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ASSESSMENT OF HEAVY METAL AND RADIOACTIVITY LEVELS IN SPINACH (*Spinacia oleracea*) GROWN AT BAHI WETLANDS IN DODOMA REGION

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ABSTRACT

This study reports on the levels of heavy metals and radionuclides in Spinach (Spinacia oleracea) grown in Bahi wetlands in Dodoma Region. The farm soil in Bahi wetland has been reported to contain elevated concentrations of ^{238}U, ^{232}Th and ^{40}K due to the existence of shallow uranium deposit in the area. In this study, spinach (Spinacia oleracea) grown in three zones of Bahi district were analyzed for heavy metals and radioactivity associated with the uranium deposit in the area. The concentrations of elements were determined by Energy Dispersive X-ray Analysis (EDXRF) of Tanzania Atomic Energy Commission, Arusha. The activities of the radionuclides were calculated from their concentration in µg/g. The concentrations of Pb and Cd in all samples were found to be higher than the maximum tolerable limits recommended by Codex 2015. The results show that, the mean activities of ^{232}Th (10.8 Bq/kg) and ^{40}K(686.9 Bq/kg)in the samples are lower than the maximum tolerable limits (1000 Bq/kg) recommended by WHO/FAO, yet higher than their activities in samples of spinach collect from a control area. Hence, regular monitoring of heavy metals and radioactivity level in farm soils and agricultural products is recommended.

Key words: Heavy metals, radioactivity, spinach, Bahi Wetland, EDXRF

INTRODUCTION

Viable uranium deposits have been discovered in Bahi wetlands in Bahi District, Dodoma Region. The uranium deposit is reported to be shallow causing the radioactivity levels in the surface soil to be high (Mbogoro and Mwakipesile 2010). The ongoing exploration process, may also contribute to the contamination of radiation to the soil. A study on assessment of the radiological status of the Bahi wetlands by Kimaro and Mohammed (2015) has indicated high activity levels of ^{226}Ra, ^{232}Th and ^{40}K in soil including the farm soil of Bahi wetlands. For instance, the mean concentration of ^{232}Th obtained from Bahi wetland was found to be higher than its concentrations in 75% of the countries reported in the UNSCEAR (2000).

At the same time a number of studies have shown the occurrence of heavy metals such as Cd, Cr, Pb, Mn, Ni, Zn, Sr, As, Hg and Cu at uranium deposit (Brennan et al. 1992, WHO 1992, Jarup 2003). The studies show strong positive correlations between the amount of radionuclides and heavy metals in the soil (WHO 1992, Jarup 2003). Therefore, it is expected that, an environment with elevated activity concentrations of natural radionuclides is also with elevated concentrations of heavy metals. Although no research on levels of heavy metals has been conducted in Bahi soil, its surface soil might also be contaminated with heavy metals.

Several economic activities are found in Bahi wetland, which include vegetable farming, fishing, salt production and paddy farming (Yanda et al. 2007). All these activities might be routes to internal intake of heavy metals and radionuclides to people of Bahi wetlands. This study has analyzed concentrations of heavy metals (Arsenic (As), Cadmium (Cd), Manganese (Mn), Mercury (Hg) and Lead (Pb) and activity concentrations levels of ^{238}U, ^{232}Th and ^{40}K in Spinach (*Spinaciao leracea*) grown at Bahi wetland. Spinach (*Spinacia oleracea*) was chosen because; leafy vegetables are reported to be good absorber of toxic metals and Spinach is the most affected (Ghiassi-Nejad et al. 2003). Therefore, there is high possibility that Spinach (*Spinacia oleracea*) grown in Bahi wetlands, have elevated concentrations of heavy metals and activity concentrations of natural radioactivity which might be detrimental to human health.

MATERIALS AND METHODS

Sample Collection

The study area (Bahi wetlands) was divided into three zones; northern zone (NZ), central zone (CN) and southern zone (SN)as shown in Fig 1. In the Northern zone, 12 samples of Spinach (*Spinacia oleracea*) were collected from Kisalalo farm 1, Kisalalo Magereza Farm 1 and Bahi Sokoni Farm 1. In the Central zone, 16 samples were collected from Chimendeli Farm 1, Bahi Makulu Farm 1, Bahi Makulu Farm 2 and Chipanga B Farm while in the Southern zone; 8 samples were collected from Chikopero Farm 1 and Chikopero Farm 2. The sample locations are shown in Table 1.

