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Accumulation of heavy metals and minerals in soil rhizosphere and organs of *Parkia biglobosa* and *Butryospermum paradoxum* growing at the lead polluted site in Niger State, Nigeria

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Abstract

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Anthropogenic activities inducing the accumulation of trace elements in Madaka village (between latitudes 6°00′ E and 7°00′ E, and 10°00′ N and 10°04′ N longitudes) of Rafi Local Government Area (Kagara, Niger State, Nigeria) have claimed many lives in the past. This study evaluated the accumulation of heavy metals and minerals in *Butryospermum paradoxum* and *Parkia biglobosa* and their soil rhizosphere at the lead polluted site around Madaka village of Rafi Local Government Area (Kagara, Niger State, Nigeria). Lead, arsenic, pH, nitrogen (%), organic carbon (%), organic matter (%), P, K, Na, Ca, Mg, N and cation exchange capacity were determined. Results showed significant differences ($p < 0.05$) between the Pb content in the soil from control (3.13 ± 1.010 mg/kg) and polluted sites (12.71 ± 1.010 mg/kg), and in the seeds of *Butryospermum paradoxum* from control (3.80 ± 0.09 mg/kg) and polluted sites (13.10 ± 0.10 mg/kg). A significant ($p < 0.05$) difference was also observed between the Pb content in *Parkia biglobosa* seeds from the control site (2.50 ± 0.10 mg/kg) and from the polluted site (14.10 ± 1.10 mg/kg). Overall, no significant differences ($p > 0.05$) were observed in the nutrient contents among all samples analysed. A significantly high concentration of Pb and As in these plants around the lead polluted site poses a great health concern. This calls for the public's attention, both governmental and non-governmental organisations, to intervene by creating awareness of the likelihood of their bioconcentration in humans and animals that consume these plants.

Keywords: anthropogenic pollution, arsenic, lead, organic carbon, trace elements.

INTRODUCTION

Artisanal mining can be defined as an unregulated informal small-scale mining system, which in the context of gold mining is known as artisanal and small-scale gold mining (ASGM) (Maria et al., 2012). Small-scale artisanal mining is practised in developing countries such as South America, Central America, Africa and Asia. Manual work is often illegal and poorly managed (Siswanto et al., 2012). For example, more than 90% of Nigeria's solid minerals are mined by artisanal and small-scale miners, who are often challenged by limited knowledge of mineral processing techniques and lack of appropriate mining methods and tools (Idowu et al., 2013). Some areas of Niger State, especially Madaka, are considered the prominent locations for artisanal and small-scale gold mining activities.

Over the years, gold mining activity has increased the leading local economy in some villages in Niger State. Children and women are increasingly involved in processing lead-contaminated gold ores, exposing themselves and their home environments to heavy metals. Mining activities can negatively impact public health, environmental safety and sustainable agriculture, and soil nutrient quality in Niger State and Nigeria. Substantial lead toxicity makes soil unsuitable for plant growth and damage biodiversity (Ghosh & Singh, 2005). Mining activities have had a tremendous negative impact on soil and plants. Mine soil is chemically, physically and biologically defective (Vega et al., 2006). Mine soil is characterised by limited cohesiveness and unstable organic matter, low nutrients and high levels of heavy metals (He et al., 2005).

The ion mechanism of lead poisoning is mainly due to the ability of lead metal ions to replace other metal ions. Divalent cations such as Ca2+, Mg2+, Fe2+ and monovalent cations such as Na+ can eventually disturb the human cell metabolism. The ionic mechanism of lead toxicity leads to significant changes in plants, animals and humans. Cell adhesion, intracellular and intercellular signalling, protein folding, maturation, apoptosis, ions, transport, enzyme regulation, and release of neurotransmitters even in picomolar concentration, lead concentration can replace calcium in the cells, which affects the concentration of protein kinase C, which regulates neural excitation and memory storage (Matta & Gjyli, 2016).

