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Vertical distribution of lead (Pb) in farmlands around contaminated goldmine in Zamfara state, Northern Nigeria

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Anthropogenic activities such as artisanal gold mining have been shown to contaminate soils. When these soils are cultivated, lead (Pb)-related human health risks are expected consequent to consumption of crops produced from such soil. This study was conducted with the aim of determining the vertical distribution of Pb in Pb-contaminated farmlands around contaminated goldmine. Eight soil profile pits were dug 1 m deep and 1 m wide in eight different farmlands, two farmlands per cardinal point (North, South, East and West). Two replicates of disturbed samples were taken from each of the profile pits at incremental depths of 20 cm from soil surface up to 100 cm. Also composite samples were randomly taken at each farm where the profile pits were sunk. The vertical distribution of Pb with the highest concentration was 2025 mg kg^{-1} in Farm II of Dareta North at the surface soil beside the gold ore processing site. Farms in Dareta South recorded lower values than Dareta North with values ranging from 1310 to 1586 mg kg^{-1}. All Pb concentration obtained in this study exceeds the international threshold value for Pb in soils (300 mg kg^{-1}) for both EU and USA. These results have great health implication on cropping activities which remains the main activities of households in the village. Management practices such as those that will render Pb to become unavailable or bio-accumulated is suggested while an active legal institution should be in place to check indiscriminate gold mining.

Key words: Vertical distribution, lead, artisanal mining, contaminated goldmine.

INTRODUCTION

Lead (Pb) is one of those several chemicals finding their way into the subsurface environment, either intentionally applied, for example in agricultural operations, or unintentionally released from leaking industrial and municipal waste disposal sites, mines and other mine tailings, or from other sources (Šimůnek et al., 2006). Even though natural soils of the Nigerian savannah are characterized by low heavy metal concentrations due to their high weathering intensity and long period of pedogenesis (Jones and Wild, 1975; Agbenin and Latifatu, 2004; Abdu et al., 2011), intensification of artisanal gold mining has increased Pb accumulation in

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soil (Mohammed and Abdu, 2013). Heavy metal pollution of soil enhances plant uptake, causing accumulation in plant tissues, eventual phytotoxicity and change of plant community (Gimmler et al., 2002). Heavy metals accumulating in soil enter the food chain, thus endangering herbivores, carnivores and consequently, humans. Accumulation of heavy metals can also cause a considerable detrimental effect on soil ecosystems, environment and human health due to their mobility and solubility which determine their speciation (Kabata-Pendias and Pendias, 1992). Although several studies have indicated that the crops grown on soils contaminated with heavy metals have higher concentrations of heavy metals than those grown on uncontaminated soil (Nabulo, 2006; Abdu, 2010), in environments with high nutrient levels, metal uptake can be inhibited because of complex formation between nutrient and metal ions (Gothberg et al., 2004). Therefore, a better understanding of heavy metal sources, their accumulation in the soil and the effect of their presence in water and soil on plant systems seems to be a particularly important.

Many chemicals which are in the soil solution and in soluble forms are referred to as solutes. The movement of these solutes through the soil to the groundwater or free water surfaces indicates process leading to the contamination of these resources. In many cases, serious human and health implications are associated with this form of pollution. These chemicals or pollutants (as solutes) are often transported in the soil by mass flow of water (convection), diffusion and/or dispersion in either the horizontal or vertical directions, or via stream flow in surface waters (Lal and Shukla, 2004).

A deadly outbreak of acute childhood lead poisoning was discovered in the first quarter of 2010 by Médecins Sans Frontières (MSF) and Nigerian health officials conducting meningitis surveillance in Zamfara State, northwestern Nigeria (MSF, 2012). The outbreak was as a result of artisanal processing of lead-rich gold ores, which is rapidly increasing and becoming more mechanized through the use of fuel powered engine to grind the ores (Plumlee et al., 2013; MSF, 2012; United Nations Environment Programme/Office for the Coordination of Humanitarian Affairs (UNEP/OCHA, 2010; von Lindern et al., 2011). The gold processing was carried out in the vicinity of the houses of villages prior to the outbreak. After the emergence of the outbreak the Village head asked the people to move the processing from their houses to a distance of about 500 m away from their houses. According to a survey carried out by MSF, Nigeria federal and state public health agencies, U.S. Centers for Disease Control and Prevention (CDC), TerraGraphics Environmental Engineering (TG), and the World Health Organization (WHO) about 400 children less than five years of age were killed and thousands more people are said to be affected, including more than 2000 children left with permanent disabilities (Plumlee et al., 2013; Dooyema et al., 2012; Lo et al., 2012; von Lindern et al., 2011). There still remains the risk of Pb movement to the food chain through the re-location and continued artisanal mining activities (UNICEF, 2011). In view of the above this study aimed at determining the vertical distribution of Pb in farmlands near contaminated goldmine.

