



# **Analysis of Heavy Metals in Soil and Maize Grown around Namungo Gold Mine in Ruangwa District, Lindi Region in Tanzania Using X-ray Fluorescence**

**Yusuf I. Koleleni<sup>1\*</sup> and Shaban A. Mbike<sup>1</sup>**

<sup>1</sup>*Department of Physics, University of Dar es Salaam, P.O.Box 35063 Dar es Salaam, Tanzania.*

## **Authors' contributions**

*This work was conducted by both authors. Author YIK designed the study. Author SAM performed the EDXRF and statistical analysis, under supervision of author YIK. The first draft was done by author SAM. Author YIK wrote the second and the final draft of the manuscript. The literature searches were done by both authors SAM and YIK. Both authors have read and approved the final manuscript for submission.*

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## **ABSTRACT**

Soils and food crops were collected from three sample villages of Chibula, Chingumbwa and Ligonje which are located nearby the Namungo gold mine. The samples of both maize and soil were prepared and analysed using Energy Dispersive X-rays Fluorescence (EDXRF) with the objective of investigating the elemental concentration levels. Most of the elements in both soil and maize were detected with high concentration levels. The results showed that Maize were accumulated with mean range concentrations of; 870.3-1296.5 mg/kg for Cd, 23.2-24.0 mg/kg for Pb, 1.3-30.7 mg/kg for Hg, 1.2-4.9 mg/kg for Cu, 39.8-115.3 mg/kg for V, 402.6-1964.8 mg/kg for Fe, and 8.6-20.1 mg/kg for U respectively. On the other hand, mean range concentrations of metal elements detected in the soil were 3.6-20.3 mg/kg for Pb, 2771.6-5969.6 mg/kg for U, 3.4-19.5 mg/kg for Hg, 0.6-8.2 mg/kg for Se, 20.9-830.4 mg/kg for As, 49.6-169.2 mg/kg for Cu and 192.2-858.8 mg/kg for V. The correlation matrix shows that most the elements are the result of mining activities which might be detrimental to the health of the consumers.

\*Corresponding author: E-mail: [ykoleleni@gmail.com](mailto:ykoleleni@gmail.com);

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## 1. INTRODUCTION

### 1.1 Heavy Metals in Soil

The impact of the high concentration level of heavy metals in the environment as well as its effect on human health has brought a new concern to the scientists. This is because the poisoning by heavy metals is known to be gradual, hidden and hard to associate with time, place and source. As such several international organisations have set tolerable levels which have made the increase in routine monitoring of environmental pollutions from different sources [1]. Reporters [2,3] shows that Pb is consumed above the permitted maximum tolerable daily intake (PMTDI) endorsed by WHO/FAO of 0.21 mg/person per day, whereas the rest were below permissible limits. The ADI for Pb was estimated to be 0.63 mg/person/day, which represents 7.4% of the total intake of the heavy metals. The order of contribution for the Pb intake is as follows: I. batatas > A. hybridus > A. esculentus > S. melongena. The last two did not differ appreciably in their Pb content and contributions.

Mining activities could pollute the surrounding environment through a range of pathways including physical disturbance of the landscape, spilling of mine tailings, emissions of dust contain heavy metals into atmosphere and generation of large quantity of acidic drainage that contains heavy metals [1]. Some heavy metals such as Cu, Zn, Mn and Co have been reported to be essential for life as they act as micronutrients for human but if a person intake exceeds a permissible limit, they may cause the health effect in human bodies [2].

Heavy metals such as Cd, Cu, Pb, Hg and Ni in excessive amount have found to be potentially carcinogenic, mutagenic as well as teratogenic. Heavy metals like some other pollutants on acute or chronic exposure severely affect different body organs [3,4]. Soils are contaminated with a heavy metal such as Pb, Cd, Cr, As, Cu, Zn, Co, Fe, Mn etc, many of which are non-essential and overtime toxic to plants, animals and human beings. This causes an undesirable change in the physical, chemical and biological characteristics of soil and affects human life, lives of animals and plants [5].

In the study by Balkhair and Ashraf [6], many soil factors, such as the ph., organic matter and

organic carbon have interacted to influence the uptake. The acidic range of the soil is known to increase the mobilisation of heavy metals, thus increasing their uptake. The field data support this argument in that the soil ph. was acidic. The values of sulfate, phosphate, nitrate and nitrite in the vegetable samples show that the leaves are richer in this anion content than in the other parts studied. It is also stated that nitrate, and nitrite contents of various parts of a plant differ in the order of leaf > stem > root > tuber > bulb > fruit > seed [6].

The long biological half-lives of most heavy metals lead to having the potential of accumulation in body organs which cause the health risk due to that there is no mechanism for their elimination from bodies [3]. Human exposure to heavy metals might occur through food, water, air, or absorption through the skin when they come in contact with humans in daily conducts [7].

### 1.2 Heavy Metals in Foodplants

Assessment of heavy metal exposure level is indispensable in determining organism health risk through contaminated vegetables [8]. Various routes of exposure to humans do exist, yet the most significant is the food chain [8,9]. A similar study by Ademoroti, 1996 [10] has reported that vegetables accumulate a considerable amount of heavy metals, especially Pb, Cr, Cu and Zn, in the roots and leaves. The concentrations of heavy metals in all of the vegetable samples analyzed were higher than the FAO/WHO guideline values of 0.1– 0.2 mg/kg Cr, 0.3 mg/kg Fe; 0.1 mg/kg Pb; 0.1 mg/kg Cu; 0.1 mg/kg Zn; 0.1 mg/kg Ni; 0.02 mg/kg Cd and 0.3 mg/kg Mn.

The results earlier reports Liu et al. [11], Muchuweti et al. [12], Kumar sharma et al. [13] demonstrated that plants grown on wastewater irrigated soils are contaminated with heavy metals and pose a health concern. The absorption and accumulation of heavy metals in plant tissues depend upon many factors. these factors include the temperature, moisture, organic matter, ph. and nutrient availability, whereas the presence of organic matter has been reported to increase the uptake of Zinc, Chromium, Lead, Iron and Copper in the wheat plant [14].

Corn cob silica (ccs), produced via a modification of the sol-gel method, can reduce heavy metal availability and stabilize contaminated soil on abandoned mining sites. Adding 5 % (w/w) ccs to mining site soil increased ph. from 4.0 to 7.7, and cation exchange capacity increased from 94.5 to 100.3 cmol+/kg. Sequential extraction showed that adding ccs decreased heavy metal availability in the soil. Mobility factor (mf) values indicated that ccs reduced pb mobility more than that of Zn or Cu in all fractions [15]. Pb concentrations in leachate from all fractions using the Toxicity Characteristic Leaching Procedure (TCLP) were greatly decreased by adding 3 % (w/w) ccs. ccs similarly reduced Zn concentrations in TCLP leachate. ccs addition did not impact cu concentrations in leachate, likely because concentrations were much lower than those of the other metals. As was generally less mobile than the heavy metals; however, as mobility and leach ability tended to increase with ccs addition because its oxyanions arsenate and arsenite have low affinity for negatively charged surfaces on the ccs. Shoot and root growth of *Spinacia oleracea* L. (spinach) was much greater in ccs-treated soil than in unamended soil. results demonstrate the utility of ccs to stabilise heavy metals in contaminated mining site soil, but this treatment may not be ideal for as-contaminated soils [15].

