

Full Length Research Paper

Bioaccumulation of heavy metals in mangoes (*Mangifera indica* L.) found in the vicinity of gold mining sites of Zamfara State, Nigeria

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The impact of gold mining on mango (*Mangifera indica* L.) grown in the vicinity of gold mining sites in Zamfara State, Nigeria have been assessed over the dry and wet seasons. Samples of mango plant parts were collected from 3 impacted sites and a control site monthly between March and August 2014, and analysed for selected heavy metals using Atomic Absorption Spectrophotometer. The results obtained indicate that Pb was the most abundant heavy metal in the mango roots (95.17 ± 68.49 mg/kg), stems (87.89 ± 64.11 mg/kg) and leaves (67.11 ± 57.11 mg/kg) found in Kwali and the least abundant metal was Ni (0.30 ± 0.44 mg/kg) in Kadauri (control site). The mean values of these metals were found to be above the WHO (1996) and Nigerian FME_{env} maximum permissible limits indicating high level of contamination from gold mining activities. The abundances of the metals followed an unsequential pattern in the order Pb > Fe > Au > Al, depending on the location, and differed significantly ($P < 0.05$) across sampling stations. Remarkably higher values of the contaminants were observed in the dry than the wet season. The sequence of heavy metal accumulation in the mango plants were Roots > Stems > Leaves > Fruits which revealed that the roots bio-accumulated the heavy metals more than the fruits. Bio-accumulation factor (BAF) values determined varied with specific heavy metals, location and the season. Most BAF values were higher than 1 indicating that *Mangifera indica* is a hyperaccumulator and could be used as bioindicator for pollution studies.

Key words: Heavy metals, *Mangifera indica*, BAF, gold mining, Nigeria.

INTRODUCTION

Mining for gold in Nigeria has been a prolong practice since the early 20th century. The genesis of gold mining dates back to 1913 when gold was discovered in Northern Nigeria (present Zamfara and Kogi States) and reached its peak in the 1930s before the Second World

War when the mines were abandoned by the colonial masters. Gold mining was resuscitated by the establishment of the Nigerian Mining Corporation (NMC) in 1980 but was later crippled due to lack of funding with the attention of government focused towards oil

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production. Gold mines, whether endogenous or exogenous ores, exist as mixtures together with various metal impurities such as silver, copper, iron, platinum, cadmium, lead and other metalloids in diverse quantities depending on the geographical region. Obtaining pure gold often involve metallurgical processing where the impurities are totally removed to yield the precious metal. These impurities or mine tailings (as they are often called), are wastes matter that must be adequately or properly disposed of in order to minimize environmental degradation. Improper disposal are responsible for the increased burden of trace and heavy metals in these areas where gold are mined. Although some of the heavy metals found as impurities in gold (such as copper and iron, manganese and zinc) are essential for proper functioning of biological systems, their occurrence in excess can be detrimental. Non-essential heavy metals of great concern include arsenic, cadmium, lead and mercury, as they form part of the World Health Organization's list of ten chemicals of major public health concern (Anette et al., 2011). Unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most heavy metals do not undergo microbial or chemical degradation (Kirpitchkova et al., 2006), and their total concentration in the environment persists for a long time after their introduction (Adriano, 2003). Changes in their chemical forms (speciation) and bioavailability are however possible (Maslin and Maier, 2000).

The element gold may also occur in nature in conjunction with quartz (SiO_2) and calcite (CaCO_3), in concentrations that would cause harm (Monday, 2010). Gold mining and processing entails breaking the ground surface to excavate the ore, crushing the ore and then using water and/or other chemicals such as cyanide and mercury to concentrate the gold through sluicing, panning, floating and leaching. This employs the use of local tools, heavy equipment that use petrol or gasoline and sometimes explosives such as dynamite (Geordie, 2011). Mining processes lead to metals being released from their stable form into the environment and removal of large quantities of overburden waste materials that are continuously dispersed through erosion, wind action and effluent draining the waste into arable land, surface and ground waters, polluting air, soil, vegetation, changing or destroying aquatic habitats, affecting agricultural lands, and causing health problems to humans (Arogunjo, 2007; Jian-Min et al., 2007). Heavy metals reduce the yield of crops thereby disturbing the metabolic processes of plants thus resulting in the growth of contaminated plants which eventually affects animals (Ogbodo et al., 2006). Distribution of heavy metals in plants depends upon availability and concentrations of heavy metals as well as particular plant species and its populations (Punz and Seighardt, 1993).

Mango (*Mangifera indica* L.) is one of the most widely

cultivated and popular fruits in the tropics and subtropics, and represents the fifth most cultivated fruit in the world, with 33.7 million tons of fruit produced in 2009 (Gerbaud, 2011). The plant is widely cultivated in Nigeria for fruit, fodder, fuel wood and other uses (Adepoju, 2015). Patches of mango plantations are found around the gold mining areas of Zamfara State, Nigeria. Plants generally are capable of absorbing and accumulating heavy metals from the surrounding environment. El-Sharabasy and Ibrahim (2010) in their study on heavy metals accumulation in mango plant and agricultural soils from agrarian communities in Egypt reported that mango plantations impacted by waste water from Ismailia canal accumulated heavy metals above the background concentration. Sabah and Fouzul (2013) studied the environmental impacts of gold mining on pollution by heavy metals in the gold mining plant of Oman. The desert plants species growing close to the gold mines showed high concentrations of heavy metals (Mn, Al, Ni, Fe, Cr and V) above the Omani and WHO standards, while similar plant species used as control showed lesser concentrations of the heavy metals. This study aimed at determining the concentration of heavy metals (Pb, Cd, As, Ni, Cu, Cr, Mn, Zn, Co, Al, Fe, Au) in mango plant parts (roots, stems/ barks, leaves and fruits) from the gold mining areas of Zamfara State, Nigeria. The concentrations of heavy metals in mango fruits were compared with WHO (1996) acceptable limits, in order to provide a basis for guiding further activities especially humans involved in illegal mining activities in the region.

MATERIALS AND METHODS

Study area

Zamfara State of Nigeria is located between latitude $12^{\circ}10'N$ and $12^{\circ}16'N$, and longitude $06^{\circ}15'E$ and $06^{\circ}25'E$, it has a total area of 39,762 square kilometres. Three gold mines namely Kwali ($05^{\circ}45.49'E$ to $11^{\circ}59.66'N$), Duke ($06^{\circ}19.56'E$ to $12^{\circ}21.45'N$) and Maraba ($06^{\circ}22.43'E$ to $12^{\circ}20.26'N$) and their surrounding villages were investigated. A control site at Kaudari ($06^{\circ}08.71'E$ to $12^{\circ}13.56'N$) was also chosen about 20 km away from the mining area.

Sample collection

Samples of mango roots, stems, leaves and fruits from each of the mining sites and the control were collected monthly for a period of six months making a cumulative total of 96 samples. Root samples were taken at a depth of 10-15 cm while the stems, leaves and fruit samples were collected using pre-cleaned acid-washed stainless knife, and washed again after each sampling to avoid cross-contamination.

Analysis of samples

All glass wares used in the analysis of samples were washed using

liquid soap, rinsed with distilled water and soaked overnight in 10% HNO₃ according to Protano et al. (2005). The samples were dried at room temperature, crushed with clean laboratory mill and sieved through 500 µm to obtain fine particles. Two grammes of the particles were placed into 250 ml beaker, a mixture of 20 ml HNO₃ and 8 ml HClO₄ were used to digest the sample on a hot plate to a final volume of 5 ml. The digest was allowed to cool, drops of deionised water added to make it up to 100 ml. It was then analysed using Flame Atomic Absorption Spectrophotometer Unicam Model 969.