MATERIALS AND METHODS

Study location

The study was conducted at Dareta village, Anka Local Government Area of Zamfara State (Figure 1) in northern Nigeria. According to WHO, 2010; UNICEF, 2011, the study area was hit with major outbreaks of Pb poisoning occurring since 2010, which are related to mining processes of Pb rich ore for the extraction of gold. Dareta is located on latitude 12°06′30″N and longitude 5°56′00″E, and has an area of 2,746 km² and a population of 142,280 according to the 2006 population and housing census (NPC, 2006). The major activity of Dareta people is farming carried out both during the rainy season and under irrigated lands. Crops cultivated under rainfall condition include cowpea, sorghum, ground nut and millet. While crops cultivated under irrigation are spinach, lettuce, cabbage and onions. Dareta village is characterized with a Sudan savannah climate having an annual average rainfall of about 579 mm.

Soil sampling, handling and preparation

Eight soil profile pits were dug to a depth and width of both 1 m in eight different farmlands (as shown in Figure 2). The living perimeter of the village was secured and profile digging proceeded along the four coordinates (North, South, East and West) starting from the first farmland after the last house, on a grid at distances 50 and 100 m. Two replicates of both disturbed and undisturbed core samples were taken from each of the profile pits at a depth of 0 to 20 cm, 20 to 40 cm and 40 to 60 cm 60 to 80 cm and 80 to 100 cm. This gave a total of twenty core samples and ten disturbed samples per sampling direction. The disturbed soil samples collected were bulked, air-dried and sieved through 2 mm sieve. The less than 2 mm samples were stored properly for physical and chemical analysis.

Analytical procedures

The particle size analysis was determined by the standard hydrometer method (Gee and Bauder, 1986). Soil pH was measured at 1:2.5 soil to solution ratio with water and 0.01 M calcium chloride ($CaCl_2$) using a glass electrode. Cation Exchange Capacity (CEC) was determined by 1 N ammonium acetate (NH_4OAc) saturation method (Anderson and Ingram, 1993). Exchangeable bases (sodium, Na^+; potassium, K^+; calcium, Ca^{2+} and magnesium (Mg^{2+}) were determined after saturating and leaching the soil with 1N NH_4OAc solution. Ca^{2+} and Mg^{2+} were obtained from titration using ethylene diamine tetra-acetic acid (EDTA) method as described by Devis and Freitas (1970) and read using Fast Sequential Atomic Absorption Spectrophotometer (AAS: Model VARIAN AA240FS). Na^+ and K^+ were determined using flame photometry. Organic carbon (OC) was determined by dichromate oxidation method (Nelson and Sommers, 1982). Total concentration of metals in the soil was determined by Fast Sequential Atomic Absorbtion Spectrophotometer (AAS: Model