Sample Preparation

In the laboratory at Physics department, the leafy part of Spinach (*Spinacia oleracea*) samples were washed thoroughly with distilled water in order to remove dust and other contamination. The Spinach samples were chopped into small pieces in order to facilitate sun drying at the same rate. The dried samples were ground using mortar and pestle and then sieved to obtain fine powder. The powdered samples were then stored in well labeled polythene bags and taken to the Tanzania Atomic Energy Commission (TAEC) laboratory for more preparation, mass measurement and analysis.

Table 1: The sampling location points for each zone and their geographic coordinates.

SN	Sampling Location	Coordinates	
		Latitudes	Longitudes
NOTHERN ZONE			
1	Kisalalo Farm 1	S5°54′ 9.91″	E35°17′50.57″
2	KisalaloMagereza Farm 1	S55°4′59.69″	E35°17′41.86″
3	Bahi Sokoni Farm	S5°20′11.47″	E35°19′11.28″
CENTRAL ZONE			
1	Chimendeli Farm 1	S6°6′33.59″	E35°22′28.70″
2	Bahi Makulu Farm 1	S6°5′20.40″	E35°21′41.76″
3	Bahi Makulu Farm 2	S6°1′59.41″	E35°20′44.16″
4	Chipanga B Farm	S6°13′28.20″	E35°21′45.72″
SOUTHERN ZONE			
1	Chikopero Farm 1	S6°11′0.24″	E35°24′47.88″
2	Chikopero Farm 2	S6°10′2.28″	E35°25′19.20″