Statistical tests

Analysis of variance (ANOVA) was used to determine whether significant difference exist among the values of different heavy metals across the three mining areas and the control site.

RESULTS

Heavy metal concentrations in mango roots

Table 1 presents the levels and abundances of heavy metals in the roots of mango plants found around the three chosen mining sites (Maraba, Duke, Kwali) and the control (Kadauri) during the dry and wet seasons. The mango roots in Maraba mining site had the following sequence in metals abundance: Pb > Fe > Au > Al > Zn > Mn > Cu > Cr > Co > As > Ni > Cd with Pb and Cd having highest and lowest values of 57.58 ± 48.25 mg/kg and 1.74 ± 2.87 mg/kg respectively. In Duke mining site, the order of occurrence of metals was Pb > Fe > Au > Al > Zn > Cd > Cu > Co > Mn > Ni > Cr > As with the highest, 62.07 ± 54.09 mg/kg and lowest, 2.05 ± 1.12 mg/kg as mean values for Pb and As respectively. In Kwali site, the metals occurred in the order Pb > Fe > Al > Au > As > Cu > Cd > Mn > Zn > Ni > Co > Cr with Pb and Cr having the highest and lowest mean values as 95.17 ± 68.49 mg/kg and 1.89 ± 2.08 mg/kg respectively. At Kadauri, the control site, heavy metals in mango roots were in the order: Pb > Fe > Au > Al > Zn > Cu > Mn > As > Cd > Co > Cr > Ni with the highest 19.80 ± 19.59 mg/kg and lowest 0.44 ± 0.65 mg/kg as average values for Pb and Ni respectively. The mean Pb value in mango root during the dry season was 83.77 ± 65.42 mg/kg, while that of the rainy season was 33.54 ± 24.41 mg/kg for the studied sites. The spatial variations of heavy metals in mango roots across sampling stations are shown in Figure 1 while the seasonal variations of heavy metals are shown in Figure 2.

Heavy metals concentration in mango stems

At Maraba site, the most abundant heavy metal in mango stem was Pb (68.82 ± 36.13 mg/kg) and least abundant was Cd (1.67 ± 1.54 mg/kg). The levels and abundances are presented in Table 2. The order of heavy metal

occurrence was Pb > Fe > Au > Al > Zn > Mn > Cu > Co > Cr > As > Ni > Cd. In Duke, the metals occurred in the following order: Pb > Fe > Au > Al > Zn > Cu > Cd > Co > Mn > Ni > As > Cr with Pb and Cr having highest and lowest mean values of 54.04 ± 30.81 mg/kg and 2.09 ± 0.65 mg/kg respectively. At Kwali mining site, the heavy metals had the sequence: Pb > Fe > Al > Au > Zn > Cu > Mn > As > Cd > Ni > Co > Cr with Cr having the least value of 1.80 ± 1.59 mg/kg, while Pb had the highest value of 87.89 ± 64.11 mg/kg. Kadauri, the control site had highest mean Fe value of 21.78 ± 11.46 mg/kg, lowest mean Ni value of 0.89 ± 0.43 mg/kg. The order of occurrence of heavy metals was Fe > Pb > Au > Al > Zn > Mn > Cu > Cr > As > Co > Cd > Ni. The dry and rainy seasons values in the mango stems were Pb (77.97 ± 53.48 mg/kg) and Ni (35.25 ± 24.18 mg/kg), respectively.

Spatial variation in the mean levels of heavy metals in mango stems across sampling stations are shown in Figure 3 while the seasonal variation of the heavy metals during dry and rainy seasons are shown in Figure 4.

Heavy metals concentration in mango leaves

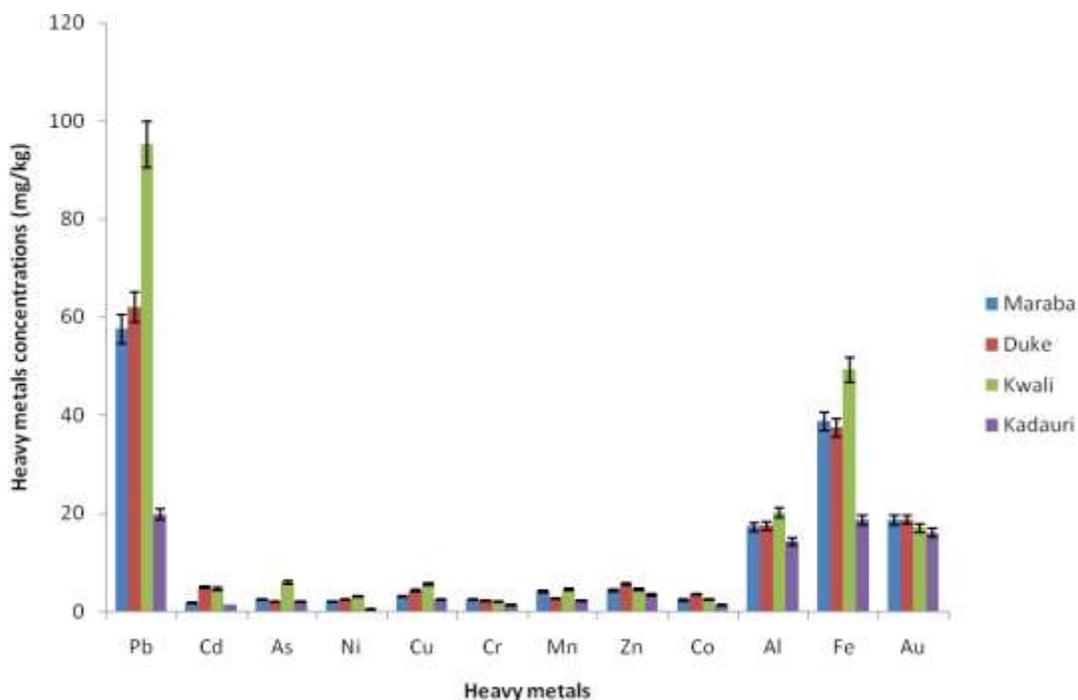
The levels of heavy metal concentrations in the mango leaves collected from the sampling sites are presented in Table 3. Mango leaves in Maraba had Pb (45.36 ± 35.04 mg/kg) as the most abundant heavy metal and Cr (1.35 ± 2.05 mg/kg), the least abundant, exhibiting the following order: Pb > Fe > Au > Al > Zn > Cu > Mn > As > Cd > Co > Ni > Cr. The Duke mining site had the highest 34.92 ± 31.27 and lowest 1.75 ± 0.89 mg/kg mean values for Fe and Cr respectively in its mango leaf with the order of occurrence; Fe > Pb > Au > Al > Cd > Zn > Cu > Ni > Mn > As > Co > Cr. The Pb concentration in Kwali mango leaf was 67.11 ± 57.11 mg/kg and that of Cr was 1.98 ± 2.25 mg/kg, exhibiting the following order: Pb > Fe > Au > Al > Zn > Mn > Cu > As > Ni > Cd > Co > Cr. In Kadauri, mango leaf had mean Pb value of 9.94 ± 4.29 mg/kg and the heavy metals concentration had the sequence: Fe > Au > Pb > Al > Zn > Cu > Mn > Cr > Cd > As > Co > Ni with Ni having a value of 0.37 ± 0.36 mg/kg. The dry season mean Pb value in mango leaves was 60.23 ± 13.47 mg/kg, while that of the rainy season was 17.85 ± 9.69 mg/kg. Spatial variations of heavy metals in mango leaves across sampling stations are shown in Figure 5 while seasonal variations are shown in Figure 6.