Whenever plants grow on contaminated soil, contaminants may be incorporated within the above ground tissue of the plants. The high observed Pb content in vegetables threatens human health. The high level of Pb is attributed to the roadside location of the garden and the transitory heavy traffic. The Pb toxicity affects many organs in humans, such as liver, kidney, lungs, and spleen, causing severe biochemical defects. High average daily intake of Pb has been also reported in Dar es salaam, Tanzania [3].

### 1.3 Energy Dispersive X-Ray Fluorescence (EDXRF)

The analysis of elements by EDXRF is made possible by the behaviour of atoms when they interact with radiation. When materials are exposed to energetic X-rays or to gamma rays, ionisation of their component atoms may take place. Ionisation consists of the ejection of one or more electrons from the atom, and may occur if the atom is exposed to radiation with energy greater than its ionisation energy [16]. X-rays and

gamma rays can be energetic enough to expel tightly held electrons from the inner orbitals of the atom. The removal of an electron in this way makes the electronic structure of the atom unstable, and electrons in higher orbitals "fall" into the lower orbital to fill the hole left behind. In falling, energy is released in the form of a photon, the energy of which is equal to the energy difference of the two orbitals involved. This energy release is in the form of emission of characteristic x-rays indicating the type of atom present in the material. Once the radiations coming from the sample are detected the quantification of all the elements may be done [16,17,18,19].

#### 1.3.1 Direct excitation of EDXRF

The EDXRF analyser also uses an x-ray source to excite the sample, but it may be configured in one of two ways. The first way is direct excitation where the x-ray beam is pointed directly at the sample as shown in Fig. 1. Filter made of various elements may be placed between the source and sample to increase the excitation of the element of interest or reduce the background in the region of interest.

The fluorescent x-rays emitted by the material sample are directed into a Silicon Lithium Detector Si (Li) which produces a "continuous" distribution of (signals), the voltages of which are proportional to the incoming photon energies. This signal is processed by a multichannel analyser (MCA) to produce an accumulating digital spectrum (peaks). The spectrum is then built up by dividing the energy spectrum into discrete bins and counting the number of pulses registered within each energy bin that can be processed to obtain analytical data. Quantitative analysis is the process in which one calculates characteristic x-rays intensity and converts to elemental concentrations [19].

#### 1.3.2 Secondary target excitation of EDXRF

The second way uses a secondary target, where the source points at the target, the target element is excited and fluoresces, and then the target fluorescence is used to excite the sample as shown in Fig. 2. A detector is positioned to measure the fluorescent and scattered x-rays from the sample and a multichannel analyser and software assigns each detector pulse an energy value thus producing a spectrum [16,17]. In order to reduce unwanted signals in the EDXRF system, collimator and secondary target are used

to improve intensity of the incident photons. The collimators are usually circular or slits and restrict the size or shape of the source beam from an exciting small area in EDXRF system.

EDXRF spectrometers require sophisticated electronics and computer software to interpret the detector output. Nowadays this is less complicated, though, due to important technological advances in multichannel analysers and faster computers, and EDXRF is often the technique of choice for fast multi-element analyses.

In lead analysis, high concentrations produce two strong spectral peaks  $L_a$  at energy 10.5 keV and  $L_b$  at 12.6 keV. Generally, the lead  $L_b$  peak is used for lead analysis. The best arsenic spectral line for measurement is the  $K_a$  peak - also at 10.5 keV. Thus lead produces an interference, whereby the lead  $L_a$  completely overlaps the desired arsenic  $K_a$  spectral peak. The lead interference becomes detrimental to arsenic measurement in two ways:

(1) Elevates the arsenic detection level.

(2) Moderately reduces arsenic precision for the same testing time compared to an identical sample with no lead.

Dispersion in EDXRF is accomplished through the use of a semiconductor-type detector [20]. Although germanium detectors are utilised, the most common type in service is the Si (Li), or lithium-drifted silicon, detector. A semiconductor detector operates based on the principle that an X-ray photon incident upon the diode material will give up its energy to form electron-hole pairs, the number of which is proportional to the energy of the photon. The high voltage applied across the diode quickly collects the released charge on a feedback capacitor, and the resulting proportional voltage pulse amplified by a charge-sensitive preamplifier. The output of the preamp is fed to the main amplifier system. The pileup rejecter, part of this system, deals with the probable event that two pulses will arrive very close together in time. From this point, the pulse is converted to a digital signal and processed in the multichannel analyser (MCA) [21].

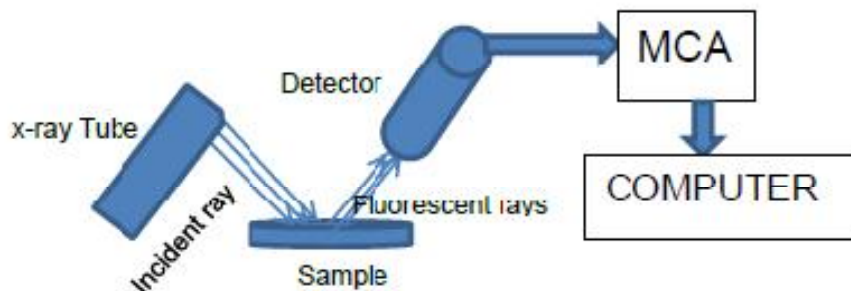


Fig. 1. A Schematic representation of direct excitation of EDXRF

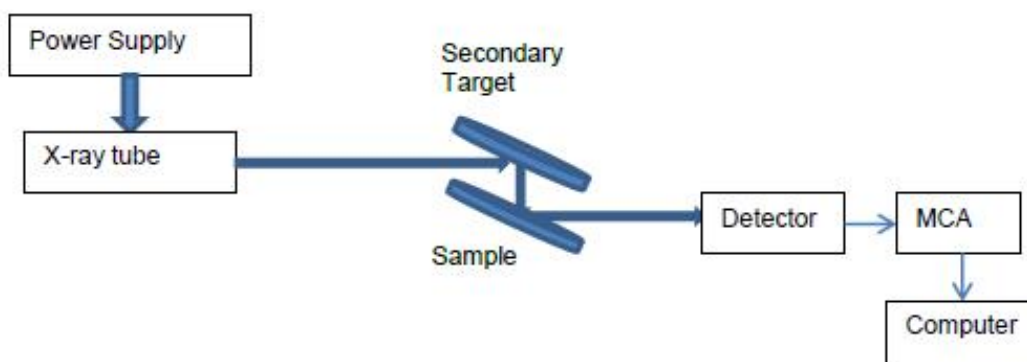


Fig. 2. Schematic illustration of secondary target excitation of EDXRF

### 1.3.3 Importance of XRF

XRF has been one of the tools of choice for environmental and geological samples for many years. For postgraduate students in the Physics Department, at the University of Dar es Salaam, Tanzania, the ability to determine major and trace components in a single analysis with the minute sample and fast preparation has been a basic practice. Current research aimed at using XRF analyses for soil and maize samples looking for heavy, toxic metals. Also, the focus is on the accuracy precision and detection limits of the technique.

