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A Survey on Heavy Metal (Metalloids) Concentration in Selected Acidic and Volcanic Soils in Tanzania

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Authors' contributions

This study was carried in full collaboration between all authors. Authors PAN, KNN and MWL designed the protocol. Author MWL performed the Lab-work. Authors PAN, and MWL prepared the first draft. Authors KNN and JNI proofread and managed preparation of the final manuscript. All authors read and approved the final manuscript.

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ABSTRACT

A total of 12 soil samples from four different sites across the United Republic of Tanzania (URT) were collected and analysed for heavy metals (metalloids) (V, Cr, Ni, Cu, Zn, As, Cd, Hg and Pb) concentration. The technique used was Energy Dispersive X-Ray Fluorescence (EDXRF). Results show that the concentrations of 77.8% of the analysed heavy metals (V, Cr, Ni, Cu, Zn, Pb and Hg) were above the phytotoxicity limits while the rest, 22.3%, (As and Cd) were below the limits. The fact that 77.8% of the analysed heavy metals have concentrations above phytotoxicity limits raises a genuine concern on the favourability of these soils for agricultural purposes.

Keywords: Heavy metals; toxic; acidic; volcanic; x-ray; phototoxic.

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1. INTRODUCTION

Heavy metals (metalloids) are naturally available in the Earth's crust [1]. In recent years, there has been a great public concern on the concentrations of heavy metals (metalloids) in agricultural soils of the world with respect to their fate in terms of bioaccumulation and biodegradability [2-4]. To date, heavy metal (metalloids) pollution in agricultural soils has become one of the most serious environmental problems of the world [5]. Be it natural or anthropogenic, heavy metals (metalloids) are always a complex problem in the environment [6].

Some of the environmental variables that affect the accumulation of heavy metals (metalloids) in soils of the world include composition of parent materials, soil properties, and human activities such as industrial processes, traffic, farming and irrigation [5]. Higher concentrations of heavy metals (metalloids) beyond the allowable limits (i.e. above phytotoxic levels) [7,8,9], are dangerous to plant species. Excessive accumulation of toxic levels of heavy metals (metalloids) beyond established phytotoxic levels may cause growth abnormalities such as alterations in germination process, leaf chlorosis or death of the whole plant [3,7,10,11].

The presence of heavy metals (metalloids) in agricultural soils can cause a significant decrease in crops yield and quality of the crops produced. Once in soil, these metals may persist for a very long time due to their fairly immobile nature [12]. Furthermore, these toxic metals can endanger human health through the food chain and may further cause deterioration of air and water quality [2].

Recent studies conducted in China, South Africa, Turkey and Romania have shown that heavy metal (metalloids) content in agricultural soils provided some fundamental information for environmental and agricultural planning [3,4,6,10,13,14]. However, very little information is available on heavy metal (metalloids) content in agricultural soils of Tanzania. The aim of this study was to establish heavy metal content (V, Cr, Ni, Cu, Zn, As, Cd, Hg and Pb) in selected acidic and volcanic soils in Eastern and Southern Highlands of Tanzania.

1. MATERIALS AND METHODS

1.1 Description of the Study Sites

Soils used in this study were collected from four (4) sites; Magadu, Mafiga, Mlingano and Sasanda (Fig. 1). The Magadu site (S 06.85°, E 037.64°) is located in Morogoro Region at an elevation of approximately 568 m above mean sea level. The site is in the agro-ecological zone E4 [15], which is characterized by semi-humid tropical lowlands, mainly plains with dominantly friable clays of low to moderate fertility. The Magadu soil was classified as Chromic Acrisol [16]. The soil in this site is highly acidic. Major food crops grown in this site are maize and beans.

The Mafiga site (S 06.80°, E 037.25°) is located in Morogoro Region at an elevation of approximately 540 m above mean sea level. The site is in the agro-ecological zone E4 [15], which is characterized by semi-humid tropical lowlands, mainly plains with dominantly friable clays of low to moderate fertility. The Magadu soil was classified as Umbric Ferralsol [17]. The soil in this site is strongly acidic. Major food crops grown in this site are maize and beans.



Fig. 1. Map of Tanzania showing three regions where the four study sites are located.
A; Magadu, B; Mafiga, C; Mlingano, and D; Sasanda

The Mlingano site (S 05.11°, E 038.87°) is located in Tanga Region at 160 m a.m.s.l. The site is in the agro-ecological zone E6 [15], which is characterized by semi-humid tropical lowlands, mainly plains with friable clays of low to moderate fertility. Soil in this site was acidic and its class is Rhodic Ferralsol [16]. Major food crop grown in this site are cassava and beans.