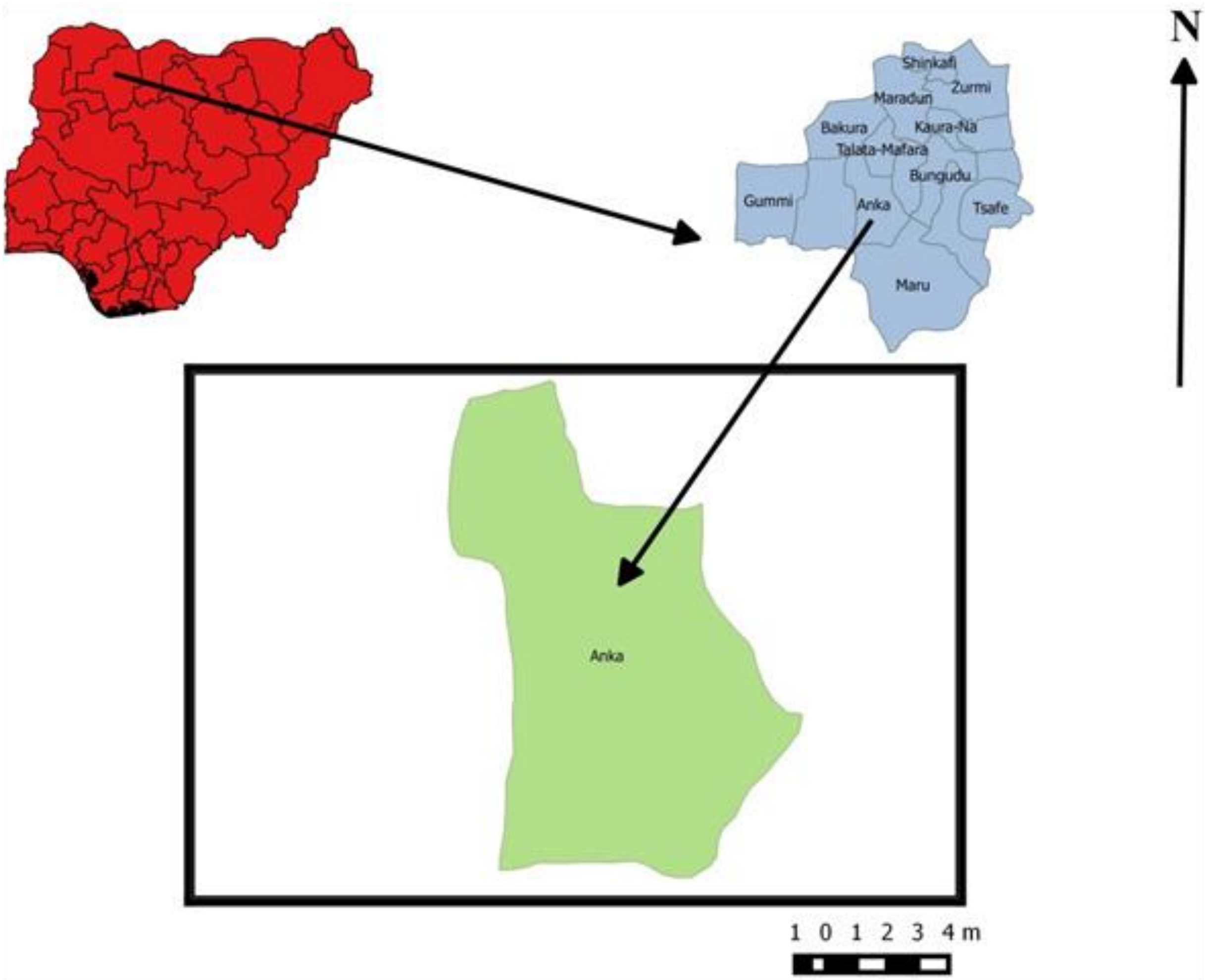

Figure 1. Map of Zamfara, showing the location of Dareta Village, where soils for the study were obtained.

VARIAN AA240FS) following aqua regia digestion as described by Lim and Jackson (1986).

The data obtained on metal concentration and the measured soil properties were subjected to simple descriptive statistics. All statistical analyses were conducted using Excel 2007 and SAS software (version 9.2; 2008).

RESULTS AND DISCUSSION

The particle size distributions of the experimental area are presented in Table 1. Soils at the 0 to 100 cm depth were predominantly clay loam, according to the USDA classification system. This coincides with reports by Jones and Wild (1975), Ogunwole and Ogunleye (2005) and that of Abdulkareem et al. (2012) that cultivated soils of the savannah region of West Africa are predominantly clay in nature down the soil profile depending upon the location. Mean values for Dareta North and Dareta South across the profile were found to be 308 and 321.00 g kg^{-1} for clay, 286 and 253.00 g kg^{-1} for silt and, 400 and 426.00 g kg^{-1} for sand as shown in Table 1. Soils of both eastern and western parts of Dareta were both predominantly clay loam at lower depths mean values of 323.00 g kg^{-1} clay, 274.40 g kg^{-1} silt and 389.00 g kg^{-1} for sand were recorded in the Dareta East. While in Dareta West, the mean values of soil fractions were 306.00 g kg^{-1} clay, 302.00 g kg^{-1} silt and 392.00 g kg^{-1} sand.

Soil pH values in the profile at lower depths (20 to 40 cm, 40 to 60 cm, 60 to 80 cm and 80 to 100 cm) were found to be neutral to slightly alkaline in water and moderately acidic to neutral in $CaCl_2$ in Dareta North and South. Mean pH of 7.76 (pH in water) and 5.95 (pH in $CaCl_2$) was observed for farm I and II in Dareta North and 7.46 (pH in water) and 6.04 (pH in $CaCl_2$) for Dareta South. Similar trend was observed in Dareta East and West where the pH in water was between neutral to slightly alkaline and strongly acidic to slightly acidic in $CaCl_2$ with means of 7.57 (pH in water) and 5.96 (pH in $CaCl_2$) for Dareta East 7.57 and 5.91 (pH in $CaCl_2$) for farm I and II in Dareta West. High Pb concentration in the