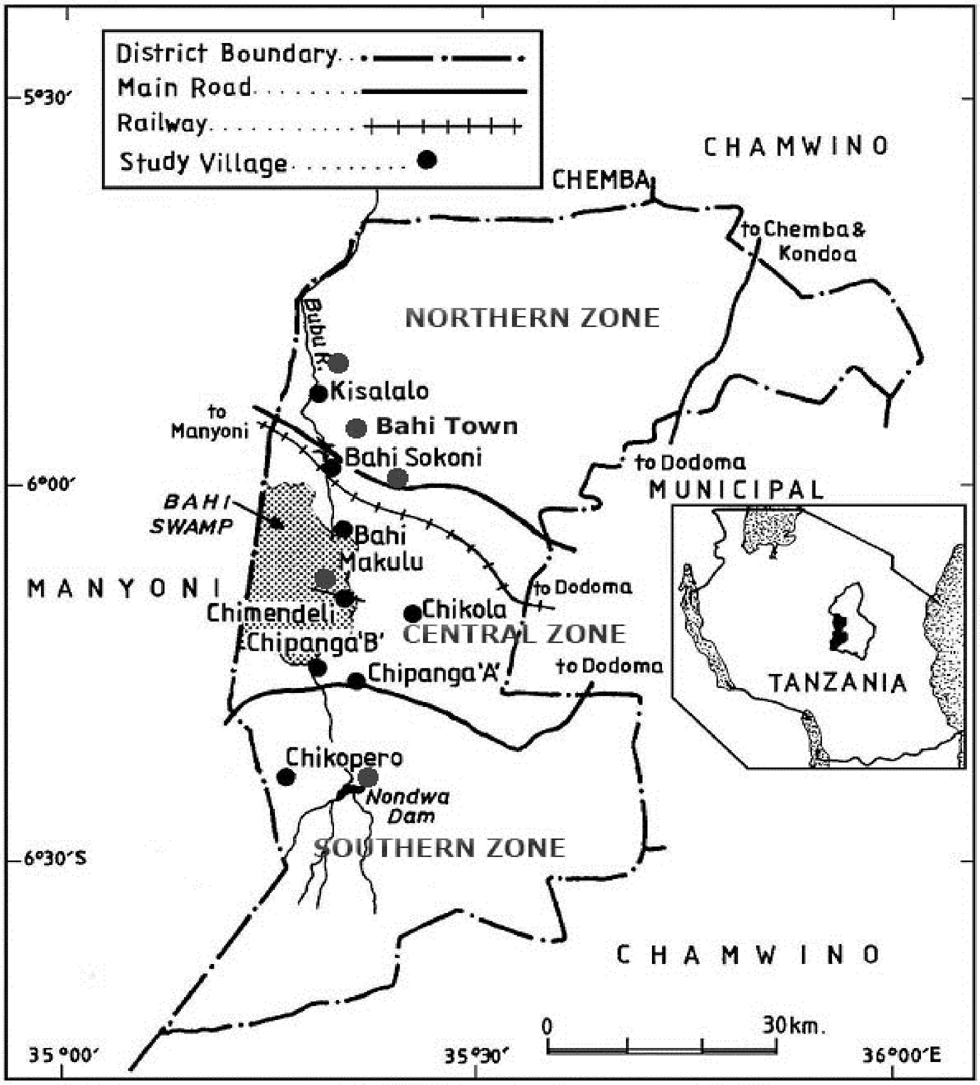

Figure 1: The map of Bahi showing the three zones and the sampling stations (Adapted and customized from Kimaro and Mohammed 2015)

At TAEC laboratory, the Spinach samples were oven dried for 24 hours at 40 ^{o}C to ensure constant weight. The samples were further ground using electrical grinder and sieved through 0.4 mm sieve and stored into clean and labeled plastic container for further procedures. 4.0 g of the sieved powder of the samples were weighed by using a digital balance and then mixed with 0.9 g cellulose binder for proper binding. The mixed powder was then put into a pulverizer to be mixed thoroughly and homogenized for 20 minutes. The homogenized mixture was put into container and inserted into a compressor. By using manual hydraulic press machine, the tablet like pellets were made through application of pressure force of 15 tons to produce intermediate thickness pellets with outer diameter of 32 mm. The pellets were kept into the sample holders and then placed into the EDXRF machine for analysis.

Sample Elemental Analysis

The elemental analyses of samples were conducted using a bench top energy dispersive spectrometer of TAEC. The machine which is operated by an automated turbo-quant X-lab Pro™ software, uses a 0.003 beryllium window X-ray tube with cooper body anode and ceramic envelope with palladium target. The tube was operated at a rate of 50 W and 50 kV voltages. The X-rays spectra were collected by a Si (Li) detector having resolution (FWHM) at Mn-Kα ≤ 160eV.

A spectrum run for 15 minutes gave a good counting statistics and resolution of the peaks. The concentration of individual elements was determined by using fundamental parameter method inbuilt in the X-lab Pro computer software in which matrix effects were accounted for. In this study accuracy of the EDXRF results of vegetables were verified using NIST reference material of trace and minor elements in Spinach leaves, (NIST 1570a). As shown in Table 2, the experimental values agreed well with the recommended values.

Table 2: An experimental and standard value of Spinach leaves NIST 1570a.

Elements	Experimental value	Reference value
Cadmium	2.52	2.89
Lead	0.18	0.2
Arsenic	< 0.15	0.07
Mercury	< 0.90	0.03
Thorium	<0.91	0.05
Uranium	<2.95	0.16

Conversion of Concentration (μg/g to Activity (Bq/kg)

In this study, the activity concentrations of ^{238}U, ^{232}Th and ^{40}K were not measured directly by Gamma ray spectrometry. Instead the samples were analyzed by EDXRF to get concentration of natural elements U, Th and K in μg/g. Then, the concentrations in μg/g were converted into activity concentration (Bq/kg) while considering their relative isotopic abundances which are 99.275%, 100% and 0.012% for ^{238}U, ^{232}Th and ^{40}K respectively. The conversions of μg/g into Bq/kg for primordial nuclides can be carried out as follows; (Yousuf and Abullah 2013).

$$A(Bq/kg) = -\frac{dN}{dt} = \lambda N = \frac{mN_A H}{A_r} . \frac{\ln 2}{t_{\frac{1}{2}}} \times 1000$$

Where; m is the mass of radionuclide in μg/g

N_A is the Avogadro number,

H is the isotopic abundance,

A_r is the relative atomic mass

$t_{\frac{1}{2}}$ is the half-life of the radionuclides

i. For ^{238}U

$$A(Bq/kg)=\frac{1\mu g/g\times 99.275\%\times 6.022\times 10^{23}\,nuclide/mole}{238g/mole}\times\frac{0.693}{1.41\times 10^{17}\sec}\times 1000=12.4Bq/kg$$

Thus, 1 µg/g of ^{238}U = 12.4 Bq/kg

ii. For 1µg/g of ^{232}Th:

$$A(Bq/kg)=\frac{1\mu g/g\times 100\%\times 6.022\times 10^{23}\,nuclide/mole}{232g/mole}\times\frac{0.693}{4.43\times 10^{17}\sec}\times 1000=4.06Bq/kg$$