The Sasanda site (S 09.16°, E 033.03°) is located in Mbeya Region at 1650 m a.m.s.l. The site is in the agro-ecological zone H5 [15], which is characterized by volcanic highlands with plateau and strongly dissected landforms covered by volcanic ash. Soil in this site was acidic and highly volcanic, and was classified as Umbric Andosol [16]. The major food crop grown in this site is maize. Some chemical parameters of the soils in this study are presented in Table 1.

Table 1. Some chemical parameters of soils collected from the four study sites

Study site	Soil parameter			
	pH _{H2O}	Organic carbon (%)	Cation exchange capacity (cmol _c kg ⁻¹)	P _{Olsen}
Magadu	4.9	1.2	11.6	31
Mafiga	5.0	1.3	15.2	2.1
Mlingano	5.3	1.2	7.3	2
Sasanda	5.5	3.4	10.1	1

Source: [16,17,18]

1.2 Soil Sampling Procedures

Sampling was carried out between April and May, 2013. A composite sample made up of 9-12 sub-samples of topsoil (to a depth of 20 cm) was collected from each selected site, and a representative sample of about one kilogram of soil was taken. The soils collected were air dried, sieved through a 2 mm-sieve and packed for further analysis.

1.3 Soil Samples Preparation

A dry weight of 12 grams of soil sample with 2.7 grams of cellulose binder were put into a bowl together with four spherical balls, each with 3 mm radius and fixed to a pulveriser machine which was further ground and homogenized. The machine was set at a speed of 150 revolutions per minute (rpm) for 15 minutes. The analyte was placed into a polished, lapped thrust piece with a smooth surface and fixed into hydraulic press machine. A pellet in tablet form was obtained by applying an average pressure of 12.5 tons. Each pellet was labeled and subsequently placed in a transparent plastic sample holder ready for measurements in Energy Dispersive X-Ray Fluorescence (EDXRF) Machine.

1.4 Analysis of Samples

All soil samples were analysed at the Tanzania Atomic Energy Commission (TAEC) using EDXRF as described by Schramm and Heckel [19]. The EDXRF used was Spectro Xepos, model; Xepos with serial No.4R0138 operated by x-lab Pro TM software [20]. The equipment has an inbuilt Turboquant (Tq 9232) algorithm for matrix effect correction. The soil metal concentration data were statistically analysed using the STATISTICA software package, version 8.

The excitation of elements in the sample is carried out using three secondary targets. Light elements from Na-V are excited using high oriented pure graphite (HOPG) target (intense monochromatic polarized X-Rays). The Elements from Cr-Zr and Pr-U are excited using Mo secondary target (intense monochromatic non-polarized X-Rays). The high energy elements Y-Ce are excited using Barkla target (Al₂O₃) (intense polychromatic polarized X-Rays). The standard secondary targets and corresponding element that are excited are summarized in Table 2 below.

Apart from the calibrations initially done by the manufacturer, routine Multichannel Analyzer (MCA) recalibration is performed once a week using recommended reference materials with known elemental concentration (i.e. IAEA-Soil-7 and Montana-Soil-II).

Table 2. Targets and corresponding elements for excitation using Turboquant TM methods

Target	Type of target	Excited elements
Mo	Secondary	Cr-Zr(K), Pr-U(L)
Al ₂ O ₃	Barkla	Y – Ce
HOPG	Bragg	Na-V

Source: [19,20]

A typical x-ray spectrum used for determination of elemental composition from a sample is presented in Fig. 2. From this spectrum two quantities are obtained. The first is the concentration (C_i) of element which is obtained from area under a given peak. The second is the minimum detection limit (MDL) which specifies the minimum concentration that can be determined by a given experimental technique. In this study, concentration values below MDL are taken as below minimum detection limit and are termed BDL (Below Detection Limit). Minimum detection limits for the metals analysed in this study are presented in Table 3.