### 1.3.4 The principle of the X-ray fluorescence spectroscopy (XRF)

The specimen is excited with the primary X-radiation. In the process electrons from the inner electron shells are knocked. Electrons from outer electron shells fill the resultant voids emitting fluorescence radiation that is characteristic in its energy distribution for a particular material. This fluorescence radiation is evaluated by the detector.

The generation of the X-ray fluorescence radiation is shown simplified in the figure above. One electron from the K shell is knocked. The resultant void is filled by either an electron from the L shell or an electron from the M shell. In the process, the  $K_{\alpha}$  and  $K_{\beta}$  radiation is generated, which is characteristic for the particular material.

In general, the sample preparation which includes drying, grinding, sieving, homogenisation and pellet pressing, significantly improves data quality, compared to unprepared, in-situ measurement. Unexpectedly poor results arise in the sample splitting and sample handling procedures. EDXRF spectrometry is based on an expression which describes the intensity of the characteristic x-rays of the  $i^{\text{th}}$  element in a multi-element sample. For monoenergetic excitation, while neglecting the enhancement effect, one can apply the following equation [16,17,18,19, 21].

If the intensity of the primary radiation is  $I_o$ , then the intensity of the characteristic x-ray due to the element  $j$  at a depth  $x$  in the sample is given by the product of the primary intensity and the three probabilities shown in equation 1 as shown in Fig. 3 [18,21,24].

$$dI_j = I_o p_1 p_2 p_3 \tag{1}$$

where  $p_1 = G_1 \exp [\mu_1 \rho x \csc \phi_1]$  is the probability that the primary radiation will reach the depth  $x$  in the sample,

$p_2 = \tau_j \rho_j \csc \phi_1 [1 - \frac{1}{j_k}] W_{kj} f_{\alpha j} dx$  is

the probability that the element  $j$  will absorb the primary radiation and results into fluorescent radiation of energy  $E_{kj}$ ,

$p_3 = G_2 \exp [-\rho x \mu \csc \phi_2] \varepsilon(E_j)$  is the

probability that the  $k$  x-rays of energy  $E_j$  will penetrate out of the sample and be detected by the detector,  $I_o$  is the intensity of the primary radiation. Substituting  $P_1$ ,  $P_2$  and  $P_3$  in the above equation we obtain;

$$dI_j = I_o G_1 G_2 \tau_j \rho_j \csc \phi_1 [1 - \frac{1}{j_k}] W_{kj} f_{\alpha j} \varepsilon(E_j) \exp[-\rho x (\mu_1 \csc \phi_1 + \mu_2 \csc \phi_2)] dx \tag{2}$$

where  $I_j$  is the intensity of the fluorescent radiation from the element  $j$  in the sample,  $G_1$  and  $G_2$  representing the solid angles subtended by the source and the detector respectively with the sample,  $\rho_j$  and  $\rho$  represent the densities

of the element  $j$  and the sample respectively,  $\phi_1$  and  $\phi_2$  are the angles form by primary characteristics x-rays respectively,  $\tau_j$  is the photoelectric cross section of the element  $j$ ,  $j_k$  is the ratio between  $\tau_j$  at the top and at the bottom of the  $k$  absorption edge,  $W_{kj}$  is the fluorescence yield for the  $k$  x-rays,  $f_{\alpha j}$  is the fraction of the  $k_{\alpha}$  x-rays of the energy  $E_j$  with respect to the  $k$  x-rays emitted,  $\varepsilon(E_j)$  is the detection efficiency of x-rays with energy  $E_j$ .

Now, the terms in equation (2) can be reduced by letting  $G_o$ ,  $K_j$  and  $a$  as in equations (3), (4) and (5).

$$G_o = I_o G_1 G_2 \csc \phi_1 \quad (3)$$

$$K_j = \tau_j (E_j) f_{\alpha_j} W_{kj} \left[1 - \frac{1}{j_k}\right] \varepsilon(E_j) \quad (4)$$

$$a = \mu_1 \csc \phi_1 + \mu_2 \csc \phi_2 \quad (5)$$

The equation (2) becomes:

$$d I_j = G_o K_j \rho_j \exp(-a \rho x) dx \quad (6)$$

Integrating equation (6) results to:

$$\int_0^d d I_j = G_o K_j \rho_j \int_0^d \exp(-a \rho x) dx \quad (7)$$

$$I_j = \frac{G_o K_j \rho_j}{a \rho} [1 - \exp(-a \rho d)] \quad (8)$$

Hence equation (7) is reduced to the final equation of the fundamental parameter method as follows:

$$I_j = G_o K_j (\rho_j d) \frac{1 - \exp(-a \rho d)}{a \rho d} \quad (9)$$

Where  $G_o$  the geometric is constant,  $K_j$  is the detection efficiency,  $d$  is the sample thickness,  $a$  is the combined absorption efficiency for

primary and fluorescence x-rays and  $\frac{1 - \exp(-a \rho d)}{a \rho d}$  is the absorption correction factor.

Equation (9) is a generalised fundamental parameter theory equation for primary fluorescence x-rays and hold for any general thickness of the sample. Most of these parameters are constant for each element in the sample making the equation universal.

### 1.3.5 Classification of sample

Various analyses techniques can be used in the quantitative analysis of the samples depending on the nature of the sample and type standard available. By using the general formula for the fundamental parameter method, sample used in XRF can be categorised into the following three categories [18].

### 1.3.6 Thin samples

For thin samples;  $a \rho d \ll 1$  this gives  $\exp(-a \rho d) \approx 1 - a \rho d$  by Taylor's expansion. In this case, the absorption factor in equation (9) can be approximated to:

$$\frac{1 - \exp(-a \rho d)}{a \rho d} \approx \frac{1 - (1 - a \rho d)}{a \rho d} = 1 \quad (10)$$

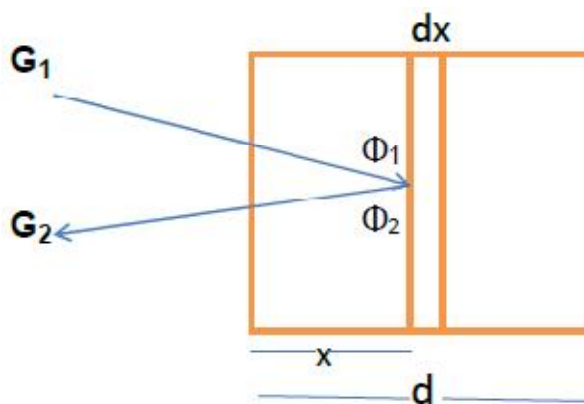


Fig. 3. Schematic figure for the excitation of the sample using x-rays [18, 21, and 24].