Thus, 1 µg/g of ^{232}Th = 4.06 Bq/kg of ^{232}Th

iii. For ^{40}K

$$A(Bq/kg)=\frac{1\mu g/g\times 0.012\%\times 6.022\times 10^{23}\,nuclide/mole}{40g/mole}\times\frac{0.693}{3.945\times 10^{16}\sec}\times 1000=0.032Bq/kg$$

Thus, 1 µg/g of ^{40}K = 0.032 Bq/kg of ^{40}K

The above conversions factors (i - iii) were used to convert mean concentrations (µg/g) of ^{238}U ^{232}Th and ^{40}K into Bq/kg.

RESULTS AND DISCUSSION

Heavy metal concentrations

Heavy metals concentrations in Spinach (*Spinacia oleracea*) are reported in Table 3. The three rows represent the mean concentrations of heavy metals in Spinach (*Spinacia oleracea*) samples collected from different zones of Bahi wetlands. Since all elements are normally distributed, the statistical presentations of the data are reported using arithmetic mean (± SEM).

In all sampling stations, the concentrations of As and Hg were found to be below the minimum detection limits of 0.15 µg/g and 0.90 µg/g, respectively of the EDXRF used in this study. Table 3 shows that, the mean concentrations of Cd and Pb are highest in the northern zone and lowest in the southern zone. The mean concentrations of both metals in Spinach grown in northern zone were about 1.7 times, respectively higher than their concentrations in samples from southern zone.

The mean concentrations of Cd and Pb in Spinach samples found in this study were compared with their mean concentrations in Spinach samples found in other studies as shown in Fig. 2.

.

Table 3: The mean activity concentrations (µg/g ± SEM) of heavy metals in Spinach (*Spinacia oleracea*) collected from three zones of Bahi wetlands

Sampling Stations	As	Hg	Cd	Pb
NZ (n = 12)	< 0.145	< 0.90	16.± 1 (15 - 18)	108 ± 7 (108 - 115)
CN (n = 16)	< 0.145	< 0.90	13 ± 2 (9.5 - 15.9)	88 ± 8 (62.3 - 115.7)
SZ (n = 8)	< 0.145	< 0.90	9 ±1 (7.6 - 12.9)	64 ± 2 (61.5 - 70.0)

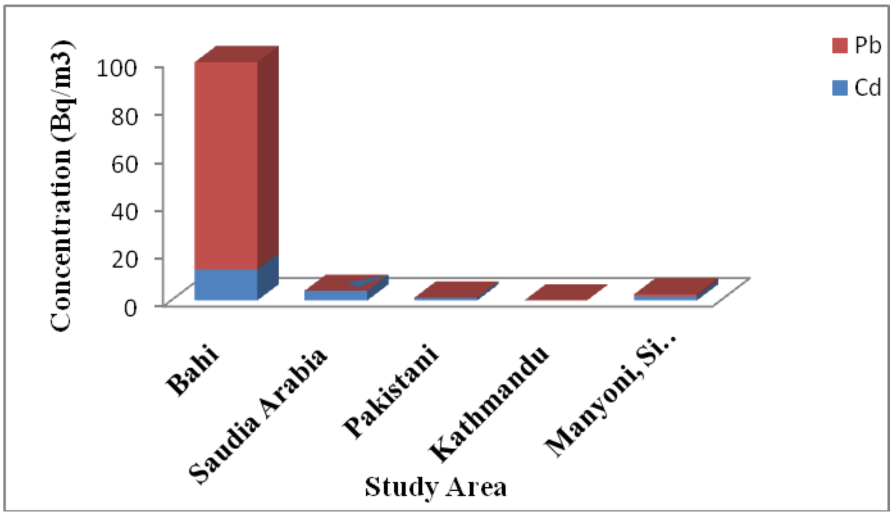

Figure 2: Comparison of the concentrations of Cd and Pbfrom this study with those reported elsewhere.

The mean concentration of Cd and Pb found in this study are higher than the values reported in four literatures reviewed in this work. For instance, the mean concentration of Cd and Pb reported in this study are more than 7 and 100 times, respectively higher than the values reported by Kapile and Makundi (2016) in spinach samples from Manyoni, Singida. The values are about 3and 40 times, respectively higher than their mean concentrations reported in Spinach (*Spinacia oleracea*) samples collected in Saudi Arabian food markets (Mohammed and Al – Qahtani 2012). Furthermore, Cd and Pb found in this study are in concentrations of about 11and 5 times, respectively higher than their mean value reported by Kafeel et al. (2014) in spinach samples grown in Sargodha, Pakistani.

