 process is called the Auger effect and the ejected electron is known as the Auger
106 electron. Auger effect predominates in low Z elements [12].
107

108 When the electron is knocked out of the atom, leaves the gap in the original shell. The
109 vacancy left in K-shell results to an unstable state of the atom and the electron from a
110 shell of lower binding energy move to the K-shell to fill the gap. The difference in
111 binding energies between the two shells forms excess energy which is emitted in
112 form of photons called fluorescence x-rays [11].
113

114 **1.5 WDXRF sequential spectrometer**

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

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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;

$$n\lambda = 2d \sin\theta \quad (1)$$

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 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) λ_{min} λ_{max}		Applications
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 hydrogenphosphate< 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

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143 **1.6 Detectors**

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

149
 150
 151 **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)

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

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

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 170 **2. MATERIAL AND METHODS**

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 172 **2.1 Study Area**

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 174 Minjingu village is situated along the rift valley escarpment on the Eastern part of
 175 Lake, Manyara region. Within the village there is a phosphate pit near the Minjingu hill
 176 Fig. 2, where phosphate is mined. The area is composed of Sedimentary rock formed
 177 by biogenic activities such as remains of bones of living birds which form layers
 178 containing phosphates. The village of Minjingu is found on the Northern part of
 179 Tanzania, along latitude 03°42' 30.9" S and longitude 035° 54' 56.3" E with the grid
 180 map of Minjingu shown elsewhere [17]. It is estimated that this village consists of
 181 about 11,000 population occupying approximately 24,000 hectares of land according
 182 to URT report [18]. The main activities of the Minjingu people are pastoralism and
 183 farming. The cultivationd in Minjingu includes; Watermelon, mug beans, maize and
 184 vegetables such as Chinese cabbages and spinach. The area of Minjingu which is
 185 used for agriculture is found on the North-Eastern part of Babati-Arusha road, while
 186 on the North-West of the same road is for pastoralism where the Minjingu phosphate
 187 mine is situated Fig. 3.
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Figure 2. Minjingu pit picture (Photo taken by the researcher on March, 2018).



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

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*).

204 The vegetables were washed by a distilled water to eliminate debris. Then samples
205 were dried at a temperature of 65⁰C for 48 hours, homogenized and grinded to the size
206 of reference materials. The WDXRF machine schematically represented in Fig. 4 was
207 used to analyse the samples. The instrument include; end window Rh-anode
208 operates at with 4 kW, x-ray generator which can operate at a maximum voltage of 60
209 kV and a maximum tube current of 170 mA. The set of crystals covered the entire
210 range of elements from Beryllium to Uranium. Up to 8 automatic crystal changers
211 were used.
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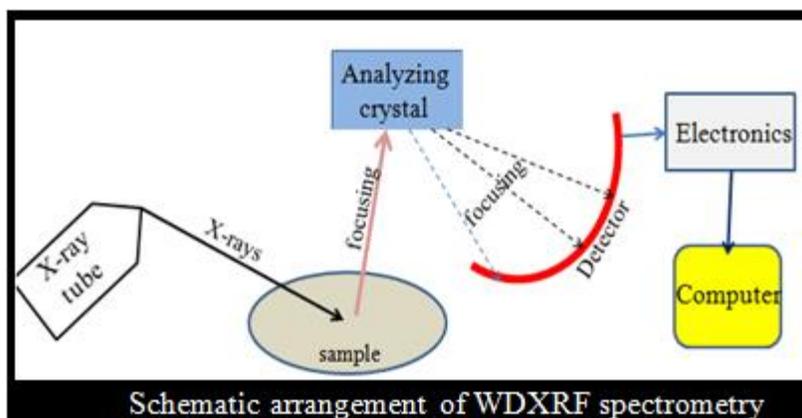


Fig. 4. Schematic arrangement of WDXRF spectrometer.

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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.