Therefore, for thin samples;

$I_j = G_o K_j (\rho_j d)$  This implies that there is no absorption for the thin samples.

### 1.3.7 Intermediate samples

For the intermediate samples with values  $0.1 < a \rho d < 0.2$ , the measured intensity varies exponentially with the thickness of the sample. This is given by

$$I_j = G_o K_j (\rho_j d) \frac{1 - \exp(-a \rho d)}{a \rho d} \quad (11)$$

### 1.3.8 Thick Samples

For the thick samples  $a \rho d \gg 1$ , in which  $\exp(-a \rho d) \approx 0$ , therefore, the exponential part of the absorption correction factor becomes;

$$\frac{1 - \exp(-a \rho d)}{a \rho d} \approx \frac{1}{a \rho d}$$

(18) becomes:

$$I_j = G_o K_j \frac{\rho_j}{a \rho} \quad (12)$$

Therefore, the intensity of intermediate and thick samples depends on the absorption factor "a".

Hence, for thin or transparent samples the matrix correction methods must be employed to correct for the absorption effects [24].

## 1.4 The Objective of this Work

In this work the objective is to investigate, the levels of Cd, Co, Cu, Ni, Pb and Zn in soils and food crop samples from mining and individual farms for their contamination in soil and accumulation in food crops. The heavy metals concentration levels from soils and maize collected from three sampled villages located nearby Namungo goldmine in Ruangwa, Lindi of Tanzania is analysed using the EDXRF technique. The model in the equations in XRF is used to obtain a quantitative mass concentration. However, the detection limits of most elements were found with an accuracy of less than 3%.

## 2. MATERIALS AND METHODS

### 2.1 Sampling and Location

Ruangwa District is located in Lindi Region in southern Tanzania. It is bordered to the north by the Liwale District, to the south by Nachingwea District and to the west by Morogoro Region. Its geographical coordinates are 10° 4' S and 38° 50' E. Namungo mines, a mining area with deposits of gold and green gemstone (tsavorite) in the hills of Namungo located in Ruangwa District of Lindi region. The mine is located 20 km away from Ruangwa town. In this study, samples were collected from farms at Chibula, Chingumbwa and Ligunje villages which are located in the area around the Namungo mine as shown in Fig. 4.



Fig. 4. A map showing the location of Ruangwa District and the study areas (<http://www.lindi.tz.go>)

A total of twenty soil samples were collected from maize fields of Chibula, Chingumbwa, Ligonje, and Mbekenyela villages. At each sampling site, a composite of five soil samples was collected separately by a random selection. Samples were collected from the centre of the fields to avoid the edge effect [22]. Twenty maize samples were collected from the corresponding soil sampling site of the maize field for computing correlations between heavy metal concentrations of soil and maize. All soil along with maize samples were kept in labelled clean polyethene bags and brought to the laboratory for preparation and analyses.

The samples were oven dried at 140°C for 24 hours to remove moisture contents to the acceptable levels. The dried samples were sieved using a 2mm mesh to remove stones. The samples were then ground into fine powder to homogenise them. Using digital balance 4.0g of the powder was measured and mixed with 0.9g of cellulose binder to form stable pellets for

analysis [22]. This process utilises the fact that the intensity of characteristic x-ray is related to elemental concentrations in the sample.

## 2.2 EDXRF, PRECISION, ACCURACY AND DETECTION LIMITS

This study used the Spectru<sup>m</sup> X-epos EDXRF system of the Tanzania Atomic Energy Commission (TAEC) The machine is operated at the voltage range between 25 to 50 kV with the current range of 0.5 to 1mA. In this model, x-rays are generated by the x-ray tube and excitation of elements in the sample is carried out using three different secondary targets depending on the atomic number of the element. Appropriate quality assurance procedures were carried out to ensure the reliability of the results. Standard reference materials (SRM) obtained from the International Atomic Energy Agency (IAEA), including Montanall soil (2711a) and Rice flour (1568a) were used for the validation of the analytical procedure.

**Table 1. Experimental values and reference values of IAEA 1568a standard Rice flour in mg/kg**

Z	Element	Experimental values	Reference values
12	Magnesium	560.3	560
13	Aluminum	4.1	4.4
33	Arsenic	0.27	0.29
48	Cadmium	0.021	0.022
29	Copper	2.3	2.4
26	Iron	7.41	7.4
80	Mercury	0.0057	0.0058
35	Bromine	8.4	8
82	Lead	0.01	<0.01
92	Uranium	0.0002	0.0003
23	Vanadium	0.005	0.007
30	Zinc	19.35	19.4
34	Selenium	0.4	0.38

**Table 2. Experimental values and reference values of IAEA 2711a soil Montana mg/kg**

Z	Element	Experimental values	Reference values
12	Magnesium	10697.2	10700
13	Aluminum	67169.6	67200
33	Arsenic	104.9	107
48	Cadmium	53.7	54.1
29	Copper	139.4	140
26	Iron	28403.0	28400
25	Manganese	674.2	675
80	Mercury	7.7	7.4
82	Lead	1398.9	1400
92	Uranium	3.0	3.1
23	Vanadium	80.0	80.7
30	Zinc	416.4	414
34	Selenium	1.8	2.0



**Table 3. The minimum detection limits in maize analysed by EDXRF system in mg/kg**

Z	Element	MDL	Z	Element	MDL
20	Calcium	10	92	Uranium	0.6
12	Magnesium	47	23	Vanadium	1.4
19	Potassium	10	34	Selenium	0.1
27	Cobalt	1.1	82	Lead	0.5
13	Aluminum	13.6	80	Mercury	0.4
33	Arsenic	0.2	25	Manganese	2.4
48	Cadmium	3.6	26	Iron	2
29	Copper	0.5	30	Zinc	1

**Table 4. The minimum detection limits in soil analysed by EDXRF system in mg/kg**

Z	Element	MDL	Z	Element	MDL
12	Magnesium	271.4	48	Cadmium	5
13	Aluminum	20	19	Potassium	10
47	Silver	3.4	20	Calcium	10
23	Vanadium	28.9	24	Chromium	17.5
25	Manganese	5	26	Iron	5
27	Cobalt	23.4	28	Nickel	2.6
29	Copper	1	30	Zinc	1
92	Uranium	3.4	80	Mercury	1.8
33	Arsenic	8.1	82	Lead	2
34	Selenium	0.7	90	Thorium	3.1

The results of measurements of SRM are summarised in Tables 1 and 2 respectively. Blank and drift standards were run after twenty determinations to maintain instrument calibration. The coefficient of variation of replicate analyses was determined for the measurements to calculate analytical precision [23].