Arsenic is one of the essential heavy metals, causing ecological and personal unease in human health. It is semi-metallic and has significant toxicity and carcinogenicity properties. It is widely present in oxides or sulphides or salts such as iron, sodium, calcium and copper. However, arsenic is a protoplasmic poison that primarily affects the sulfhydryl group of cells, causing the malfunctioning of cell respiration, cell enzymes and mitosis (Matta & Gjyli, 2016).

Handmade mining activities are the primary source of heavy metal pollution near the mine sites, and the consequences are harmful since fruits and seeds form part of the food. They are considered to contain a variety of complex plant chemistry and secondary metabolites, which can protect the human body from various biological and non-biological stresses, and against diseases. When consumed, fruits are easily digestible and are associated with increased intake of minerals, vitamins and enzymes. Since ancient times, they have been a natural staple food in the human diet (Meera et al., 2011). Therefore, in addition to being used as dietary supplements, fruits and seeds have a central role in healthcare by increasing life and improving the general well-being of humans.

In the rural areas, the contributions of multipurpose indigenous agro-managed fruit trees such as *Butryospermum paradoxum* and *Parkia biglobosa* for food supply is essential for food security. They serve as a safety net during hunger periods, when stored food supplies are dwindling, and harvestings are not yet available. Therefore, the possibility of heavy metal presence in the edible part of *Parkia biglobosa* and *Butryospermum paradoxum* and their consequent bioaccumulation in humans has become a matter of concern (Singh & Kalamdhad, 2011). These two plants are processed into condiments and oil used for culinary and other purposes by the inhabitants of this place. However, heavy metal levels present in *Parkia biglobosa* and *Butryospermum paradoxum* native to mining places have not been thoroughly investigated and documented. There is also a shortage of information about heavy metals in these two trees. Therefore, it is necessary to check for the toxic inorganic contaminants level in the soil rhizosphere and these plant parts.

Therefore, this study aimed to determine the heavy metal and mineral accumulation in *Butryospermum paradoxum* and *Parkia biglobosa* and their soil rhizosphere at the lead polluted site around Madaka village of Rafi Local Government Area (Kagara, Niger State, Nigeria). This will go a long way in giving the policymaker the direction on cautioning the use of these plant parts as a food source by this affected community.

MATERIALS AND METHODS

Description of the study area

This research was carried out between May and July 2019. The study area was a mining site in Madaka, the Rafi Local Government Area of Kagara (Niger State, Nigeria). Madaka is a lead polluted town, while Kagara town was used as a control site. Madaka is about 33.5 km from Kagara. It lies between 6°00′ E and 7°00′ E, and 10°00′ N and 10°04′ N (Fig. 1). The region has two distinct seasons: the dry and the rainy season. The mean annual rainfall in the area is 1200 mm, while the minimum and maximum mean annual temperatures are 26°C and 34°C, respectively. The site's vegetation is typical Guinea savannah, which comprises tall grasses with a series of trees within the vegetation. The trees become more abundant along the River Channel.

Sample collection

Twelve sampling trees were identified, marked for collection and used for this study. Six samples of the plants and soils were collected at each site: Madaka and Kagara, three for each plant species. The soil rhizosphere was collected from 5 cm depth around the plants. The leaves and seeds of the two plants were collected following the methods by Jones & Case (1990). The plant samples were identified at the Department of Plant Biology, Federal University of Technology, Minna, Nigeria. The voucher specimens number FUT/PLB/FAB/003 for *Parkia biglobosa* and FUT/PLB/SAP/004 for *Butryospermum paradoxum*.

Processing and digestion of samples

The samples were processed for analysis following the method by Sina & Traore (2002).

The fruit husk and pulp were removed by hand and then air-dried for two weeks in the Laboratory, Department of Plant Biology, Federal University of Technology, Minna. The samples were then ground using a pestle and mortar. Finally, the ground samples were sieved to obtain a uniform particle size for each sample (Rana et al., 2010) and kept in a polythene bag.