The mean concentrations of Cd in samples from Bahi were found to be 65 times higher than 0.2 µg/g set as the maximum tolerable limit (MTL) of Cd in food (WHO 1992). Cd is a toxic element, which has been classified as carcinogenic (Codex 2015). Ingested Cd is retained in kidneys and liverwith a biological half life ranging from 10 to 30 years (WHO 2008). At the same time, the concentrations of Pb in samples from Bahi wetlands were found to be much higher than the 0.3 µg/g set by Codex alimentarius (2015) as MTL (Codex 2015). Lead is non-essential element as it is toxic even in trace amount (WHO 2010). High concentrations in foodstuff have been reported to cause a number of diseases, such as cardiovascular, renal, nervous and skeletal systems (WHO 1992).

Activity concentrations

In all sampling stations, the concentration of ^{238}U was found below the minimum detection limit of 2.8 µg/g of the EDXRF system used in this study; hence 34.7 Bq/kg was taken as the MDA for ^{238}U in this study. The average activity concentrations of radionuclides (^{232}Th and ^{40}K) in Spinach (*Spinacia oleracea*) collected from Bahi wetlands and control region are summarized in Table 4. The first three rows represent the mean activity concentrations of radionuclides in samples collected from the three zones of Bahi wetlands. The fourth row present mean activity concentrations in samples collected from control area.

The values of activity concentrations of ^{232}Th in all three zones were found to be similar and about 1.6 times higher than the mean value found in control samples. Higher activity concentrations of ^{232}Th in samples from Bahi than in control might be due to the presence of high values of ^{232}Th in farm soil as reported by Kimaro and Mohammed (2015). ^{40}K was found to be highest in northern zone followed by central zone. The ^{40}K value found in northern zone is about 2 and 16 times its activity concentration found in southern zone (SZ) and control area, respectively.

In the present study, ^{40}K was detected in relatively large activity concentrations than ^{232}Th and ^{238}U in all analyzed samples. The mean activity concentration of ^{40}K was ~77 times higher than the mean activity concentration of ^{232}Th and about 24 times higher than the MDL for ^{238}Uin spinach samples from Bahi. For control samples, the mean activity concentration of ^{40}K was ~ 6 times higher than the mean activity concentration of ^{232}Th and about 1.5 times higher than the MDL of ^{238}U for the system used in this study. Higher activity concentrations of ^{40}K than those of ^{232}Th are also reported by Kimaro and Mohammed (2015) in farm soils from Bahi. Therefore, it was expected that crops grown in these soil will have higher concentrations of ^{40}K than ^{232}Th. Moreover, several reviewed literatures have reported similar observation that ^{40}K is present more in environmental samples than ^{238}U, ^{232}Th and their progenies (Ababneh et al. 2009, Boukhenfouf and Boucenna 2011).

Table 4: The mean activity concentrations (Bqkg^{-1} ± SEM) of radionuclides in Spinach (*Spinacia oleracea*) from Bahi Wetland

	Activity Concentrations		
Sampling Zones	**^{238}U**	**^{232}Th**	**^{40}K**
NZ (n= 12)	< 34.7	11.1±0.5 (10.3 - 12.4)	849 ±26 (785.7 - 870.0)
CZ (n = 16)	< 34.7	11.1 ± 0.4 (10.5 - 12.3)	789 ± 10 (775 - 809)
SZ (n = 8)	< 34.7	10.3 ± 1 (8.6 - 11.2)	422.6 ± 6.6 (412.4 - 431.8)
Control (n = 4)	< 34.7	7.7 ± 0.1 (7.8 - 7.6)	54.2 ± 6.6 (45.9 - 70.3)

The mean activity of ^{232}Th and ^{40}K in Spinach (*Spinacia oleracea*) samples found in this study were compared with their activities in Spinach samples found in other studies in literature. The results showed that, ^{232}Th reported in this study has higher activity concentrations than the mean values in three literature reviewed in this studies (Fig. 3). However, the mean activity of ^{232}Th in this study is 2 times lower than the value reported by Ferdous et al. (2013). At the same time, the mean activity concentration of ^{40}K in Spinach (*Spinacia oleracea*) is about 2 times higher than the mean concentrations reported by Abojassim et al. (2016) and Ferdous et al. (2013) in samples from Iraq and India, respectively. Nevertheless the activity of both radionuclides in spinach samples from Bahi are lower than the 1000 Bq/kg, a safe standard limits of radionuclides in vegetables set by FAO/WHO.