The Detection limit is the minimum concentration of a particular element that can be determined by the EDXRF instrument. It is the capability of the analysing instrument to distinguish the peak intensity ( $I_p$ ) from the fluctuations of the background intensity ( $I_b$ ) due to counting statistics or background noise. In this study, MDL was determined by the X-lab Pro™ software using equation 13 [17, 18, and 19] and shown in Tables 3 and 4.

$$MDL = \frac{3xC_i}{I_p - I_b} \sqrt{\frac{I_b}{T_b}} \quad (13)$$

Where:

$T_b$  = background time used to measure the background intensity,

$C_i$  = is the concentration of the analysed concentration,

$I_p$  = intensity of peak and  $I_b$  = Intensity of background.

### 3. RESULTS AND DISCUSSION

#### 3.1 Elemental Concentrations in Maize Samples

Table 5 presents the mean concentration results of both essential and toxic elements detected in maize samples collected from Ruangwa district around Namungo gold mine area.

The differences in mean concentrations of elements in maize from sampled villages with those obtained in the control area are shown in Figs. 5(a) to 5(c)

The results show that XRF is a relatively simple, easy and powerful method for analysing solid samples. The technique is particularly well suited to the determination of major elements of all sample thicknesses. In addition, X-Ray fluorescence has the following advantages [24,25,26,27]:

- Large penetration depth which gives more surface sensitivity
- Elementary selectivity
- Relatively simple, cheap and quick analyses
- Detection limits. XRF is a reliable method for trace element analyses at the ppm level although the technique is relatively

- insensitive to the rare earth elements (e.g. La, Ce etc.).
- It is non-destructive techniques uses "Dry" method and therefore requires minimal sample preparation (for trace element analysis).
- Large dynamic range.
- Accurate analyses of a range of elements.
- Few consumables.
- Archaeometrists have applied XRF to solve their ancient mysteries.
- Forensic scientists utilise XRF spectrometry to match samples associated with suspects (i.e. dirt or sand on clothing or shoes) to samples from crime scenes. As for other applications, here XRF can help elucidate an elemental fingerprint, without the need to analyse the evidence destructively.
- Non-destructive: The X-radiation has absolutely no lasting influence on the material; it fully retains its quality.
- Fast: The XRF method needs very simple sample preparation and short measurement times range in the seconds, rarely longer than one minute.
- Clean: No chemicals are used.
- Safe: Method without the use of environmentally hazardous chemicals, X-radiation poses no risk for the operator due to the protective instrument design.

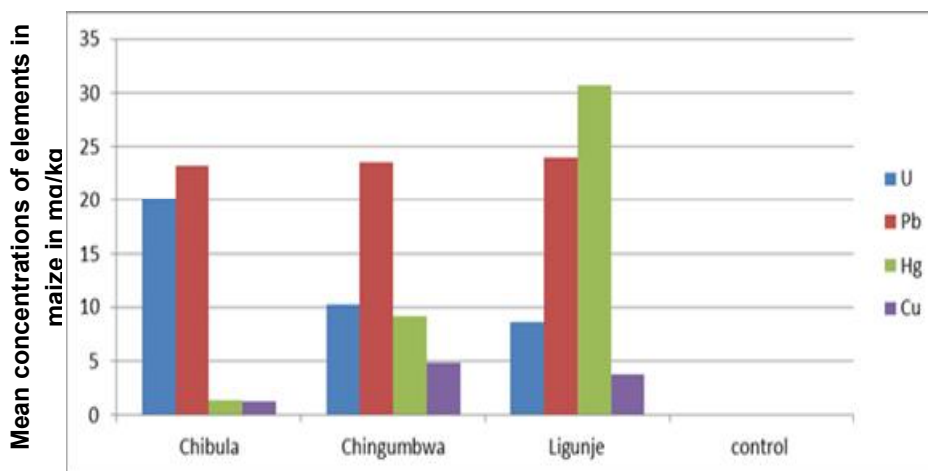
- Universally applicable: The XRF method is suitable for material analysis and counting thickness measurement in a very broad range of applications.

Certainly, the advantages stated together with purchasing cost make XRF favourable compared to Particle Induced X-Ray Emission and Neutron Activation Analysis which both need very expensive machines,

### 3.2 Comparison of Elemental Concentration values in the Maize from Ruangwa District with Values Reported in the Literature

The concentration levels of elements determined in maize from areas around Namungo gold mine in this study were compared with other concentration levels reported in the literature.

Generally, there were previous reports that showed higher or lower concentration levels than values obtained in this study. A study conducted around Dabaoshan mine in China reported high levels of Pb (1.44 mg/Kg) and Cd (0.82 mg/Kg) in rice [34]. And this is respectively lower by 16.7 and 23.1 times than the maximum concentration value of 24.0mg/kg recorded in this study. The study conducted around Gwari Artisanal goldmine Kaduna state-Nigeria reported mean concentrations in maize to be 11.61 mg/kg and 102.34 mg/kg for Pb and Zn respectively [35].

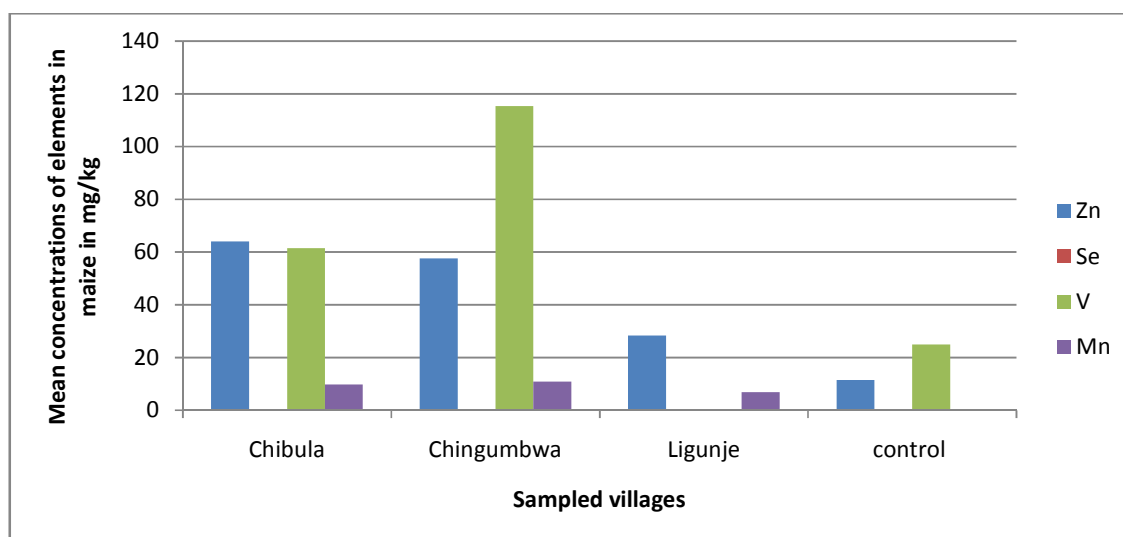


Three sampled villages

Fig. 5 (a) The differences in mean concentrations of elements in maize from sampled villages with those obtained in the control area are shown with Chibula, Chingumbwa and Ligonje