Table 3. Minimum detection limits

N	Elements		MDL
	Symbol	Name	LOD
23	V	Vanadium	31.95
24	Cr	Chromium	16.63
28	Ni	Nickel	2.33
29	Cu	Copper	1.43
30	Zn	Zinc	1.00
33	As	Arsenic	0.91
48	Cd	Cadmium	5.96
80	Hg	Mercury	1.41
82	Pb	Lead	1.28

For spectral line intensity (I_i), given as counts in Fig. 2, the software of the EDXRF corrects it for background and converts the results to concentration (C_i) of the elements present in the sample after making interference (K_i) and matrix effects (M_a) corrections as follows [21].

$$C_i = K_i * I_i * M_a$$

The MDL, as a capability of the analytical techniques to distinguish peak intensity (I_i) from the fluctuations of the background intensity (I_b) due to counting statistics, or the background noise is obtained as described elsewhere [21,22]. Once the sample has been inserted in the EDXRF, in addition to C_i its algorithm also determines MDL based on the following expression.

$$MDL = \frac{3x C_i}{I_i - I_b} \sqrt{\frac{I_b}{T_b}}$$

T_b is the time used to measure the background intensity.

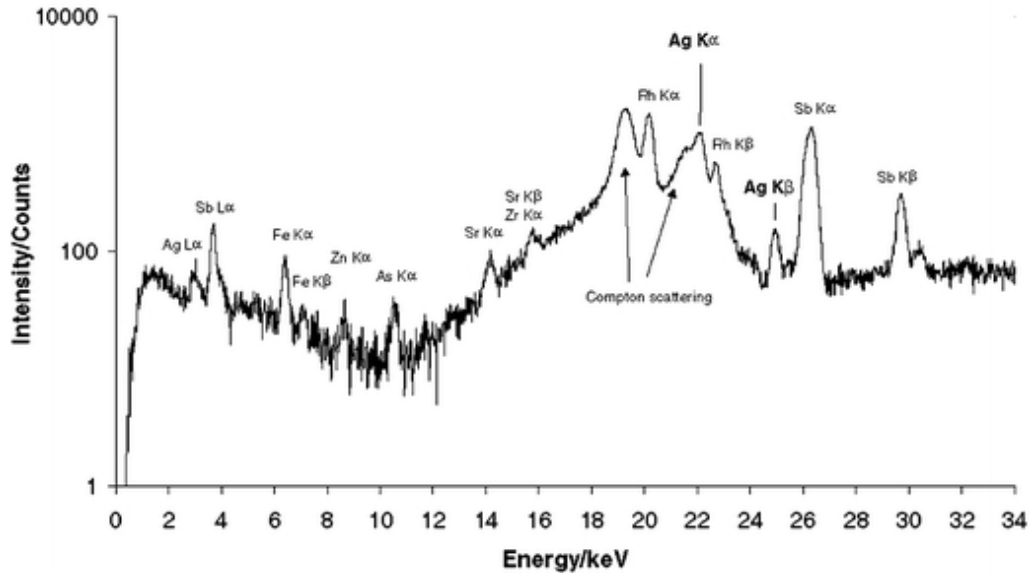


Fig. 2. Example of K α and K β characteristic lines in EDXRF analysis

2. RESULTS AND DISCUSSION

2.1 Concentration of Heavy Metals in the Soil Samples

Table 4 contains the levels of the nine elements studied. These elements which include V, Cr, Ni, Cu, Zn, As, Cd, Hg and Pb are considered phytotoxic when present in excessive quantities [3-4,6-10,13-14,23-29]. Their concentrations (mean \pm standard error) for each of the four sites are presented in Table 4. This table serves as the baseline for heavy metals (metalloids) in the selected acidic and volcanic soils of the four study sites in URT.

Table 4. Baseline concentrations in $\mu\text{g/g}$ (mean \pm standard error) of heavy metals in soil samples from the selected sites

Name	Soil from				Phytotoxicity Limits*
	Mafiga	Magadu	Mlingano	Sasanda	
Vanadium	193.12 \pm 4.95	93.24 \pm 16.81	182.15 \pm 0.56	38.60 \pm 3.06	2
Chromium	122.84 \pm 7.40	75.33 \pm 1.93	113.48 \pm 1.68	65.74 \pm 2.63	1
Nickel	55.34 \pm 1.85	46.94 \pm 1.38	56.50 \pm 3.27	18.96 \pm 0.24	30
Copper	62.69 \pm 1.94	27.86 \pm 1.87	61.60 \pm 2.71	31.81 \pm 0.95	100
Zinc	66.84 \pm 4.07	51.29 \pm 0.28	67.91 \pm 2.80	89.58 \pm 2.29	50
Arsenic	0.67 \pm 0.19	2.15 \pm 0.17	0.45 \pm 0.25	0.51 \pm 0.26	10
Cadmium	BDL**	0.34 \pm 0.36	BDL**	BDL**	3
Mercury	0.31 \pm 0.06	0.59 \pm 0.35	0.28 \pm 0.09	0.25 \pm 0.09	0.3
Lead	13.34 \pm 0.51	8.77 \pm 0.15	12.56 \pm 0.51	32.95 \pm 0.48	50