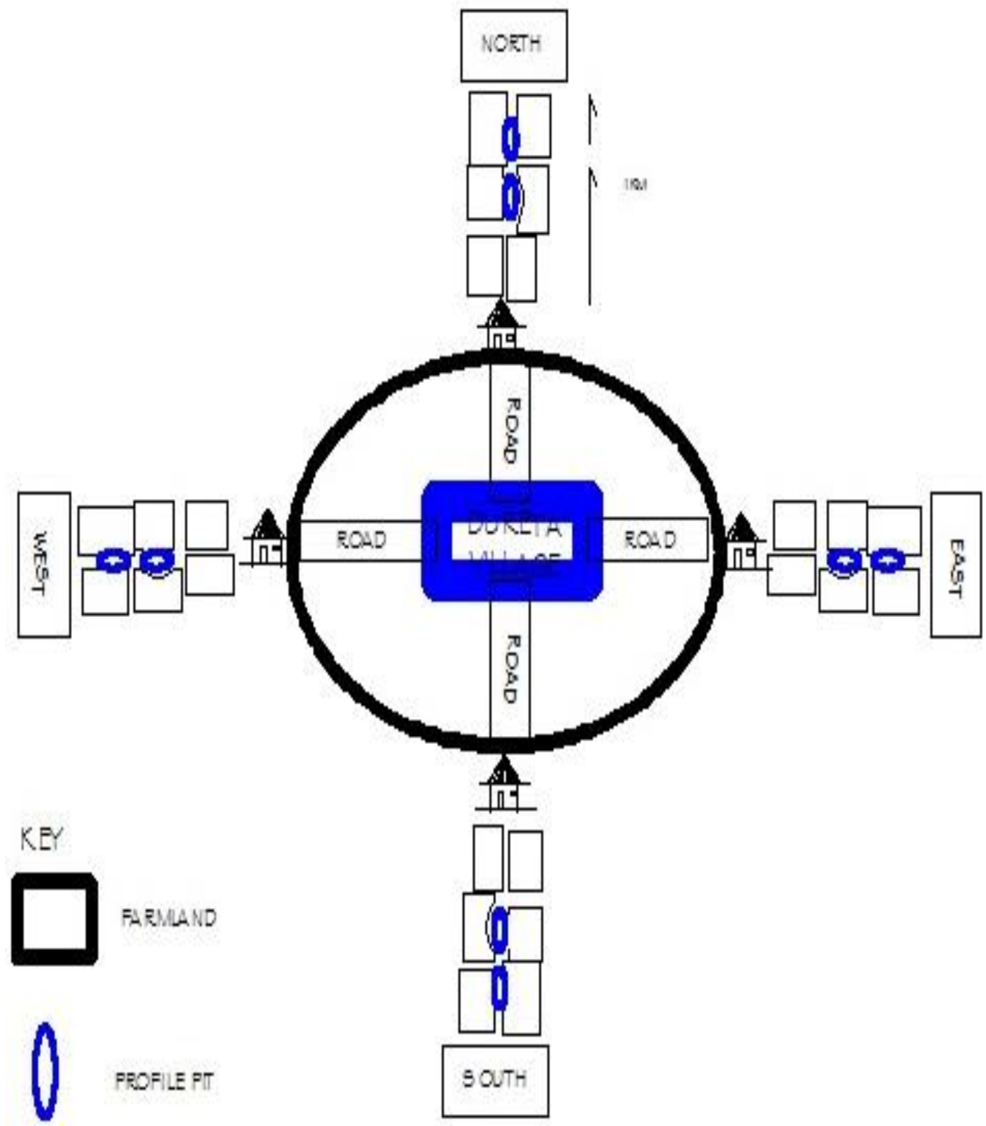

Figure 2. Field layout of the sampling points in the study location with respect to the last house in Dareta village.

Table 1. Mean particle size distribution of soil profile (0-100 cm) in the different cardinal directions of Dareta village.

Sampling direction	Clay (g kg^{-1})	Silt (g kg^{-1})	Sand (g kg^{-1})	Textural class
Dareta North	308.00	286.00	400.00	Clay Loam
Dareta South	321.00	253.00	426.00	Clay Loam
Dareta East	323.00	274.40	389.60	Clay Loam
Dareta West	306.00	302.00	392.00	Clay Loam

Mean values is for two farms across sampling direction.

study area is favoured by high pH values across the sampling directions as reported by Alloway (1995), where he states that; in heavily pollute soils, high Pb concentration is greater in soils with higher pH than in soils with low pH concentration. Mean values of CEC at lower soil depths (0 to 100 cm) of the northern and Southern part of the study area were 12.58 $cmol_{(+)}kg^{-1}$ and 15.00 $cmol_{(+)}kg^{-1}$ respectively (Table 2). Mean CEC

Table 2. Mean of profile soil chemical properties in different sampling directions of Dareta village (0-100 cm).