Heavy metals concentration in mango fruits

The levels of heavy metal concentrations in the mango fruits grown around the sampling sites are presented in Table 4. In Maraba, the mean concentration of Fe in mango fruit was 29.38 ± 20.16 mg/kg. The metals occurred in the order: Fe > Pb > Au > Al > Cu > Zn > Mn >

Table 1. Mean, ranges and standard deviation of heavy metal concentrations (mg/kg) in mango roots from the three mining areas and the control.

Metals	Maraba	Duke	Kwali	Kadauri	F-value	P-test
Pb	57.58 ± 8.25 (14.11 - 39.30)	62.07 ± 54.09 (21.33 - 159.04)	95.17 ± 68.49 (28.91 - 191.84)	19.80 ± 19.59 (5.96 - 58.43)	2.21	P <0.05
Cd	1.74 ± 2.87 (0.02 - 2.71)	4.91 ± 6.88 (0.61 - 3.39)	4.59 ± 4.78 (2.04 - 11.32)	1.39 ± 1.37 (0.11 - 7.11)	1.02	P < 0.05
As	2.31 ± 2.53 (0.03 - 7.18)	2.05 ± 1.12 (0.11 - 15.22)	5.93 ± 3.95 (0.24 - 12.89)	1.91 ± 2.58 (0.18 - 3.96)	2.98	P <0.05
Ni	2.03 ± 1.82 (0.18 - 5.39)	2.47 ± 3.11 (0.17 - 6.83)	3.11 ± 3.86 (0.08 - 9.77)	0.44 ± 0.65 (0.02 - 1.75)	1.10	P <0.05
Cu	3.03 ± 1.70 (0.96 - 5.85)	4.17 ± 3.17 (1.43 - 9.11)	5.54 ± 3.90 (0.81 - 11.12)	2.46 ± 2.44 (0.31 - 7.19)	1.29	P > 0.05
Cr	2.46 ± 2.53 (0.03 - 7.09)	2.22 ± 1.94 (0.21 - 4.92)	1.89 ± 2.08 (0.06 - 4.84)	1.26 ± 0.99 (0.17 - 2.31)	0.42	P > 0.05
Mn	3.99 ± 3.46 (1.19 - 8.99)	2.58 ± 1.29 (1.47 - 4.82)	4.46 ± 3.19 (2.08 - 10.17)	2.14 ± 1.98 (0.33 - 5.82)	1.06	P > 0.05
Zn	4.25 ± 2.89 (1.61 - 9.86)	5.54 ± 4.67 (1.42 - 13.28)	4.43 ± 2.56 (2.01 - 9.19)	3.41 ± 2.48 (1.10 - 6.85)	0.43	P > 0.05
Co	2.30 ± 2.06 (0.57 - 6.02)	3.53 ± 3.16 (0.75 - 8.61)	2.32 ± 2.27 (0.10 - 5.84)	1.31 ± 1.42 (0.03 - 3.81)	0.92	P <0.05
Al	17.19 ± 9.17 (9.38 - 29.31)	17.48 ± 10.31 (9.81 - 31.98)	20.14 ± 21.35 (3.92 - 61.90)	14.24 ± 18.09 (1.50 - 49.90)	0.14	P <0.05
Fe	38.74 ± 31.00 (15.28 - 98.39)	37.38 ± 30.53 (4.88 - 88.19)	49.27 ± 43.82 (17.12 - 130.28)	18.57 ± 11.56 (6.11 - 33.05)	0.99	P <0.05
Au	18.57 ± 7.29 (12.06 - 31.98)	18.72 ± 6.17 (9.76 - 26.30)	16.98 ± 5.68 (10.68 - 24.17)	16.05 ± 3.79 (10.18 - 21.14)	2.12	P>0.05

**Figure 1.** Spatial variation of heavy metals in mango roots across the sampling stations.

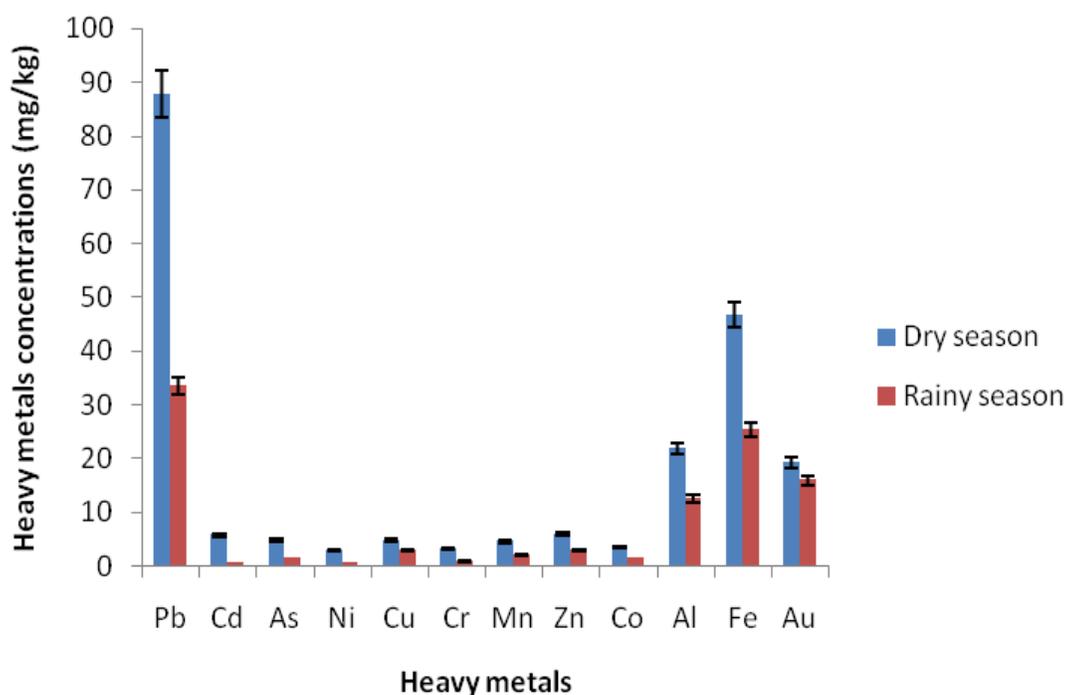


Figure 2. Seasonal variation of heavy metals (mg/kg) in mango roots.

Table 2. Mean, ranges and standard deviation of heavy metal concentrations (mg/kg) in mango stems from the three mining areas and the control.