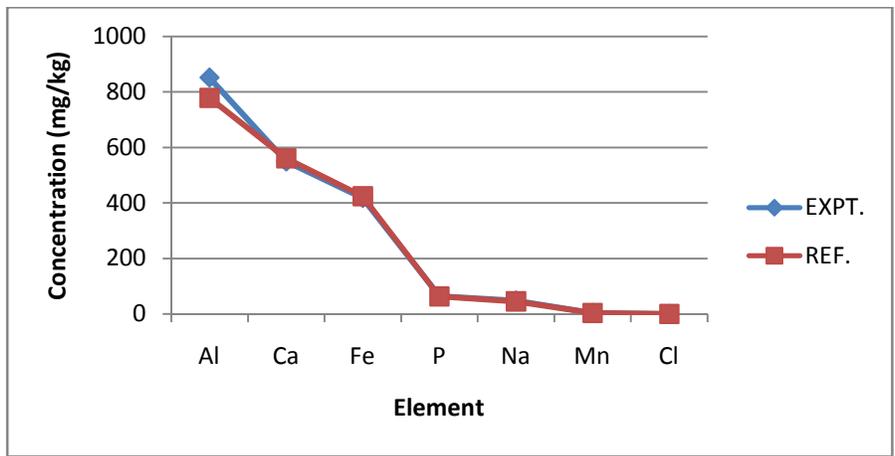


Fig. 5. Experimental and reference (Soil 7) samples results of AMGCLAB.

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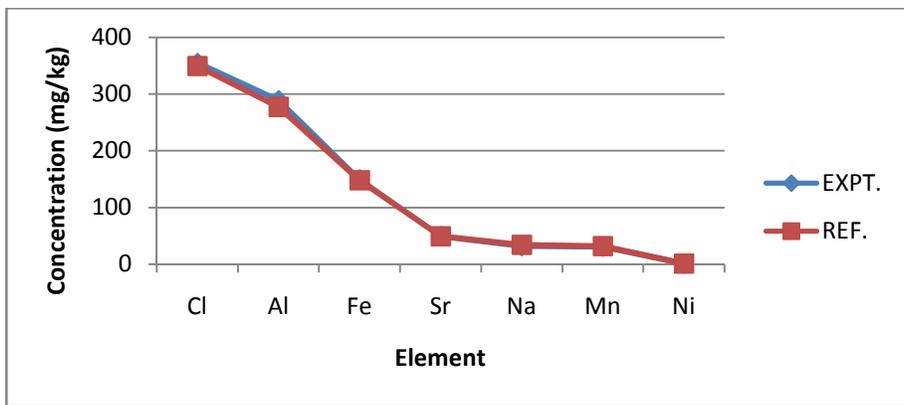


Fig. 6. Experimental and reference values for cabbages IAEA 359.

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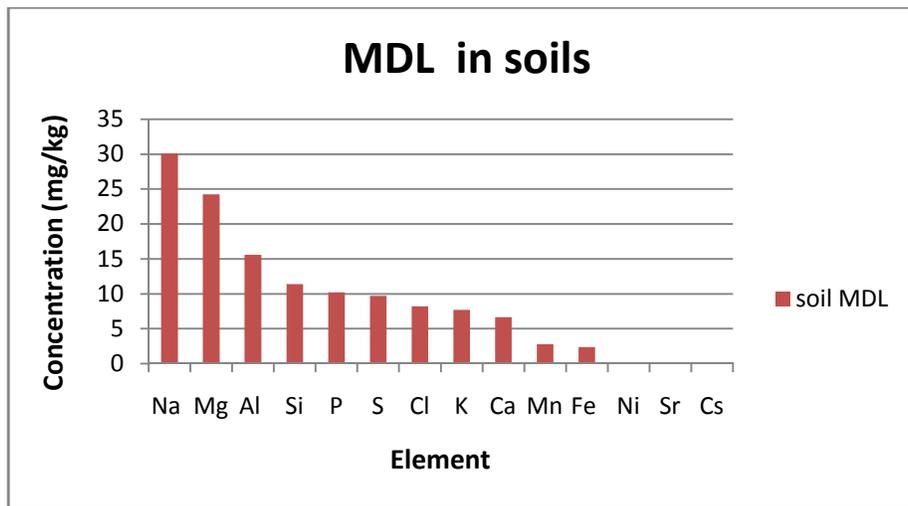
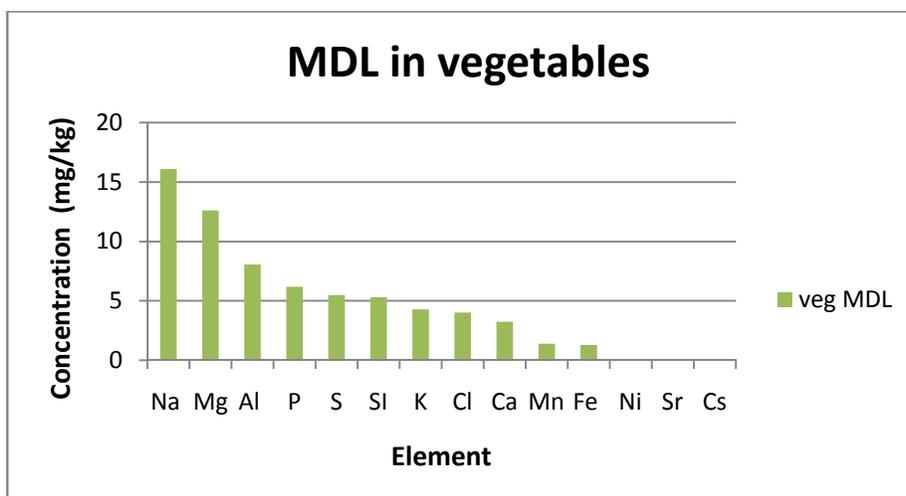