**Table 5. The mean concentrations (mg/kg) of toxic elements obtained in the maize samples from Ruangwa district; Arithmetic mean (A. Mean ± SEM)**

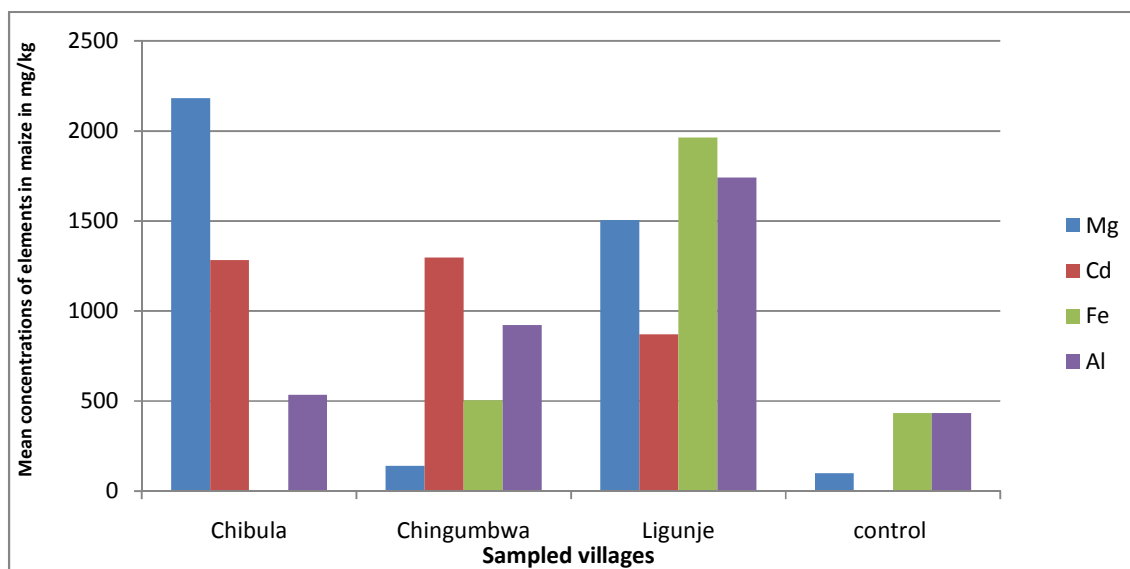
Element	Chibula (Station 1)	Chingumbwa (Station 2)	Ligunje (Station 3)	Mbekenyela (control area)
Mg	2181.4±30.3	140.1±10.5	1505.4±6.6	100.9±5.4
Pb	23.2±0.2	23.5±0.6	24.0±0.0	BDL
Hg	1.3±0.3	9.2±1.7	30.7±3.8	BDL
Cu	1.2±0.2	4.9±0.9	3.8±0.5	BDL
Zn	64.0±0.9	57.6±1.6	28.3±0.8	11.5±0.3
Cd	1283.9±90.4	1296.5±843.9	870.3±187.4	BDL
V	61.5±4.7	115.3±3.8	39.8±1.1	24.9±4.7
Mn	9.8±1.5	10.9±0.3	6.9±0.9	BDL
U	20.1±0.5	10.2±0.2	8.6±0.4	BDL
Se	0.1±0.0	0.3±0.0	BDL	BDL
Fe	402.6±3.9	505.7±5.5	1964.8±55.7	433.9±17.5
Al	535.3±7.7	921.4±36.3	1741.7±67.3	433.9±17.5



**Fig. 5 (b). The differences in mean concentrations of elements in maize from sampled villages with those obtained in the control area are shown with Chibula, Chingumbwa and Ligunje**

**Table 6. Comparison of mean concentrations (mg/kg) of toxic metals in the maize with Maximum Tolerable Limits (MTLs) set by International Organisations (FAO/WHO)**

Element	Chibula (Station 1)	Chingumbwa (Station 2)	Ligunje (Station 3)	MTLs	References
Fe	402.6	505.7	1964.8	425	[28]
Cu	1.2	4.9	3.8	2	[29]
Zn	64.0	57.6	28.3	60	[28]
Cd	1283.9	1296.5	870.3	0.5	[29]
Hg	1.3	9.2	30.7	0.2	[30]
Pb	23.2	23.5	24.0	2	[29]
U	3837.6	5969.6	2771.6	0.0005	[31]
Mn	9.8	10.9	6.9	100	[32]
V	858.8	525.5	192.2	0.0005	[31]
Al	535.3	921.4	1741.7	100	[33]



**Fig. 5 (c). The differences in mean concentrations of elements in maize from sampled villages with those obtained in the control area are shown with Chibula, Chingumbwa and Ligonje**

This is about 2.1 times lower than the maximum level of Pb (24.0mg/kg) obtained in this work. It is about 42 times higher than the maximum level of Zn (64.0mg/kg) reported in this work. However, similar findings were obtained from different studies conducted in Tanzania for instance, Machiwa [36] reported mean concentrations of Cu and Zn in rice collected from four different locations of Mwanza, Geita, Bunda and Magu to be respectively higher by 3.7 and 21.7 times than the value reported in this study, and the levels were associated with mining activities in those areas. Tungaraza et al. [37] reported the mean level of Hg (0.026mg/kg) in rice grown in Mugusu mining area in Tanzania which is below the MTLs of 0.2 mg/kg. This is about 40 times higher than the minimum level of 1.3mg/kg and is about 1183 times higher than the maximum level of 30.7mg/kg as reported in this study. The soil-plant transfer coefficient, also known as enrichment factor, enumerates comparative variations in heavy metals' bioavailability to plants. The coefficient depends on both soil and plant properties. The accrual of metals from soil to plant depends on factors like plant species absorption capacity, soil type, and a metal chemical form [3]. The levels of heavy metals for Fe, Zn, Pb, and Cu have high concentrations of Pb and Fe was higher than the established standards, while those of Zn and Cu were slightly low. The findings indicate that when the irrigating water is polluted by Pb and Fe the possible

sources of heavy metals like Pb and Cu could be road runoff and atmospheric deposition [38,39].