Metals	Maraba	Duke	Kwali	Kadauri	F-value	P-test
Pb	68.82 ± 36.13 (15.01 - 98.04)	54.04 ± 30.81 (25.90 - 98.50)	87.89 ± 64.11 (29.06 - 179.81)	15.68 ± 5.64 (6.38 - 21.01)	3.51	P < 0.05
Cd	1.67 ± 1.54 (0.81 - 5.71)	4.27 ± 4.46 (0.11 - 5.81)	3.60 ± 3.52 (1.08 - 6.17)	0.93 ± 0.57 (0.19 - 3.61)	1.70	P < 0.05
As	2.36 ± 1.82 (0.18 - 3.81)	2.14 ± 1.96 (0.84 - 10.29)	3.81 ± 1.71 (0.28 - 10.11)	1.40 ± 1.29 (0.13 - 1.92)	2.09	P < 0.05
Ni	2.01 ± 1.27 (0.54 - 3.81)	2.32 ± 1.98 (0.71 - 5.32)	2.79 ± 4.43 (0.83 - 12.28)	0.89 ± 0.43 (0.13 - 1.42)	1.35	P < 0.05
Cu	3.19 ± 1.53 (1.27 - 5.01)	4.48 ± 3.52 (0.54 - 8.98)	4.50 ± 3.42 (0.32 - 8.92)	2.39 ± 1.52 (0.28 - 5.03)	0.88	P < 0.05
Cr	2.70 ± 1.49 (0.51 - 4.65)	2.09 ± 0.65 (1.04 - 2.88)	1.80 ± 1.59 (0.19 - 3.99)	1.53 ± 0.81 (0.41 - 2.36)	1.04	P > 0.05
Mn	4.18 ± 2.79 (1.48 - 9.14)	2.92 ± 2.34 (0.48 - 7.24)	3.98 ± 2.22 (1.01 - 7.24)	2.41 ± 1.58 (0.39 - 3.83)	0.83	P > 0.05
Zn	4.97 ± 2.19 (2.85 - 9.05)	4.90 ± 3.43 (1.08 - 9.81)	4.66 ± 2.72 (1.91 - 9.51)	3.07 ± 1.54 (1.22 - 5.19)	0.73	P > 0.05
Co	2.78 ± 0.83 (1.83 - 4.17)	3.03 ± 2.95 (0.61 - 8.59)	2.44 ± 1.61 (0.82 - 4.45)	1.19 ± 1.09 (0.02 - 2.48)	1.21	P < 0.05
Al	14.38 ± 9.27 (5.31 - 31.82)	15.97 ± 9.70 (4.23 - 30.84)	22.71 ± 23.96 (2.71 - 69.82)	11.12 ± 7.77 (1.81 - 21.80)	0.69	P < 0.05
Fe	45.17 ± 32.43 (17.06 - 87.31)	43.66 ± 33.59 (9.46 - 91.41)	51.41 ± 40.33 (11.12 - 103.30)	21.78 ± 11.46 (9.17 - 38.94)	1.02	P < 0.05
Au	19.92 ± 14.67 (10.08 - 49.29)	18.53 ± 6.64 (10.83 - 29.30)	22.70 ± 10.99 (10.17 - 41.22)	14.45 ± 5.98 (8.11 - 23.95)	2.31	P < 0.05

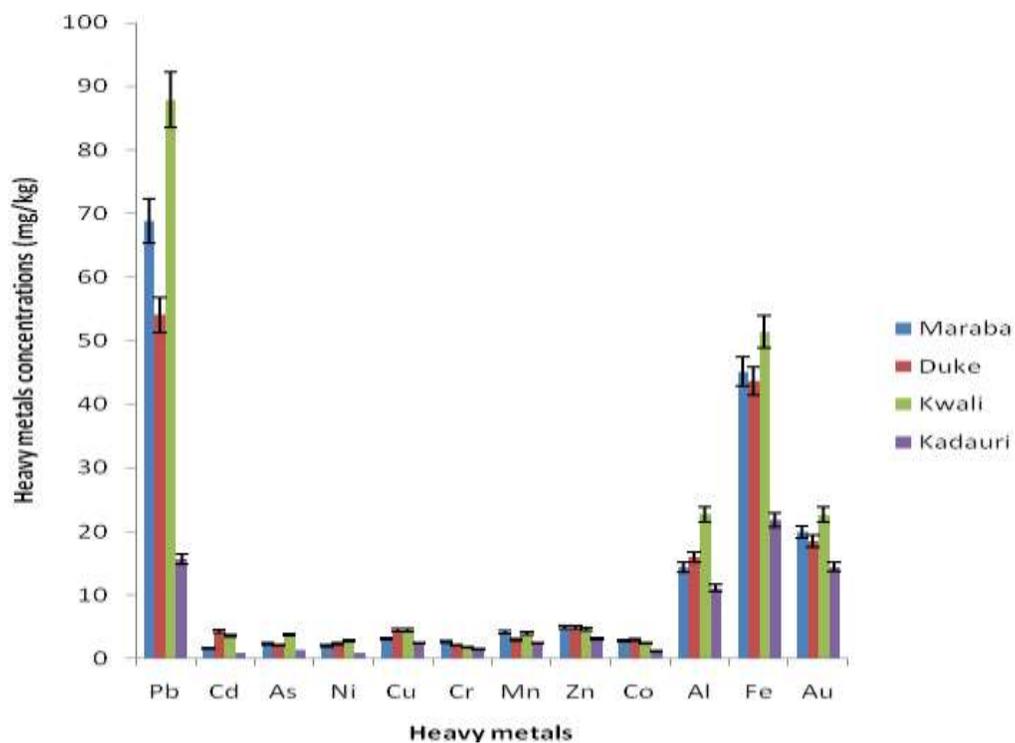


Figure 3. Spatial variation of heavy metals in mango stems/ barks across the sampling stations.