* Source: [7,8,9]. ** Below Detection Limit

2.1.1 Chromium (Cr)

The measured concentration of element Chromium was above the phytotoxic ($1\mu\text{g/g}$) limit in soil as recommended [7] in all the four sites; Mafiga ($122.84\pm 7.40\mu\text{g/g}$), Magadu ($75.33\pm 1.93\mu\text{g/g}$), Mlingano ($113.48\pm 1.68\mu\text{g/g}$) and Sasanda ($65.74\pm 2.63\mu\text{g/g}$). Furthermore, the concentrations of Chromium from the four sites were found to be above the average values in soils elsewhere i.e. $64\mu\text{g/g}$ in Canada [29], $53.9\mu\text{g/g}$ in China [28] and $37\mu\text{g/g}$ in U.S.A [24], indicating that these values are beyond the acceptable limits in soil for plant growth. The effects of such elevated levels of Chromium may result in alterations in the germination process, stunted growth, reduced yield and mutagenesis in plants [3].

2.1.2 Nickel (Ni)

Nickel was found to be higher than the phytotoxic limit in soil, which is $30\mu\text{g/g}$ [7] in three sites; Mafiga ($55.34\pm 1.85\mu\text{g/g}$), Magadu ($46.94\pm 1.38\mu\text{g/g}$) and Mlingano ($56.50\pm 3.2\mu\text{g/g}$) and was found to be lower in Sasanda ($18.96\pm 0.24\mu\text{g/g}$). In addition to that, the measured concentrations of Nickel were higher than the average values in soils elsewhere i.e. $0.18\pm 0.03\mu\text{g/g}$ in Nigeria [1] and $13\mu\text{g/g}$ in U.S.A [24], implying that these values are beyond the acceptable limits both in plants and soil. Such elevated levels of Nickel may cause a decrease in leaf area, chlorosis, necrosis and stunting in plants [30].

2.1.3 Copper (Cu)

The concentration of Copper was found to be lower than the phytotoxic limit in soil, which is $100\mu\text{g/g}$ [7,8] in all the four sites; Mafiga ($62.69\pm 1.94\mu\text{g/g}$), Magadu ($27.86\pm 1.87\mu\text{g/g}$), Mlingano ($61.60\pm 2.71\mu\text{g/g}$) and Sasanda ($31.81\pm 0.95\mu\text{g/g}$). However, Copper concentrations in this study were found to be above the average values in soils elsewhere i.e. $20\mu\text{g/g}$ in China [28], $17\mu\text{g/g}$ in U.S.A [24] and $0.89\pm 0.25\mu\text{g/g}$ in Nigeria [1], which is a sign that these values are beyond the allowed limits in soil. In lieu of that, the four study sites seem to have higher levels of Copper in soil that may result in chlorosis in plants, yellow colouration, inhibition of root growth and less branched roots [7].

2.1.4 Zinc (Zn)

The concentration of element Zinc was above the phytotoxic limit in soil, which is $50\mu\text{g/g}$ [16] in all the four sites; Mafiga ($66.84\pm 4.07\mu\text{g/g}$), Magadu ($51.29\pm 0.28\mu\text{g/g}$), Mlingano ($67.91\pm 2.80\mu\text{g/g}$) and Sasanda ($89.58\pm 2.29\mu\text{g/g}$). Furthermore, the concentrations of Chromium from the four sites were found to be above the average values in soils elsewhere i.e. $48\mu\text{g/g}$ in U.S.A [24] and $0.04\pm 0.003\mu\text{g/g}$ in Nigeria [1]. The effects of such elevated levels of Zinc may result in some negative effects to plants i.e. stunting and reduction of leaves elongation [31].

2.1.5 Arsenic (As)

Arsenic was found to be lower than the phytotoxic limit in soil, which is $10\mu\text{g/g}$ as recommended [7],[9] in all the four sites; Mafiga ($0.67\pm 0.19\mu\text{g/g}$), Magadu ($2.15\pm 0.17\mu\text{g/g}$), Mlingano ($0.45\pm 0.25\mu\text{g/g}$) and Sasanda ($0.51\pm 0.26\mu\text{g/g}$). These measured Arsenic concentrations were also lower than the average values in soils elsewhere i.e. $9.21\mu\text{g/g}$ in China [28] and $5.2\mu\text{g/g}$ in U.S.A [24]. Although the measured concentrations of Arsenic in all four sites are lower than the recommended values, a more specific and detailed study is

recommended to be undertaken in all the sites to come up with a clear and sound conclusion on the favourability of the soils for plants growth.