The response of maize (*Zea may L.*) to heavy metals (Cd, Cr, Cu, Pb and Zn) contamination was investigated in field experiments to predict the potential of the plant to extract metal toxicants. Experimental field was amended with increasing loads (2–10 kg/h) of either metal salts and/or metal-cow manure blend (metal/cow manure ratio 1:10). Maize plants were grown and monitored for changes in growth rate. Maize plant tissue metal concentrations were determined using the standard method. Physicochemical parameters of the parent soil (control) determined were 6.20, 8.93%, 6.81 meq/100-g, 0.54% and 87.50 mg/kg for soil pH, soil organic matter (OM); cation exchange capacity (CEC), total nitrogen and phosphorus respectively. Soil particle size analysis showed the predominance of the sand component (74.20%), followed by clay (23.70%) and the silt (2.10%). Pseudo total metal content (mg/kg) was 4.35, 3.00, 6.25, 0.50 and 14.25 for Cd, Cr, Cu, Pb and Zn respectively. The low levels of these metals in the parent soil suggested the need for spiking to assess and predict plant tissue metal concentration in the contaminated soil. The plants were generally greenish with linear growth attributes proportional to metal doses, suggesting some level of forbearance. The range of maize tissue metal concentration for Cd, Cr, Cu, Pb and Zn were 3.50 – 42.80,

3.40 – 21.80, 7.80 – 48.10, 2.50 – 30.40 and 10.20 – 44.75 respectively. Cu was most extracted from the plant while Cr was the least. Predictive models for plant tissue metal concentration were derived from soil pH, OM, plant available and pseudo-total metal with a close range of values. The models predicted the metal concentration in maize plant very well, and the relationship is significant ( $0.01 \leq p \leq 0.05$ ). However, extrapolation of the present experimental results and its broader application to other plants, still need further investigation [40].

### 3.3 Elemental Concentrations in Soil Samples

Table 7 presents the mean concentration results of both essential and toxic elements recorded in soil samples collected from Ruangwa district around Namungo gold mine area.

### 3.4 Comparison of Elemental Concentrations in the Soil from Ruangwa District with Values Reported in the Literature

The concentrations of elements obtained in soil from areas around Namungo gold mine in this study were compared with other concentrations reported in the literature. The observation made in China by a study conducted around Dabaoshan mine in China reported high concentrations of Cu (276 mg/kg - 703 mg/kg), Zn (181mg/kg-1100 mg/kg) and Cd (3.0 mg/kg - 5.5 mg/kg) in paddy soils of China [34]. The

study conducted around Gwari Artisanal goldmine Kaduna state-Nigeria, showed that the mean concentrations of Lead (Pb), and Zinc (Zn) in soil were, 20.83 mg/kg and 61.82 mg/kg respectively. Additionally, the study showed that the concentration of Zn in soil is higher across all sampling locations while for Pb and Zn the concentrations were higher in some locations [35]. The study conducted at the Obuasi gold mine in Ghana using atomic absorption spectrometry reported the mean concentrations of As, Cu, Pb and Zn in soils around the active tailings dams to be 581mg/kg, 39.64mg/kg, 24.22mg/kg and 72.64mg/kg respectively [41]. The study conducted in Tanzania by Machiwa [36] in the Lake Victoria basin reported mean concentrations of Cd(8.70 mg/kg), Hg(19.99 mg/kg), Pb(19.34 mg/kg), Zn (65.46 mg/kg), and Cu (14.58 mg/kg) in the paddy soils collected from 18 sites within the basin. The Lake Victoria was chosen for the heavy metals investigation based on increasing mining activities.

The Study was done by Kihampa and Asante [42] in Singida Region of Tanzania in the vicinity of small-scale Goldmine at London and Sambaru revealed heavy metal concentrations in soil ranging from 1.7 to 53.8 mg/kg, 8.7 to 22.24 mg/kg, 0.42 to 2.6 mg/kg and 3.19 to 24.42 mg/kg for Mercury (Hg), Lead (Pb), Zinc (Zn) and Copper (Cu) respectively. However, the Tanzanian standard recommended limits for some metals in soil set by Tanzania Bureau of Standard (TBS) of Cr, Cu, Zn, Pb, Ni, As and Cd to be 100 mg/kg, 200 mg/kg, 150 mg/kg, 200 mg/kg, 100 mg/kg, 1 mg/kg, and 1 mg/kg respectively [43].

**Table 7. The mean concentrations (mg/kg) of essential and toxic elements obtained in soils from Ruangwa district; Arithmetic mean (A. Mean ±SEM)**

Element	Chibula (Station 1)	Chingumbwa (Station 2)	Ligunje (Station 3)	Mbekenyela (control area)
Mg	23582.4±96.9	7343.8±100.7	11340.7±35.3	1776.1±49.7
V	858.8±58.7	525.5±90.5	192.2±83.8	141.1±29.3
Ni	82.5±0.6	190.6±1.8	32.3±0.8	7.1±0.8
Cu	49.6±1.4	169.2±1.2	90.6±1.6	21.5±0.9
Zn	71.9±0.4	134.6±0.4	57.1±0.3	37.5±0.1
As	369.1±2.8	830.4±0.3	20.9±0.8	BDL
Se	5.5±0.4	8.2±0.1	0.6±0.0	BDL
Fe	43323.3±62.6	70610.3±89.8	39437.5±68.0	338.3±18.3
Hg	19.5±0.3	7.5±0.3	3.4±0.1	BDL
Pb	19.1±0.4	20.3±0.2	3.6±0.6	BDL
Al	57788.2±198.2	63466.9±56.7	92661.4±428.1	5558.1±79.7
U	3837.6±146.1	5969.6±210.7	2771.6±90.7	BDL

It has also been reported that the level of Hg (0.26 mg/kg) in agricultural soils in Mugusu gold mining in Geita district of Tanzania is high due to the mining activities taking place near the agricultural soils [37]. Heavy metals in soil should not exceed the maximum allowable limits which are 0.1 mg/kg, 0.2 mg/kg, 1.0 mg/kg, 0.1 mg/kg, 1.0 mg/kg, 2.0 mg/kg, 5.0 mg/kg, 0.1 mg/kg, 5.0 mg/kg, 0.005 mg/kg and 5.0 mg/kg for Cd, As, Cr V, Co, Cu, Fe, Pb, Mn, Hg and Zn respectively [35]. The daily tolerable exposure to which a person is expected to have without any significant risk of harmful effects during a lifespan. for Pb, Zn, Cu, and Fe is 0.004 mg/kg/day, 0.3 mg/kg/day, 0.04 mg/kg/day, and 0.7 mg/kg/day, respectively [44]. The high observed Fe levels could be attributed to the nature of the parental material of soils in the study site. Also, Fe and Zn could be emanating from phosphate fertilisers, wastewater disposal, organic wastes dumping, use of sludge, and burning of the fossil fuels in the area [38], while Pb and Cu are stemming from nearby traffic activities and use of agrochemicals, respectively [39].

### 3.5 Linear Correlation Analysis

Linear correlation analysis is a useful tool in identifying common source of heavy metals. Elements with a common source vary in the same manner and as a result, have a high correlation coefficient.

From the Table 8 above it is evident that, the correlation of elemental concentrations may be categorised depending on the correlation coefficient value r: high correlation (r= 0.5-1.0; P=0.05), moderate correlation (r=0.3-0.5; P=0.05) and low correlation (r=0.1-0.3).by [20, 21]. The elements with high correlation include: U-Hg, U-Pb, Ni-V, Cu-V, Cu-Ni, As-V, As-Ni and As-Cu.