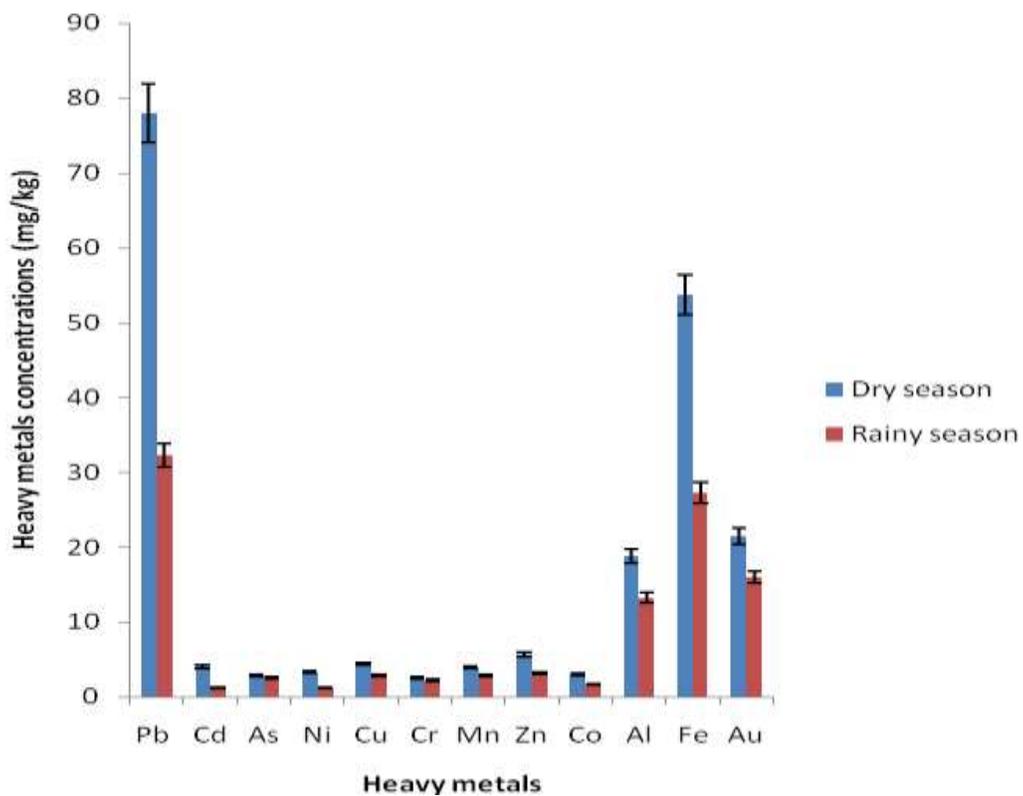
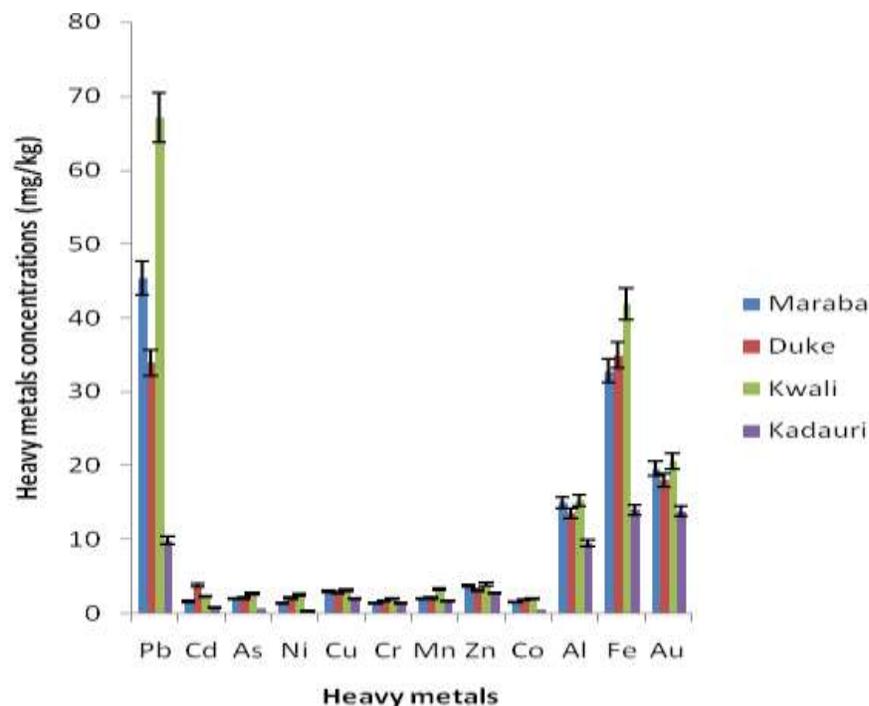


Figure 4. Seasonal variation in heavy metal concentrations (mg/kg) in mango stems/ barks.

Table 3. Mean, ranges and standard deviation of heavy metal concentrations (mg/kg) in mango leaves from the three mining areas and the control.

Metals	Maraba	Duke	Kwali	Kadauri	F-value	P-test
Pb	45.36 ± 35.04 (11.18 - 104.60)	33.93 ± 24.79 (11.20 - 69.99)	67.11 ± 57.11 (17.06 - 161.26)	9.94 ± 4.29 (4.11 - 15.22)	2.66	P < 0.05
Cd	1.64 ± 2.29 (0.01 - 5.84)	3.83 ± 5.17 (0.09 - 11.68)	2.29 ± 3.47 (0.02 - 9.16)	0.77 ± 0.78 (0.02 - 2.11)	0.89	P < 0.05
As	1.99 ± 2.37 (0.05 - 6.29)	2.08 ± 2.61 (0.09 - 6.98)	2.67 ± 2.29 (1.09 - 7.28)	0.74 ± 0.75 (0.05 - 1.92)	0.87	P < 0.05
Ni	1.47 ± 1.04 (0.18 - 3.15)	2.09 ± 1.06 (0.36 - 6.40)	2.58 ± 4.14 (0.08 - 10.49)	0.37 ± 0.36 (0.08 - 0.93)	1.02	P < 0.05
Cu	3.01 ± 1.89 (1.02 - 5.39)	2.85 ± 2.58 (0.19 - 6.18)	3.15 ± 2.01 (0.03 - 5.27)	2.05 ± 0.88 (0.41 - 3.18)	0.39	P > 0.05
Cr	1.35 ± 2.05 (0.03 - 5.27)	1.75 ± 0.89 (0.41 - 3.18)	1.98 ± 2.25 (0.02 - 4.84)	1.49 ± 1.06 (0.01 - 2.89)	0.17	P > 0.05
Mn	2.05 ± 2.67 (0.36 - 6.48)	2.09 ± 0.94 (0.95 - 3.81)	3.25 ± 2.65 (1.01 - 7.25)	1.73 ± 1.24 (0.19 - 3.44)	0.73	P < 0.05
Zn	3.73 ± 1.75 (1.85 - 6.40)	3.13 ± 2.25 (1.11 - 7.28)	4.01 ± 2.58 (2.12 - 8.99)	2.77 ± 1.42 (1.08 - 5.01)	0.45	P < 0.05
Co	1.63 ± 1.76 (0.28 - 5.18)	1.85 ± 2.03 (0.06 - 5.30)	2.05 ± 2.32 (0.18 - 6.09)	0.62 ± 0.78 (0.02 - 1.99)	0.73	P < 0.05
Al	15.02 ± 7.31 (9.19 - 28.51)	13.63 ± 12.45 (3.59 - 31.72)	15.35 ± 12.95 (4.04 - 39.81)	9.57 ± 6.49 (1.88 - 19.24)	0.41	P < 0.05
Fe	32.85 ± 29.75 (15.20 - 91.71)	34.92 ± 31.27 (5.24 - 81.77)	41.87 ± 36.03 (9.11 - 98.24)	14.07 ± 7.74 (5.26 - 22.99)	1.05	P < 0.05
Au	19.58 ± 11.83 (10.01 - 42.31)	18.06 ± 8.26 (8.21 - 30.12)	20.60 ± 12.36 (8.35 - 39.73)	13.83 ± 3.92 (9.02 - 19.00)	3.94	P < 0.05

**Figure 5.** Distribution of heavy metals in mango leaves across the sampling stations.

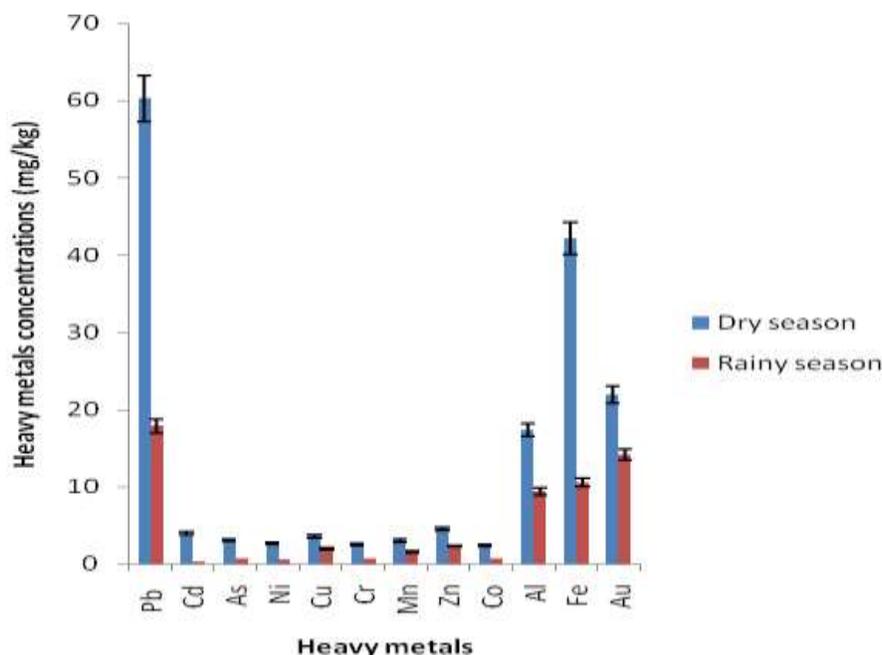


Figure 6. Seasonal variation in heavy metals concentration (mg/kg) in mango leaves.