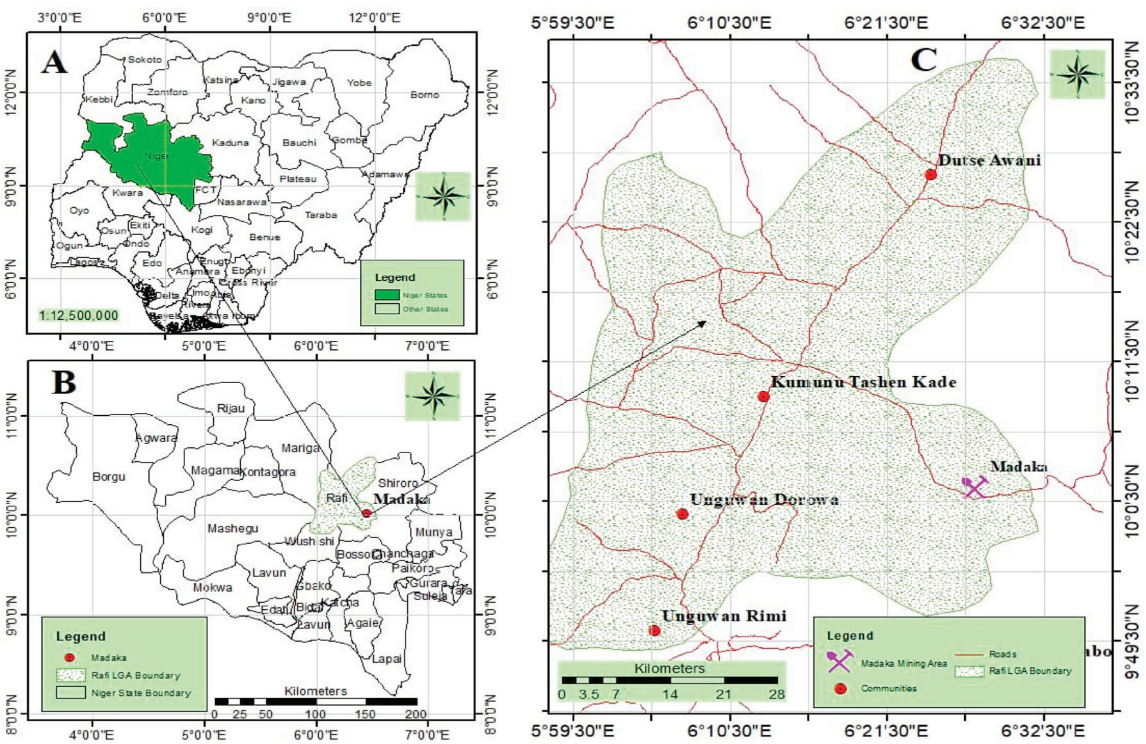

Fig. 1. Map of Madaka village illustrating lead polluted site from artisanal mining in Rafi Local Government Area of Niger State, Nigeria

Samples were digested using HNO_3, H_2O_2 and HCl as described by Edgell (1988). HNO_3 and HCl were added in 1 : 1 ratio (10 cm^3) to 2 g of the sample and mixed thoroughly. The samples were heated to 95°C in the heating chamber. After the samples were digested, it was then cooled and diluted to 100 cm^3 with water and filtered with filter paper before analysis.

Analyses of plant and soil samples

The methods described by Pirie (1955) were used for the mineral and proximate determination of the following parameters: moisture content, ash content, crude fibre, crude lipid, nitrogen and crude protein, carbohydrate, P, Na, K, Ca, Mg and N. The methods described by Uriyo & Singh (1974) were used for the determination of soil pH, carbon, exchangeable anion, cation exchange capacity and nitrogen.