Sampling direction	pH (water)	pH ($CaCl_2$)	CEC ($cmol_{(+)}kg^{-1}$)	OC ($g\ kg^{-1}$)	Na ($cmol_{(+)}kg^{-1}$)	K ($cmol_{(+)}kg^{-1}$)	Ca ($cmol_{(+)}kg^{-1}$)	Mg ($cmol_{(+)}kg^{-1}$)
Dareta North I	7.58	5.86	14.00	4.70	0.40	0.45	9.42	2.85
Dareta North II	7.94	6.04	11.16	3.46	0.30	0.37	6.68	3.63
Mean	**7.76**	**5.95**	**12.58**	**4.08**	**0.35**	**0.41**	**8.05**	**2.24**
Dareta South I	7.6	6.14	12.08	5.04	0.26	0.35	7.99	2.98
Dareta South II	7.32	5.94	17.92	2.16	0.56	0.40	9.59	4.13
Mean	**7.46**	**6.04**	**15.00**	**3.60**	**0.41**	**0.38**	**10.29**	**3.05**
Dareta East I	7.58	5.96	12.74	3.72	0.27	0.30	7.70	2.63
Dareta East II	7.56	5.96	14.30	2.94	0.20	0.30	10.75	2.89
Mean	**7.57**	**5.96**	**13.52**	**3.33**	**0.24**	**0.30**	**9.23**	**2.76**
Dareta West I	7.72	5.82	15.90	4.54	0.35	0.30	11.26	3.81
Dareta West II	7.42	6.00	13.12	4.72	0.57	0.46	7.96	4.84
Mean	**7.57**	**5.91**	**14.51**	**4.60**	**0.46**	**0.38**	**10.61**	**4.32**

Mean represents values from five samples taken for each soil property, I = farm I, II = farm.

of 11.52 $cmol_{(+)}kg^{-1}$ were obtained for Dareta East and 14.51 $cmol_{(+)}kg^{-1}$ for Dareta West. This classifies the soils as low to highly fertile by Soil Survey Staff (1993). The moderately high CEC obtained might be attributed to high percentage of clay values (180 g kg^{-1} and 200 g kg^{-1}) obtained in the Dareta North and South. Owing to the low OC content of the studied soil in Dareta North and South, this finding did not corroborate that which states that CEC of savanna soils are influenced more by organic carbon than the clay content (Jones and Wild, 1975; Wuddivira, 1998). The results for the OC at the surface soil (0 to 100 cm) are presented in Table 2. The results ranged from 0.6 to 11.00 g kg^{-1}. Mean soil organic carbon contents obtained are 3.30 g kg^{-1} in Dareta North, 3.20 g kg^{-1} in Dareta South, 8.40 g kg^{-1} in Dareta East and 4.10 g kg^{-1} in Dareta West.

Results of the vertical distribution of Na, Ca and Mg in Dareta village are presented in Figures 4 to 6. No clear trend with respect to the exchangeable bases was observed. Higher mean Na contents were obtained in Dareta South (0.41 $cmol_{(+)}kg^{-1}$) and Dareta West (0.46 $cmol_{(+)}kg^{-1}$) than other cardinal directions as shown in Table 2. In Dareta South I and II, mean values of 0.26 $cmol_{(+)}kg^{-1}$ and 0.56 $cmol_{(+)}kg^{-1}$ were obtained respectively. The high Na content obtained from Dareta South and Dareta West might be as a result of Na being held with a much lower energy on soil colloids than either K or the divalent Ca and Mg ions and is, therefore, easily lost through leaching (Tisdale and Nelson, 1975).