This observation might indicate a common source of these elements. In the study conducted

by Youcef and El-Gaward [45] on the Accumulation and Translocation of Heavy Metals in Eggplant grown in Contaminated soil reveals sewage sludge caused significance accumulation of metals in the fruits. A pot experiment was conducted to investigate the effects of the rock phosphate application on accumulation and translocation of heavy metals from the soil to the roots, shoots and fruits of eggplant which also applicable to maize grown in a sewage sludge-amended soil contaminated with Cd, Pb and Ni were 30, 30 and 60 mgkg<sup>-1</sup>, respectively. The obtained results demonstrated that the sewage sludge application caused a significant accumulation of metals in the fruits of eggplant and maize. The concentrations of these metals in the fruits were in the order of Pb > Cd > Ni. The fruits of eggplant were not safe for human consumption, because the levels of heavy metals exceeded the permissible limits. These, heavy metals in different parts of eggplant can be ranked in the order of roots > shoots > fruits, were (mgkg<sup>-1</sup>). The soil-plant transfer factor (TF) showed that the order of uptake of metals by eggplant was: Cd > Ni > Pb. This calls for concern especially in the case of Pb and Cd which are highly toxic and of no known biological use. Therefore, Eggplant should not be cultivated in the farms and fields which use sewage sludge contaminated with heavy metals as an amendment [45].

One of the most significant biosphere contamination problems worldwide is derived from heavy metals. Heavy metals can be highly reactive and toxic according to their oxidation levels. Their toxic effects are associated with the increased production of reactive oxygen species (ROS) and cellular damage induced in plants. The study focused on the effects of nickel (Ni), copper (Cu), and zinc (Zn) applied to the soil on the antioxidant response and allergen production in the aromatic plant basil (*Ocimum basilicum* L.) following a combined physiological, biochemical and analytical approach [46].

**Table 8. Correlation coefficient of concentration values of different elements in soils from sampled villages in Ruangwa District. The correlation is statistically significant at P≤ 0.05**

	V	Ni	Cu	As	Hg	Pb	U
V	1						
Ni	0.99	1					
Cu	0.81	0.79	1				
As	0.98	0.99	0.70	1			
Hg	0.01	0.03	-0.58	0.16	1		
Pb	0.76	0.78	0.24	0.85	0.64	1	
U	-0.13	-0.10	-0.68	0.02	0.99	0.53	1

The highest physiological and cellular damage in basil plants was caused by Cu and Zn. Increasing concentrations of Cu resulted in a further increase in cellular damage and nitro-oxidative stress, correlating with an induction in the activity of reactive oxygen and nitrogen species metabolism enzymes. Treatment with Cu led to increased concentration of the allergenic protein profiling while increasing concentrations of Cu and Zn led to a decrease in the concentration of total proteins (likely due to proteolysis) and antioxidant capacity. Interestingly, severe Cu stress resulted in the accumulation of specific proteins related to transpiration and photosynthetic processes [46]. In some cases, heavy metal contamination in Nigeria soils is reported. The intake of toxic heavy metals in edible food crops has been a potential threat to human and animal health. Hence, a study on the soil to food crop relation regarding heavy metals accumulation is expedient a total of 640 edible food crop samples (pumpkin 64, passion fruit 96, maize grain 96, sugarcane stem 64 and tubers of cassava 320) were collected. Results: The results revealed that the levels of Cd ranged from 0.07 to 9.80 mg/kg, Co 0.05–38.1 mg/kg, Cu 0.33– 16.9 mg/kg, Ni 3.81–93.1 mg/kg, Pb 4.45–47.7 mg/kg and Zn 5.02–81.4 mg/kg in topsoils. There was no significant difference ( $P > 0.05$ ) in the levels of these heavy metals in sub-soils and among farms. Except in pumpkin, the nickel concentration in all the investigated food crops exceeded regulatory limits set by the World Health Organization and the Food and Agriculture Organization. Similarly, the concentration of Cd and Co in pumpkin exceeded regulatory limits. Soil-plant transfer factors indicated low accumulation into crops except for Co in maize and Ni in cassava. Conclusion: Therefore, the soil may require mild remediation action to minimise possible sources of Co and Ni contamination such as irrigation and fertiliser application practices. The concentration of Cd in food crops could be of health concern if such crops are ingested [47]. The results of did not correlate Pb-V, Pb-Ni, Pb-As and Pb-Hg.

#### 4. CONCLUSION

This study aimed to investigate the heavy metal concentrations in soils and food crops (mainly maize) and estimate the potential health risks of heavy metals to humans via consumption of polluted food crops grown around Namungo gold mine area in Ruangwa district. Samples of both maize and soil were collected from three villages

of Chibula, Chingumbwa and Ligonje followed by preparation for analysis of heavy metal concentrations using EDXRF spectroscopy.

The capability of EDXRF shows that the technique is easy and powerful for analysing solid samples like soil and other minerals as well as any food crops like corn. The technique is particularly well suited to the determination of major as well as minor elemental concentrations of all sample thicknesses. It has considerable penetration depth which gives more surface sensitivity, elementary selectivity with reliable detection limits. It is a non-destructive, accurate technique for a range of elemental analyses. The XRF method needs very simple sample preparation and short measurement times range in the seconds, rarely longer than one minute. Certainly, the advantages stated together with purchasing cost make XRF favourable compared to Particle Induced X-Ray Emission and Neutron Activation Analysis which both need very expensive machines.

The detected levels found were above the Maximum Tolerable Limits (MTLs) set by International Organisations (FAO/WHO) as shown in Table 5 and 6. The results showed that Maize were accumulated with mean range concentrations of; 870.3-1296.5 mg/kg for Cd, 23.2-24.0 mg/kg for Pb, 1.3-30.7 mg/kg for Hg, 1.2-4.9 mg/kg for Cu, 39.8-115.3 mg/kg for V, 402.6-1964.8 mg/kg for Fe, and 8.6-20.1 mg/kg for U respectively. On the other hand, mean range concentrations of metal elements detected in the soil were 3.6-20.3 mg/kg for Pb, 2771.6-5969.6 mg/kg for U, 3.4-19.5 mg/kg for Hg, 0.6-8.2 mg/kg for Se, 20.9-830.4 mg/kg for As, , 49.6-169.2 mg/kg for Cu and 192.2-858.8 mg/kg for V, .

To investigate possible sources of these elements the correlation matrix was performed. Results from correlation matrix appear that most elements attributed to mining activities taking place at Namungo goldmine. Therefore the consumption of maize products from Ruangwa is on the toxic elements side which is detrimental to the health caused by mining operations and steps need to be taken to reverse the situation.

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### COMPETING INTERESTS

The authors have declared no competing interests exist in this paper.

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