The Pb, As, and some nutrient (P, K, Ca, Na, Mg and N) concentrations of digested samples were determined by Microwave Plasma Atomic Emission Spectroscopy (MP-AES, *Agilent 4100*). The *Agilent MP Expert* software was used to subtract the background signal from the analytical signal. A background spectrum from a blank solution was recorded and automatically subtracted from each standard, and the sample solution analysed at varying wavelengths.

Statistical analysis

All the triplicate data generated were analysed using Statistical Package for Social Sciences (*SPSS*, version *20.0*). Independent sample Student's *t*-test was used to compare the mean of data for significant differences. The $p < 0.05$ was considered statistically significant.

RESULTS

Heavy metal concentration in soil rhizospheres

In the soil rhizosphere of *Butryospermum paradoxum*, a significantly ($p < 0.05$) higher concentration of lead (12.71 ± 1.01 mg/kg) was recorded at the polluted site in Madaka compared to that (3.13 ± 1.01 mg/kg) at the control site in Kagara (Table 1). No significant ($p > 0.05$) differences were noticed in the arsenic concentration of *Butryospermum paradoxum* soil rhizospheres between polluted and control sites. The lead and arsenic concentrations of *Parkia biglobosa* soil rhizosphere from the Madaka village site were significantly higher than the values recorded at the Kagara control site.

Mineral composition of soil rhizosphere

Analysis of mineral composition in the soil rhizosphere of *Butryospermum paradoxum* (Table 2) and *Parkia biglobosa* (Table 3) revealed no significant ($p > 0.05$) differences among all the soil parameters analysed.

Nutrient composition in seeds

The results (Tables 4–5) showed the nutrient composition in the seeds of *Parkia biglobosa* and *Butryospermum paradoxum* at the Madaka and Ka-

Table 1. Heavy metal concentration in soil rhizosphere of *Butryospermum paradoxum* and *Parkia biglobosa* at the Madaka and Kagara sites

Treatments	Heavy metals	
	Pb (mg/kg)	As (mg/kg)
Kagara *Butryospermum paradoxum*	3.13 ± 1.01	25.56 ± 1.01
Madaka *Butryospermum paradoxum*	12.71 ± 1.01	26.37 ± 1.01
p	0.00	0.38
Kagara *Parkia biglobosa*	2.17 ± 1.01	31.77 ± 1.01
Madaka *Parkia biglobosa*	8.18 ± 1.01	34.94 ± 1.01
p	0.02	0.02

Table 2. Mineral composition of soil rhizosphere of *Butryospermum paradoxum* at the Madaka and Kagara sites. Abbreviations: OC – organic carbon, OM – organic matter, EA – exchangeable anion, CEC – cation exchange capacity

Parameters	Treatments		*p*
	Kagara	Madaka	
pH	5.86 ± 0.50	6.20 ± 0.70	0.55
OC (%)	1.65 ± 0.90	3.60 ± 2.04	0.21
OM (%)	2.52 ± 1.52	3.13 ± 2.14	0.71
N (%)	0.21 ± 0.21	0.15 ± 0.01	0.12
P (mg/kg)	18.52 ± 1.60	22.23 ± 4.70	0.64
K (mg/kg)	1.52 ± 1.52	0.30 ± 0.17	0.18
Na (mg/kg)	0.60 ± 0.14	0.53 ± 0.60	0.90
Ca (mg/kg)	3.52 ± 1.13	3.49 ± 2.10	0.99
Mg (mg/kg)	9.50 ± 3.03	3.91 ± 2.02	0.20
EA (cmol/kg)	1.02 ± 0.44	1.32 ± 0.44	0.80
CEC (cmol/kg)	14.11 ± 2.43	9.84 ± 3.61	0.20

Table 3. Mineral composition of soil rhizosphere of *Parkia biglobosa* at the Madaka and Kagara sites. Abbreviations: OC – organic carbon, OM – organic matter, EA – exchangeable anion, CEC – cation exchange capacity