Fig. 7. The Minimum Detection Limits (MDL) for elements in soil analyzed by WDXRF.

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244 Fig. 8. The Minimum Detection Limits (MDL) for elements in vegetables by WDXRF.
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247 Minimum Detection Limits (MDL) for soils (Fig. 7) and vegetables (Fig. 8) were
248 calculated from the formula given by Koleleni and Mbike [21], Koleleni and Mosha
249 [22]. The WDXRF machine in this study has shown very low detection limits especially
250 for vegetables. The achievement were due to optimized curved crystals, good
251 arrangement of collimators and sequential measurement aided by two detectors
252 which reduced the background intensity of the machine significantly.
253

254 3.2 Comparison of heavy metal concentrations in soil of this study and other studies

255
256 In Table 3, India [23] and Namibia [24] studies shows high content of iron than the
257 current study except Poland [25]. Fe concentration values in these countries are high
258 though the Fe recommended limits are unknown; this may harm the population
259 surrounding these areas. The Mn and Ni concentration values were found to be lower
260 in this study compared to other studies. This may be due to differences in natural
261 formation of soils.
262

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

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

272 enriching the nearby soils. The presence of these elements in soils might be exposing
 273 the dwelling community into deleterious health problems. Cd and Pb went missing in
 274 Minjingu soils. However, these toxic metals were present in India, Namibia and
 275 Poland. These countries might be having the same geological backgrounds, hence
 276 similar content of elements [26].
 277

278 3.3 Elemental concentrations in vegetables

279 Elements such as Ni, Mn, Sr, Cl, Al, Cs and Fe were found in Minjingu. Comparing
 280 field and control mean results reveals that, field vegetables were embedded with Ni
 281 toxic metal with values of 13 ± 0.1 mg/kg in Table 4 This amount is about 130 times the
 282 allowable limits of 0.1 mg/kg [27].
 283

284 Table 4. Comparison of heavy metal concentration (mg/kg) in vegetables in this study
 285 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	-	-	-

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

287 Table (4) shows that Minjingu vegetables contain higher concentration values of Fe
 288 than those reported in Iran, Nigeria and China. The matured Minjingu vegetables has
 289 much iron content because iron increases with plant age [30].The amount of iron in
 290 Minjingu (620 mg/kg) is above MTLs of 425 mg/kg [31] and also the intake of Fe
 291 beyond 3.0 g is toxic to the body which is usually accompanied with symptoms such
 292 as inter-intestinal bleeding and restlessness [32].
 293

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

301 Table 5. Vegetable range of concentration (mg/kg) of metals from four sites of
 302 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

303 BDL-Below Detection Limit

304 Table 5 shows the highest range of Cl, Fe and Al contained in Nkaiti and Mbulungu.
 305 These places are 7 and 5 km, respectively away from the phosphate mine. The highest
 306 range of concentration observed in these places might be influenced by the heavy
 307 metal resulting from of contaminated atmospheric particulates from the factory, and
 308 phosphate ore. They are being deposited in high amount in vegetable leaves [33, 34].
 309 Considering Idara ya maji which is only 1km from the polluting source, contains
 310 significant amount of Cl. Apart from Nkaiti, Idara ya maji contain greater range values
 311 of Ni (0-4 mg/kg). The Cl and Ni metals contained in vegetables of this place might be
 312 reaching via various means such as air transportation, water runoffs, smoke and dust
 313 chemicals all the way from the Minjingu industry
 314