Table 4. Mean, ranges and standard deviation of heavy metal concentrations (mg/kg) in mango fruits from the three mining areas and the control.

Metals	Maraba	Duke	Kwali	Kadauri	F-value	P-test
Pb	24.86 ± 21.22 (9.11 - 56.08)	27.00 ± 19.25 (12.19 - 53.83)	35.78 ± 20.86 (19.01 - 64.02)	11.87 ± 2.55 (9.05 - 15.01)	1.24	P<0.05
Cd	1.79 ± 1.97 (0.05 - 3.85)	4.66 ± 5.82 (0.02 - 12.91)	3.14 ± 4.74 (0.01 - 10.11)	0.52 ± 0.44 (0.11 - 0.99)	0.84	P<0.05
As	1.30 ± 0.97 (0.01 - 2.19)	1.49 ± 1.15 (0.10 - 2.64)	1.63 ± 1.83 (0.10 - 3.89)	1.70 ± 0.59 (0.95 - 2.13)	0.09	P>0.05
Ni	1.35 ± 1.38 (0.14 - 2.71)	1.74 ± 0.32 (1.27 - 1.95)	3.71 ± 5.19 (0.06 - 11.10)	0.30 ± 0.44 (0.01 - 0.96)	1.11	P<0.05
Cu	3.58 ± 2.30 (1.47 - 5.85)	3.06 ± 1.51 (1.71 - 4.72)	4.79 ± 3.28 (1.62 - 7.89)	2.86 ± 1.36 (2.08 - 4.89)	0.59	P<0.05
Cr	1.52 ± 1.29 (0.01 - 2.85)	1.31 ± 0.84 (0.74 - 2.55)	1.96 ± 2.64 (0.11 - 5.71)	2.20 ± 1.33 (1.05 - 3.64)	0.24	P>0.05
Mn	2.34 ± 1.15 (0.97 - 3.41)	2.16 ± 1.00 (1.25 - 3.28)	2.95 ± 2.13 (1.10 - 5.29)	3.90 ± 2.99 (1.19 - 7.83)	0.62	P<0.05
Zn	3.40 ± 1.93 (1.84 - 5.96)	4.79 ± 3.79 (0.92 - 9.72)	3.43 ± 2.18 (1.29 - 5.36)	5.13 ± 2.73 (2.50 - 7.99)	0.43	P<0.05
Co	1.45 ± 1.18 (0.11 - 2.87)	3.69 ± 2.59 (0.36 - 6.38)	1.73 ± 1.85 (0.11 - 3.57)	1.45 ± 1.25 (0.01 - 2.81)	1.49	P<0.05
Al	10.97 ± 0.74 (9.95 - 11.64)	14.12 ± 13.24 (5.25 - 34.08)	14.31 ± 5.88 (7.28 - 21.57)	7.84 ± 3.81 (5.11 - 12.58)	0.75	P<0.05
Fe	29.38 ± 20.16 (12.30 - 58.04)	42.22 ± 20.66 (21.66 - 61.49)	41.99 ± 33.45 (11.30 - 85.72)	23.10 ± 11.99 (11.98 - 38.91)	0.69	P<0.05
Au	16.89 ± 4.84 (12.21 - 21.08)	20.41 ± 7.12 (12.46 - 29.02)	16.48 ± 5.60 (9.11 - 21.49)	15.28 ± 4.89 (8.18 - 18.66)	3.41	P<0.05

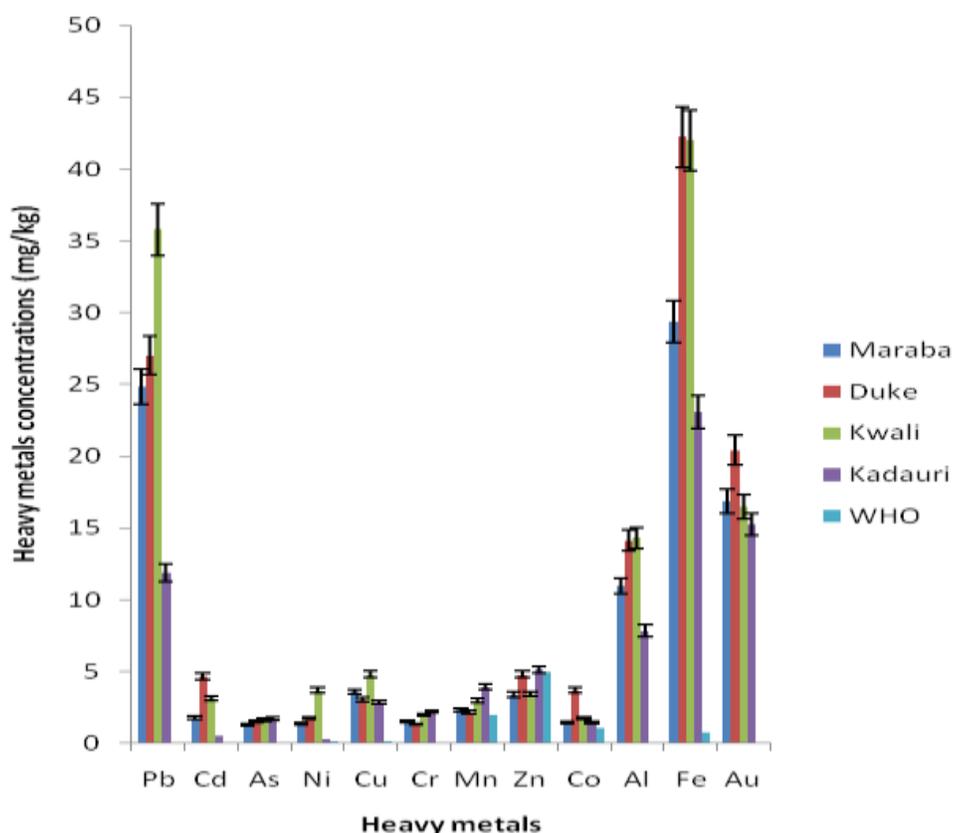


Figure 7. Spatial variation of heavy metals in mango fruits across the sampling stations.

Cd > Cr > Co > Ni > As with As having value of 1.30 ± 0.97 mg/kg. Mango fruit from Duke mining site had an average Fe concentration of 42.22 ± 20.66 mg/kg and gave the sequence: Fe > Pb > Au > Al > Zn > Cd > Co > Cu > Mn > Ni > As > Cr with Cr value of 1.31 ± 0.84 mg/kg. Kwali mining site had average Fe concentration of 41.99 ± 33.45 mg/kg in mango fruit with the order: Fe > Pb > Au > Al > Cu > Ni > Zn > Cd > Mn > Cr > Co > As and As value of 1.63 ± 1.83 mg/kg. Kadauri mango fruit had mean Fe value of 23.10 ± 11.99 and the metals were in the order Fe > Au > Pb > Al > Zn > Mn > Cu > Cr > As > Co > Cd > Ni with Ni value of 0.30 ± 0.44 mg/kg. In mango fruit, the dry season mean Pb value stood at 35.97 ± 20.18 mg/kg and the rainy season mean value was 13.78 ± 4.44 mg/kg. Mean levels of metals in mango fruits across sampling stations in comparison to WHO (1996) standards are shown in Fig.7 while metal levels during dry and rainy seasons are shown in Figure 8.