Parameters	Treatments		
	Kagara	Madaka	*p*
pH	5.80 ± 0.40	5.60 ± 0.70	0.73
OC (%)	1.10 ± 0.73	2.30 ± 0.61	0.54
OM (%)	3.30 ± 1.23	3.10 ± 1.04	0.51
N (%)	0.30 ± 0.22	0.20 ± 0.10	0.14
P (mg/kg)	19.90 ± 6.70	18.80 ± 1.90	0.80
K (mg/kg)	0.42 ± 0.20	0.50 ± 0.14	0.70
Na (mg/kg)	0.50 ± 0.22	0.60 ± 0.10	0.70
Ca (mg/kg)	2.54 ± 0.60	2.72 ± 1.22	0.83
Mg (mg/kg)	4.74 ± 3.40	6.91 ± 3.34	0.50
EA (cmol/kg)	0.63 ± 0.20	0.91 ± 0.02	0.04
CEC (cmol/kg)	9.20 ± 3.40	11.60 ± 1.90	0.34

Table 4. Mineral contents of *Butryospermum paradoxum* seeds at the Madaka and Kagara sites

Parameters	Kagara	Madaka	*p*
Mg (mg/kg)	3.10 ± 0.10	3.88 ± 0.10	0.50
Na (mg/kg)	2616.70 ± 284.31	3083.33 ± 448.14	0.02
K (mg/kg)	8950.00 ± 312.30	10966.70 ± 2414.71	0.23
P (mg/kg)	2037.34 ± 556.70	1988.10 ± 337.80	0.90
N (mg/kg)	2.91 ± 0.10	2.52 ± 0.42	0.20

Table 5. Mineral contents of *Parkia biglobosa* seeds at the Madaka and Kagara sites

Parameters	Kagara	Madaka	*p*
Mg (mg/kg)	33.10 ± 0.03	4.01 ± 0.01	0.19
Na (mg/kg)	2733.33 ± 288.70	2783.33 ± 104.10	0.80
K (mg/kg)	11033.33 ± 1626.60	11166.70 ± 838.70	0.91
P (mg/kg)	2933.90 ± 451.10	2798.43 ± 221.40	0.62
N (mg/kg)	2.81 ± 0.20	3.81 ± 3.31	0.05

gara sites, respectively. There was no significant ($p > 0.05$) difference in Mg, Na, K, P, and N. However, Mg, Na, K, P, and N contents of *Parkia biglobosa* did not show a significant ($p > 0.05$) difference.

Heavy metal concentration in seeds and leaves

Heavy metal concentration in seeds and leaves of *Butryospermum paradoxum* at the lead polluted site in Madaka and the control site (Kagara) were significantly ($p < 0.05$) different (Table 6). The Pb content in *Butryospermum paradoxum* seeds (13.10 ± 0.10 mg/kg) at the polluted site was significantly ($p < 0.05$) higher than at the control site (3.80 ± 0.09 mg/kg). The As content in *Butryospermum paradoxum* seeds (4.12 ± 0.13 mg/kg) at the polluted site was significantly ($p < 0.05$) higher than that at the control site (3.72 ± 0.10 mg/kg). There was no significant ($p > 0.05$) difference in the Pb and As contents between the leaves samples.

The Pb content in the seeds of *Parkia biglobosa* (14.10 ± 1.10 mg/kg) at the polluted site (Table 7) was significantly ($p < 0.05$) higher than the value recorded at the control site (2.50 ± 0.10 mg/kg). However, no significant ($p > 0.05$) difference was observed in As contents of the samples.