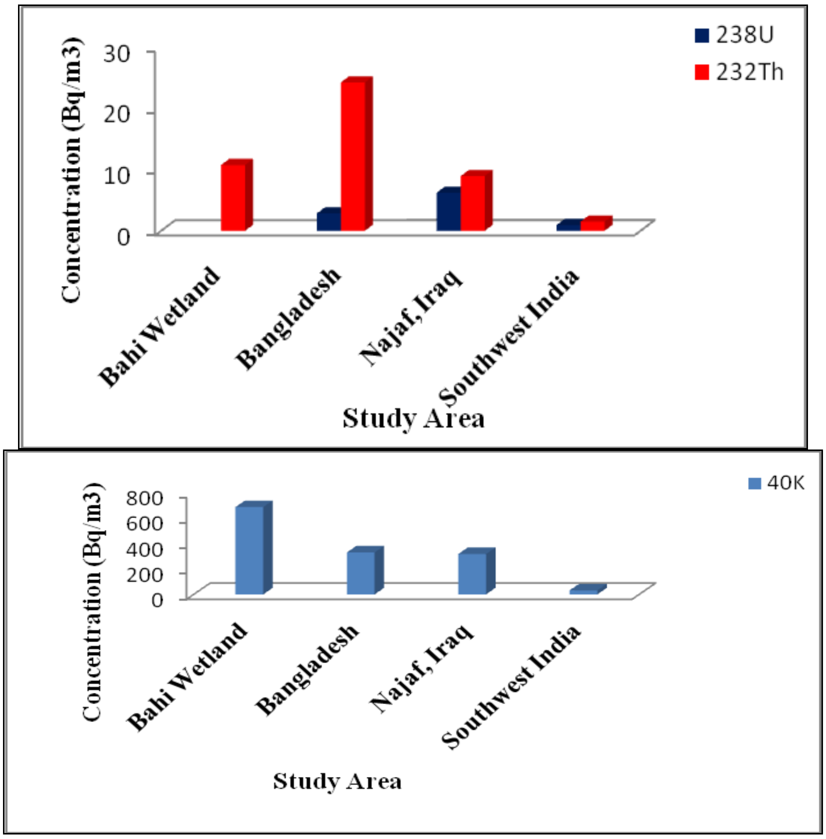

Figure 3: Comparison of the activity concentrations of ^{238}U, ^{232}Th and ^{40}K from this study with those reported elsewhere. The activity concentrations of ^{238}U in Bahi is below MDL of 34.7 Bq/kg

CONCLUSION

This study determined the concentrations of heavy metals and radionuclides in Spinach (*Spinacia oleracea*) grown in Bahi wetlands using Energy Dispersive X-ray fluorescence technique. Two toxic heavy metals namely Cd and Pb and two radionuclides ^{232}Th and ^{40}K were determined in concentrations above the MDL of the EDXRF technique used in the present study. The concentrations of Arsenic, Mercury and Uranium were detected below the MDL of the system. The results showed that, the mean activity concentrations of ^{232}Th and ^{40}K in Spinach (*Spinacia oleracea*) collected in the study area are higher than their concentrations in samples from control area and higher than their activity in spinach samples from Iraq and India. However, their activity concentrations are lower than those reported in Bangladesh.

The mean concentrations of Cd and Pb in this study are much higher than the values reported by Kapile and Makundi (2016) in samples from Singida, region. The mean concentrations are also higher than the values reported in spinach from Saudi Arabia, Pakistani and Kathmandu. The results show also that, the mean concentrations of Cd and Pb in Spinach **(***Spinacia oleracea*) from Bahi Wetland (86.6 µg/g and 12.8 µg/g) are 433 and 642 times, respectively higher than their permissible limits set by Codex (2015). Therefore, Spinach **(***Spinacia oleracea*) grown in Bahi wetland is contributing to exposure of the Bahi population to metal toxicity which might be detrimental to their health. Research which will include more number of samples is recommended.

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CONFLICT OF INTEREST STATEMENT

The authors declare that there are no conflicts of interest

AUTHOR'S CONTRIBUTIONS

All authors read and approved the final manuscript

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