Distribution of heavy metals contaminants in mango plants

The most abundant heavy metal was Pb (95.17 ± 68.49 mg/kg) in mango roots at Kwali, with As (1.30 ± 0.97

mg/kg) in mango fruits at Maraba, being the least abundant. The overall mean Pb concentration in mango roots for the 3 sites throughout the study period was 58.65 ± 30.85 mg/kg. The general distribution of heavy metals in the mango plants investigated from the 3 mining sites followed the order: Pb > Fe > Au > Al > Zn > Cu > Mn > Cd > As > Co > Ni > Cr. The distribution of the heavy metals by mango parts based on Pb concentrations from the study sites (except Fe in fruits at Kwali) followed the sequence: Roots > Stems > Leaves > Fruits which revealed that the roots bio-accumulated the heavy metals more than the fruits and other parts of the mango tree. The greatest impact on the mango tree occurred at Kwali site where all the mango parts investigated (roots, stem/bark, leaves and fruits) had elevated concentrations of heavy metals above 37.0 mg/kg, several orders of magnitude above WHO (1996) permissible limits of the metals in fruits, Figure 7, except Zn. The mean levels of metals across mango parts are shown in Figure 9.

Bio-concentration of heavy metals by the mango plants

The ability of organisms or plants to bio-concentrate and

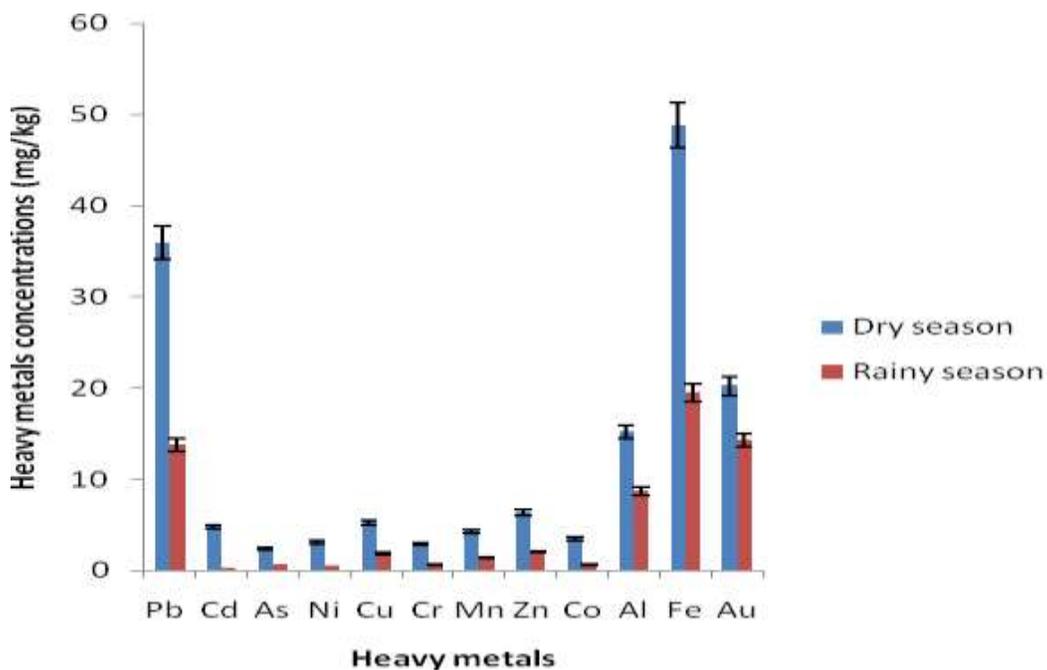


Figure 8. Seasonal variation in heavy metals concentration in mango fruits.

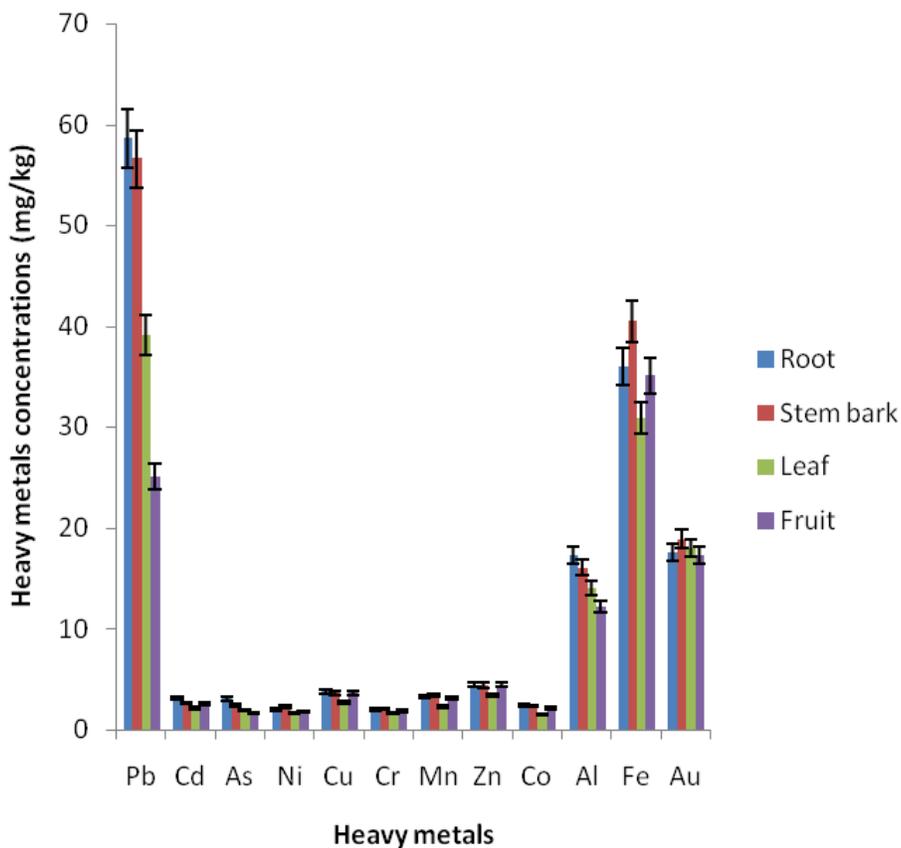


Figure 9. Overall distribution of heavy metals in mango plant parts.

Table 5. BAF values of mango plants analysed from the study sites in the dry season (March/April 2014).