Table 6. Heavy metal concentration in seeds and leaves of *Butryospermum paradoxum* at the Madaka and Kagara sites

Treatments	Heavy metals (mg/kg)	
	Pb	As
Kagara, seeds	3.80 ± 0.09	4.12 ± 0.13
Madaka, seeds	13.10 ± 0.10	3.72 ± 0.10
p	0.000	0.0133
Kagara, leaves	6.11 ± 1.10	3.778 ± 0.11
Madaka, leaves	8.83 ± 0.10	3.819 ± 0.10
p	0.053	0.599

Table 7. Heavy metal concentration in seeds and leaves of *Parkia biglobosa* at the Madaka and Kagara sites

Treatments	Heavy metals (mg/kg)	
	Pb	As
Kagara, seeds	2.50 ± 0.10	3.10 ± 0.10
Madaka seeds	14.10 ± 1.10	3.84 ± 0.32
p	0.001	0.085
Kagara, leaves	6.41 ± 3.55	3.10 ± 0.21
Madaka, leaves	10.80 ± 0.53	3.10 ± 0.04
p	0.101	0.598

Table 8. Nutrient contents in leaves of *Butryospermum paradoxum* at the Madaka and Kagara sites

Parameters	Kagara	Madaka	*p*
Mg (mg/kg)	3.10 ± 0.10	3.88 ± 0.10	0.50
Na (mg/kg)	2616.70 ± 248.31	3083.33 ± 448.14	0.20
K (mg/kg)	8950.00 ± 312.30	10966.70 ± 2414.71	0.23
P (mg/kg)	2037.34 ± 556.70	1988.10 ± 337.80	0.90
N (mg/kg)	2.917 ± 0.10	2.52 ± 0.42	0.20

Table 9. Nutrient contents in leaves of *Parkia biglobosa* at the Madaka and Kagara sites

Parameters	Kagara	Madaka	*p*
Mg (mg/kg)	3.73 ± 0.06	3.81 ± 0.01	0.97
Na (mg/kg)	2733.33 ± 837.16	2966.67 ± 246.64	0.67
K (mg/kg)	7833.33 ± 448.14	9200.30 ± 289.76	0.52
P (mg/kg)	2222.11 ± 437.31	3233.36 ± 924.87	0.16
N (mg/kg)	16.71 ± 21.65	4.13 ± 0.06	0.38

Nutrient composition in leaves

The results of the analysis revealed that nutrient composition in leaves of *Butryospermum paradoxum* (Table 8) and *Parkia biglobosa* (Table 9) at the Madaka and Kagara sites had no significant ($p > 0.05$) differences between the studied samples.

DISCUSSION

This study suggested that heavy metals at the illegal mining site did not significantly influence the mineral compositions in the soil rhizosphere, leaves and fruits of *Parkia biglobosa* and *Butryospermum paradoxum*, the native tree species of the sites. In addition, heavy metal and nutrient analyses of the two plants have revealed that they are not in equal proportions. Therefore, the higher concentration of lead observed in the soil rhizosphere of *Butryospermum paradoxum* at Madaka lead polluted site might be due to artisanal gold mining being practised in this vicinity.

Although the values are currently not higher than the WHO (1996) recommended value, if the practice is not regulated, there may be a high level of Pb accumulation in the soils. More so, soil with a high lead concentration is prone to limited cohesion and instability with low organic matter and low nutrients. This suggestion conforms with the finding of He et al. (2005), who have reported a high level of heavy metals in mine soil. Ghosh & Sing (2005) have found that mining activities usually bring about land degradation and heavy metal accumulation. Similarly, gold mining activity may be the primary factor responsible for the observed higher concentration of Pb and As in *Parkia biglobosa* from the soil rhizosphere of the lead polluted site compared to that of the control site. This is because most artisanal gold miners have limited knowledge of mineral processing techniques that are environmentally friendly. A similar reason has been previously given by Idowu et al. (2013). The presence of heavy metals at the control site might be due to automobile emissions since it is situated along the federal highway. However, many factors such as height, texture and organic matter concentration may also be attributed to higher As content, which appears to be found in *Parkia biglobosa* at the polluted site. This corroborates the earlier findings of Rieuwerts et al. (1998), who have reported a high amount of metal in soil with the characteristics mentioned above. In addition, the following mineral composition: pH, organic carbon, organic matter, N, K, Na, Ca, Mg, exchangeable anions and cations exchange capacity from the rhizosphere of *Butryospermum paradoxum* and *Parkia biglobosa*, which did not vary significantly, probably due to the presence of other plants coexisting with *Butryospermum paradoxum* and *Parkia biglobosa*, and providing a mechanism of stabilising these mineral elements.