In Dareta East and Dareta West, the trend varies where values obtained indicates medium to high exchangeable K contents. Values range 0.18-044 $cmol_{(+)}kg^{-1}$ in the Dareta East and 0.20 to 0.77 $cmol_{(+)}kg^{-1}$ in the Dareta West. No clear distribution with respect to K content was observed. This may be attributed to more intense weathering, release of labile K from organic residues, application of K fertilizers and upward translocation of K from lower depth along with the capillary use of ground water (Sai Kumar et al., 2013). Calcium in Dareta village recorded high mean values of 8.05 $cmol_{(+)}kg^{-1}$ in the Dareta North and 10.29 $cmol_{(+)}kg^{-1}$ in the Dareta South (Table 2). Similar patterns of high Ca contents were also obtained in both eastern and western parts of the study area with mean values of 9.23 $cmol_{(+)}kg^{-1}$ and 10.61 $cmol_{(+)}kg^{-1}$ respectively. The content of exchangeable Ca in the soils appeared to be directly related to leaching intensity, as affected by the amount effective precipitation received (Shobayo, 2010), thus, Ca was lower at the surface than the underlying subsoil. The predominance of Ca over cations may be related to high Ca content of harmattan dust material added annually and/or to parent materials high in Ca (Malgwi, 2001). This dominance of Ca over other exchangeable bases is in consonance with results of several other researchers (Esu, 1987; Mosugu, 1989; Kparmwang, 1993; Zarafi, 1993; Abdullahi, 1997; Maniyunda, 1999; Yaro et al., 2002). Magnesium values are generally in the high range as shown in Table 2 even though soils

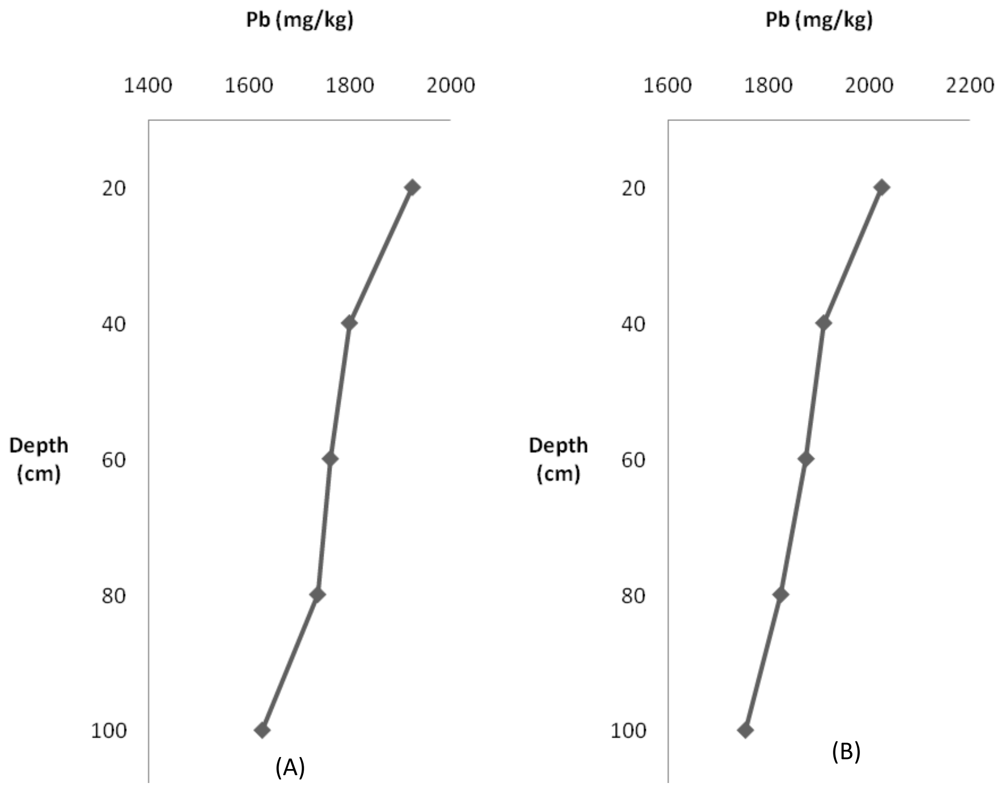

Figure 3. (a) Vertical Distribution of Pb in Dareta North 1, (b) Vertical Distribution of Pb in Dareta North II.

were rated to have low to medium concentration. In the Dareta, North, a mean value of 2.24 $cmol_{(+)}kg^{-1}$ was observed. While in Dareta South, a mean value of 3.05 $cmol_{(+)}kg^{-1}$ was obtained. Increase in Mg content with depth in soil may be attributed to the leaching of Mg from the surface to the subsoil as this is thought to have no effect soil structure and therefore does not influence infiltration during lysimeters studies.