Specific heavy metals	Maraba	Duke	Kwali
Pb	1.98	2.94	6.24
Cd	16.18	65.16	55.62
As	19.18	16.73	24.04
Ni	2.46	4.62	11.48
Cu	1.89	3.60	4.43
Cr	1.07	1.77	1.89
Mn	1.06	1.41	2.23
Zn	0.46	0.93	0.63
Co	0.57	1.65	1.20
Al	0.73	1.51	0.90
Fe	1.53	2.33	2.65
Au	0.08	1.24	1.59

bio-accumulate chemicals and toxic compounds have been used to scientifically assess the potential risks such chemicals may have on humans and the surrounding environment (Anot and Gobas, 2006; Harad and Smith, 1997). It also helps to understand the extent of impact the toxicant may exert on the biota. The mango parts were evaluated for their bio-accumulation factors (BAFs) by adopting the method utilized by Anot and Gobas (2006), which involves determining the ratio of the concentration of the specific metal in the mango part to the concentration in the surrounding soils in Zamfara. Tables 5 and 6 show the BAF values of the mango plants investigated during the dry and wet seasons from the 3 impacted sites.

BAF values show the extent of bio-accumulation of the toxicants by the *M. indica*. The higher the BAF, the lower the degree of toxicant levels in the specie indicating low impact on the fruit tree *M. indica*. In other words, higher BAF value indicated low availability of the metal and less impact on the plant. These could be deduced from the relationship $1.0 < \text{BAF} > 1.0$ for toxicant bio-accumulation in plants, when $\text{BAF} < 1.0$, it depicts high impact while $\text{BAF} > 1.0$, designates low impact. The BAF values varied with the specific heavy metals, their location and season (Tables 5 and 6). Higher BAF values were observed in the wet season indicating less contamination of *M. indica* in the wet than the dry season.

Pollution status of the *M. indica*

A comparison of the health status of *M. indica* in the study area with WHO (1996) permissible limits reveal severe contamination of the mango plants (Table 7) especially in the dry season. The mean concentrations of the heavy metals in the roots, foliage (leaves), stem and

mango fruits were markedly higher than values obtained from previous studies (Ogundele et al., 2015; Opaluwa et al., 2012; Pugh et al., 2002). The health implication of this could be disastrous if the miners and local residents are not warned concerning the consumption of mango fruits harvested in the mining vicinity. Gradual accumulation of the toxins is possible if precautionary measures are not taken such as replacing *M. indica* and any other fruit or medicinal tree in the mining environment with non-edible and non- medicinal trees.

DISCUSSION

Heavy metals in the gold mining areas of Zamfara State, Nigeria occurred in large amounts especially Pb and Fe. They were transported from soil moisture into the *M. indica* parts mainly through the root system before being transferred to other parts of the plant. This explained the higher abundance of the metals in the roots more than other parts of the mango plant. The metal levels in the roots, stem, leaves and fruits determined across the sampling stations showed significant difference ($P < 0.05$) with the mining areas having higher values than the control. This could be as a result of uncontrolled and direct discharge of the mining waste into the ambient environment from where these metals were absorbed (Tsafa et al., 2012). Also, Yang et al. (2014) investigated the relationship between soils and plants containing heavy metal concentrations in Nepal and reported that the capability of heavy metal transfer to the plants was significantly increased by soils heavy metal concentrations and bioavailability of the specie that could influence the soil-plant transfer process. Heavy metals can accumulate in different plant parts although the accumulation rate may differ from part to part or organ to

Table 6. BAF values of mango plants analysed from the study sites in the wet season (July / August 2014).

Specific heavy metals	Maraba	Duke	Kwali
Pb	1.07	0.89	1.44
Cd	0.14	0.76	0.15
As	2.23	4.28	22.43
Ni	1.92	2.11	0.51
Cu	0.99	0.84	1.17
Cr	81.83	19.80	7.83
Mn	2.0	1.85	1.96
Zn	0.79	0.39	0.81
Co	15.80	16.90	18.75
Al	1.0	0.95	1.41
Fe	1.08	1.01	1.01
Au	1.0	1.0	0.87

Table 7. Comparative evaluation of heavy metal levels in mango parts with permissible limits in plants (mg/kg)

Specific heavy metals	Roots (Kwali)*	Leaves (Kwali)*	Fruit (Kwali)*	Wheat (Ekmeypapar et al., 2012)	Plant (Ogundele et al., 2015)	WHO (1996)
Pb	95.17	67.11	35.78	1.0	397	2
Cd	4.59	2.29	3.14	-	<0.03	0.02
As	5.93	2.67	1.63	-	-	-
Ni	3.11	2.58	3.71	20	2.80	10
Cu	5.54	3.15	4.79	8.2	43.3	10
Cr	1.89	1.98	1.96	-	nd	1.30
Mn	4.46	3.25	2.95	115	-	-
Zn	4.43	4.01	3.43	20	28.5	0.6
Co	2.32	2.05	1.73	-	-	-
Al	20.14	15.35	14.31	-	-	-
Fe	49.27	41.87	41.99	301	-	-
Au	16.98	20.60	16.48	-	-	-

*Present study (most impacted site).

organ (McLaughlin et al., 1999) depending on the absorption potential of the organ. The variations reported in the mango parts (root, stem leaf and fruit) were very significant indicating the extent to which toxicants can be transported in tissues especially in highly impacted areas. Similar heavy metal accumulation pattern of root > stem > leaf > fruit system was observed by George et al. (2000) in their study on accumulation of heavy metals by vegetables grown in mine wastes. However, Sun et al. (2013) reported a bioaccumulation pattern of leaf > root > stem > tuber from agricultural soils in Dehui, China. These pattern of toxicant transfer within a short period of 6 months as observed portrayed danger to the cultivation of vegetables, root crops and fruit trees in gold mining or any other industrial area.

The heavy metal levels in all mango parts showed significant difference ($P < 0.05$) between seasons with dry season having higher values than the wet season. This could be attributed to the dilution and leaching action of rain during the wet season (Yahaya et al., 2010). López-Millán et al. (2009) reported that high concentration of heavy metals have remarkable negative effects on plant growth which may include reduction in mineral concentrations, browning of the roots and changes in photosynthetic activity of the impacted plants. Heavy metals have the ability to migrate from contaminated soil to plant tissues (Stasinou and Zabetakis, 2013). As the metal concentration increases, migration commences from the roots to fruits and leaves of the plants (Rodríguez-Celma et al., 2010). Heavy metal

bioaccumulation and transfer in plants are the main exposure pathways by which humans can be harmed through food chain (Cui et al., 2004; Yu et al., 2006).

Fruits are the most important part of the plant which humans consume directly and through which they could be directly exposed to heavy metals. The concentration of heavy metals in mango fruit above permissible limit is of great concern because it points to the fact that it is risky to harvest and trade with mango fruits or vegetables cultivated near gold mining areas, since such fruits may not be fit for human consumption. The study revealed that eating mango fruit during dry season poses more risk to metal uptake than during the wet season. Most of the BAF values obtained during the study were greater than 1. This implies that *M. indica* is a hyperaccumulator (Khan et al., 2015) and could be used as bio-indicator for pollution studies.

Conclusion

In this study, heavy metal concentrations in the mango plants from the mining areas were higher compared to the control. The observed concentrations varied with the different parts of the mango plant. Heavy metals have significantly negative effects on plant growth and through the process of accumulation and food-chain transfer, may reach humans the ultimate consumer of fruit trees. It is imperative that illegal mining activities should be totally controlled and abolished by the Federal Environmental Protection Agencies or the Federal Ministry of Environment of Nigeria. The different mining companies in Nigeria should be compelled to follow every due process and comply with regulatory standards as stipulated in the Nigeria's Mineral and Mining Act of 2011. This approach shall minimise the uncontrolled discharge of mine waste into the ambient environment. Efforts should be intensified by environmental regulatory agencies in Nigeria to create awareness on the health hazards that could result if contaminated mango fruits are consumed.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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