The Mg, Na, K, P and Na of *Butryospermum paradoxum* and *Parkia biglobosa* seeds at the lead polluted site do not differ much from those of the control; this may be due to root types, and the mode of transporting the elements across to the shoot system. However, we could not lay our hands on any information regarding how these elements are transported across the shoot. However, Adebayo et al. (2017) have reported a low amount of these elements in gold mining soil, making the plants growing on it at a disadvantage in acquiring some of these nutrient elements due to the high level of competition within and between these plants. Lead content that appears much in the seeds of *Butryospermum paradoxum* at the polluted site than that of the control site may be attributed to transporting lead from the root through the xylem to the shoot and distributed pattern around the seed portion. This agrees with the finding of other studies (Bartrem et al., 2014; Lo et al., 2012). They have reported heavy metal accumulation in the fruits and leaves of arable and cash crops. Much difference in lead contents of the leaves recorded at the polluted site than that of the control site may be due to phytovolatilisation, which might have helped reduce the volume of lead in it through evapotranspiration. In addition, the high amount of phosphorus recorded in the study can also help in lead depletion in plant parts. This is also in line with the finding of Ambika et al. (2016), who have reported the accumulation and reduction of lead in plants in the presence of cadmium and phosphorus.

Arsenic content in the seeds and leaves of *Butryospermum paradoxum* does not show any significant difference ($p > 0.05$). However, that of the polluted site was higher than that of the control site. This may be because of lead and arsenic in its soil, in an impure form. This is in line with Salgare & Acharekar

(1992) finding. They have said the effect of heavy metals might bring about the availability of other heavy metals in soil and plants growing at the polluted sites.

The results obtained for seeds of *Parkia biglobosa* maybe because of interference with the soil organic substances, which likely increases the chances of this heavy metal uptake by *Parkia biglobosa*. This assertion conforms with the finding of Wuana & Okieimen (2011). They have reported that the dissolved soil organic substances impact heavy metal transformation by increasing the solubility of heavy metals, root growth and plant uptake. However, the Pb content in the leaves does not show the difference. This might be because of phytovolatilisation of this metal from the leaves to the atmosphere. This is in line with Shabir et al. (2012), who have reported phytovolatilisation of Hg, As and Se. The As content in the seeds and leaves of *Parkia biglobosa* does not show many discrepancies; this may be because of enzyme activities on this metal in these organs, degrading the metal to the minimum level of less toxic over time. This is in line with Kumar et al. (2019) study, who have reported the plant's ability to metabolise heavy metals during nutrient acquisition. The following nutrient elements do not show any significant difference ($p > 0.05$); Mg, Na, K, P and N in seeds of *Parkia biglobosa*. This may be attributed to the biodegradation of heavy metals by biochemical and physiological enzymes, which tend to reduce the impact on the distribution of these nutrients in these organs. This is in line with the finding of Yan et al. (2020). They have suggested that the effects of heavy metals reduce plant growth due to changes in their biochemical and physiological activities.

CONCLUSIONS

The heavy metal content in the soil rhizosphere, seed and leaves of *Butryospermum paradoxum* and *Parkia biglobosa* at the two sites varied significantly, exceeding the recommended threshold of WHO, making the plants at the two sites unsafe for animals and humans. Our finding also revealed a high amount of lead and arsenic in the soil rhizosphere, seeds and leaves of *Butryospermum paradoxum* and *Parkia biglobosa* at the two sites. At the same time, their nutrient composition did not show much variation.

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