Vertical distribution of Pb in Dareta village

The vertical distribution of Pb in Dareta village is presented in Figures 3 A-H for farm I and farm II, across the sampling directions. In farm II of Dareta North, the Pb concentration ranges from 1627 to 2025 $mgkg^{-1}$ with the highest concentration (2025 mg kg^{-1}) observed at the surface soil is located near the gold ore processing site. Farms in Dareta South recorded lower values than Dareta North with values ranging from 1310 to 1586 $mgkg^{-1}$. Lower concentrations at lower depths were observed in surface soils of Dareta East and Dareta West. Lead concentrations as low as of 604 and 625 mg kg^{-1} were observed in farms I and II of Dareta East respectively, and 740 and 876 mg kg^{-1} for farms I and II in Dareta West respectively. Caution should be carried out when selecting sites for sample collection. This will ensure representative sampling of the study area as the Pb pollution is not evenly represented in the area. High concentrations of Pb down the soil profile suggest geological sources of Pb across the sampling directions

The trend for high concentration of Pb in the upper depths than the lower depths may be as a result of superficial enrichment through human activities such as mining. It could also reflect metals affinity for organic matter (Agbenin, 2002). Lead fixation by organic matter has been shown to be more important than fixation by hydrous oxides (Li and Shuman, 1996), and the surface horizons of most soils contain higher organic matter relative to the successive lower horizons. High concentrations of Pb observed at lower depth suggested that Pb was translocated via facilitated transport with the colloidal clay particles during elluviation, hence deposition of clay was accompanied by that of Pb as clay increased with increase in depth. Similar observations were made by Mohammed and Abdu (2013) on Pb distribution in the same soils of Dareta It could also be as a result of capillary rise of Pb polluted ground water. The source of pollution of the ground water is most likely from the washing of metal ores in streams and household. Where the water saturating this horizon is polluted, it could result in accumulation of metals at this zone relative to other zones; hence contamination from a receding ground water table may occur with time.

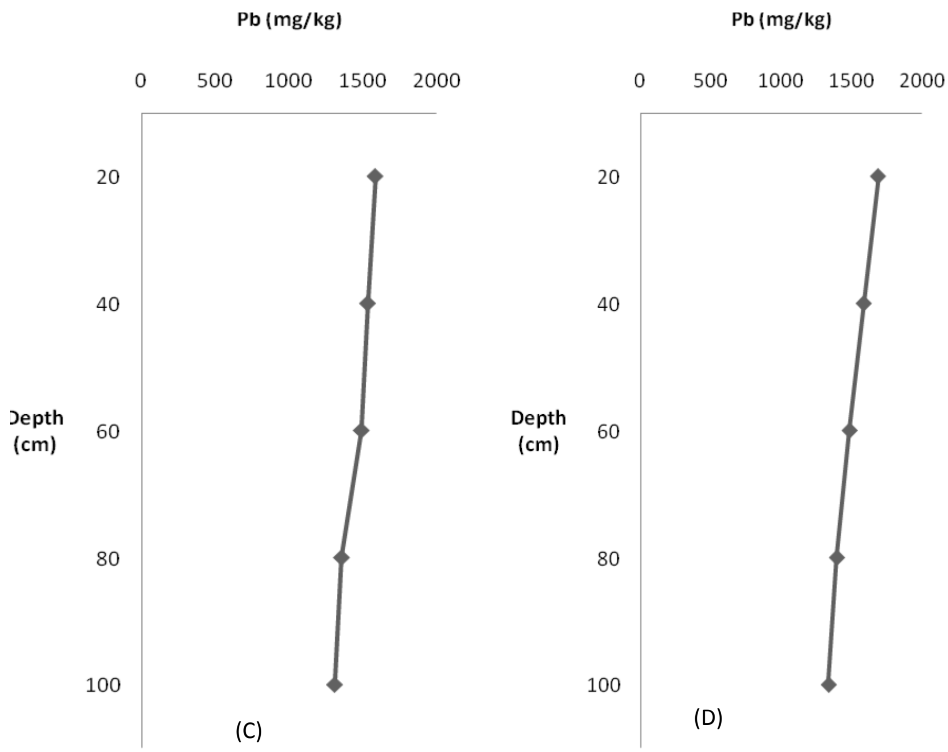

Figure 3. (c) Vertical Distribution of Pb in Dareta South 1, (d) Vertical Distribution of Pb in Dareta South II.