315 Mbulungu indicates high concentration range of Mn, Sr and Cs. Table 5 shows the
 316 highest range of Mn from 32-142mg/kg. Amin reported in Pakistan the range of Mn
 317 between 90 to 128.70 mg/kg [35]. The amount of Mn reported by Amin is lower than
 318 that obtained in this study. The highest range of Ni was found in Nkaiti (0-13 mg/kg)
 319 while Okorosaye-Orubite and Igwe[36] recorded the highest range of Ni (5.37 ± 0.4 -
 320 12.5 ± 0.16 mg/kg), this amount is lower than that found in this study. Therefore
 321 phosphate mine may be considered as the main contributing factor to the increasing
 322 range levels of Ni.
 323

324 Generally the field area contained the higher concentration range levels as compared
 325 to the control site. The nearby place to the mine like Idara ya maji, which is 1km from
 326 the mine, was thought to be contaminated with heavy metal by means of water run
 327 offs and air. But for the distant places 5 and 7 km from the mine, suggests that
 328 vegetables were contaminated by means of aerosol movement.
 329

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

332 (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	-	66.55mg/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	-	-	-

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

335 (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	-	-	-	-

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Cs	14±0.5	-	-	-	-
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338 ^aThis study, ^b[38], ^c[39], ^d[40], ^e[41].

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

350
 351 Al and Cs were absent in sweet potato leaves of India, Bangladesh and Dar es Salaam
 352 as it were in spinach of these places, but present in the current study. As compared to
 353 spinach, sweet potato leaves contain lowest levels of heavy metals generally in all
 354 studies listed on Table 6 (b). This may be ascribed to roots and nature of vegetable
 355 specie forming a barrier to absorption of heavy metals leading to poor uptake of these
 356 metals in sweet potato leaves. So the consumption of sweet potato leaves in Minjingu
 357 is encouraged rather than spinach.

358 The elements Fe, Ni, Sr, Mn, Cl, Al and Cs contained in Chinese cabbages, Ethiopian
 359 mustard and cowpea leaves of Minjingu were not found elsewhere in the literature.

360

361 3.4 Correlation coefficient Analysis

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363 Correlation coefficient “r” is any number that falls between -1 to +1 to determine if two
 364 paired sets of data are related. The correlation coefficient *r* provides the magnitude
 365 and direction of a linear association between two variables. The correlation coefficient
 366 *r* of -1 or +1 shows a perfect linear relationship, while *r*=0 shows no evidence for
 367 correlation [42]. Dependent and independent variables are perfectly correlated at +1
 368 and -1, strong relationship is exhibited at 0.75 and 1 (-0.75 and -1), moderate
 369 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
 370 weak relationship. At 0.25< (-0.25<) there is hardly or no relationship at all [43]. The
 371 correlation coefficient was used in this study to identify a probable common source of
 372 heavy metals in vegetables.

373

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

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381 At the significance level of *p*≤0.05 the *r* shown the weak correlation between Mn and
 382 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
 383 (*r*=0.24), Fe and Ni (*r*=-0.20) and a very weak correlation was observed between Fe and
 384 Sr (*r*=0.15), Ni and Cl (*r*=0.13). Comparing these results with Basha and Rajaganesh
 385 [46] in Andhra Pradesh-India, there was a very strong correlation between Fe and Al
 386 (*r*=0.71) while in this study it was *r*=0.73. This good correlation of Fe and Al may
 387 indicate that contamination of these metals originates from the natural sources as Fe

388 and Al are among the most abundant elements on the earth's surface [26] and from
 389 the accumulated heavy metal deposited in soils

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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

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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 deteriorating health effects [47].

4. CONCLUSIONS

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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 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 declare that, there is no any competing interest

COMPETING INTERESTS

AUTHORS' CONTRIBUTIONS

Both Authors YIK and ST designed together the study, performed the analysis, wrote the paper and managed the literature searches.Both authors have read and approved the manuscript for submission

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