2.1.6 Cadmium (Cd)

Cadmium concentration was below detection limit in three sites; Mafiga, Mlingano and Sasanda, and was detectable in Magadu ($0.34 \pm 0.36 \mu\text{g/g}$). The measured concentration was also below the phytotoxic limit in soil which is $3 \mu\text{g/g}$ as recommended [7,9]. Furthermore, this measured concentration was found to be lower than the average values in soils elsewhere i.e. $1.4 \mu\text{g/g}$ in Canada [10]. Therefore, the measurements made in the four sites reveal that all selected acidic and volcanic soils in Tanzania contain very low concentrations of Cadmium, a scenario that indicates that these soils support plants and microbial life.

2.1.7 Mercury (Hg)

The concentration of Mercury was slightly above the phytotoxic limit in soil, which is $0.3 \mu\text{g/g}$ as recommended [7], in two sites; Mafiga ($0.31 \pm 0.06 \mu\text{g/g}$) and Magadu ($0.59 \pm 0.35 \mu\text{g/g}$). The concentration was found to be lower at Mlingano ($0.28 \pm 0.09 \mu\text{g/g}$) and Sasanda ($0.25 \pm 0.09 \mu\text{g/g}$). However, the measured concentrations of Mercury from all the four sites were higher than the average values in soils elsewhere, i.e. $0.04\text{--}0.15 \mu\text{g/g}$ in China [6], [14], [26]. These levels of Mercury concentration indicate a possibility of slight danger for plants that are found in the two sites whose concentrations are above the limit.

2.1.8 Lead (Pb)

Lead was found to be lower than the phytotoxic limit in soil, which is $50 \mu\text{g/g}$ as recommended [7] in all the four sites; Mafiga ($13.34 \pm 0.51 \mu\text{g/g}$), Magadu ($8.77 \pm 0.15 \mu\text{g/g}$), Mlingano ($12.56 \pm 0.51 \mu\text{g/g}$) and Sasanda ($32.95 \pm 0.48 \mu\text{g/g}$). However, the concentrations of Lead from the four sites were found to be above the average values in soils elsewhere i.e. $1.4 \mu\text{g/g}$ in Canada [10]. The effects of such elevated levels of Lead may result in some negative effects to plants i.e. dark-green leaves as recommended [3].

2.1.9 Vanadium (V)

The concentration of Vanadium was found to be higher than the phytotoxic limit in soil, which is $2 \mu\text{g/g}$ as recommended [7] in all the four sites; Mafiga ($193.12 \pm 4.95 \mu\text{g/g}$), Magadu ($93.24 \pm 16.81 \mu\text{g/g}$), Mlingano ($182.15 \pm 0.56 \mu\text{g/g}$) and Sasanda ($38.60 \pm 3.06 \mu\text{g/g}$). These concentrations show that all the selected acidic and volcanic soils in Tanzania contain higher concentration of Vanadium, which may be potentially toxic to the life of plants grown in the four sites.

3. CONCLUSION

The results showed that 77.8% of the analysed heavy metals (Cr, Ni, Cu, Zn, Hg, Pb and V) in this study contain concentrations above the phytotoxicity limits as recommended [16-18]. This means, all four soil types (Mafiga, Magadu, Mlingano and Sasanda) do possess a health threat to plants' life in terms of heavy metals (metalloids) concentrations once these soils are used for agricultural purposes. The main reason for the elevated concentrations of heavy metals (metalloids) in the four study sites is the extensive use of fertilizer and agricultural pesticides during farming for their food crops. Studies have indicated that application of these agrochemicals were associated with increased concentration of selected

heavy metals in the soil [1-2,4,6,11,14,24-26,32-34]. The fact that, soil from Sasanda contained very low concentration of Nickel compared to other three sites maybe explained in accordance with the type of the parent material existing in Sasanda i.e. volcanic pumice and ash, that is completely different from what exists in the other three sites. The types of minerals present in volcanic ash are dependent on the chemistry of the magma from which it was erupted. In this way, the composition of the parent material at Sasanda seems to contain more of Iron, Magnesium and metals of the like, and therefore, lacks elements of the likes of Arsenic.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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