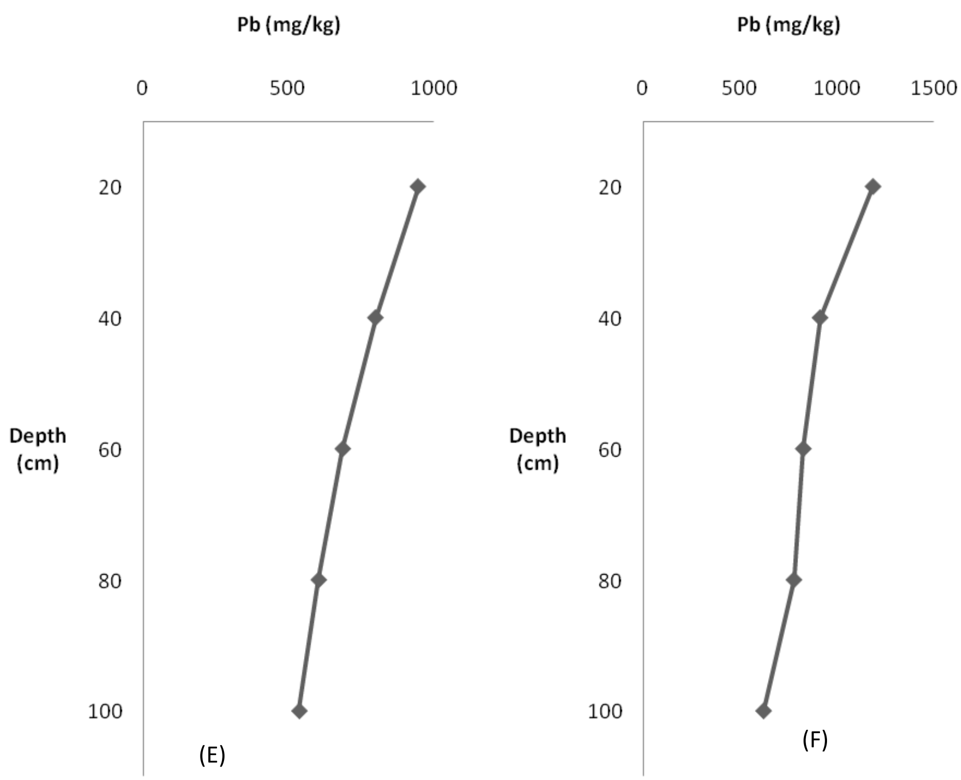

Figure 3. (e) Vertical Distribution of Pb in Dareta East 1, (f) Vertical Distribution of Pb in Dareta East II.

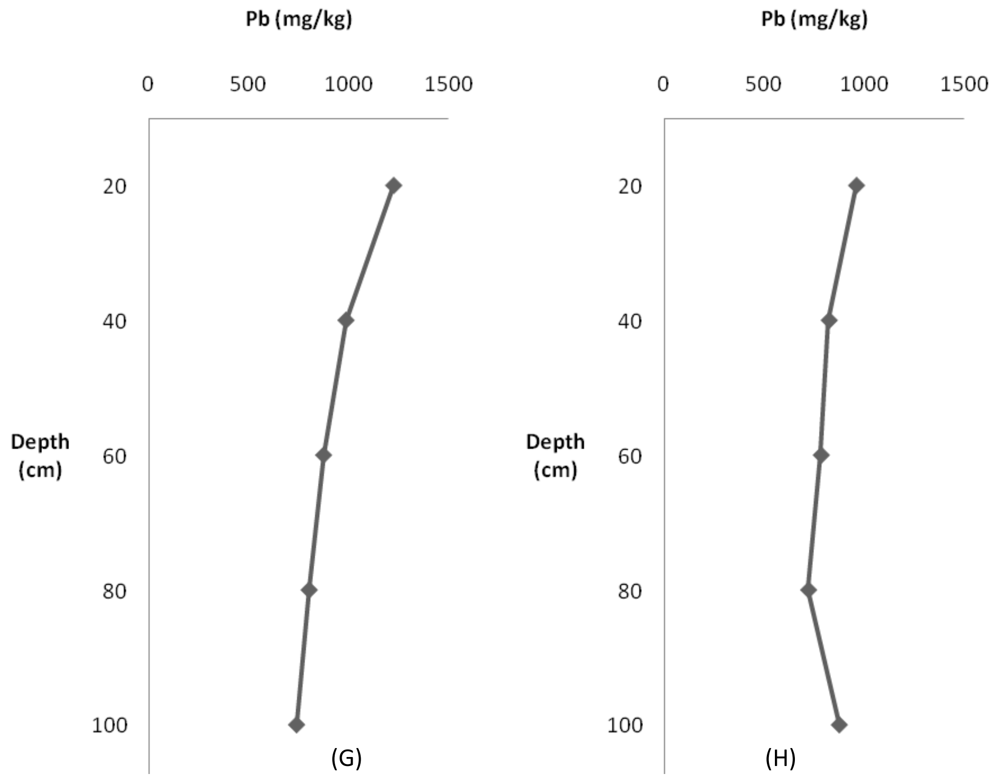

Figure 3. (g) Vertical Distribution of Pb in Dareta West 1, (h) Vertical Distribution of Pb in Dareta West II.

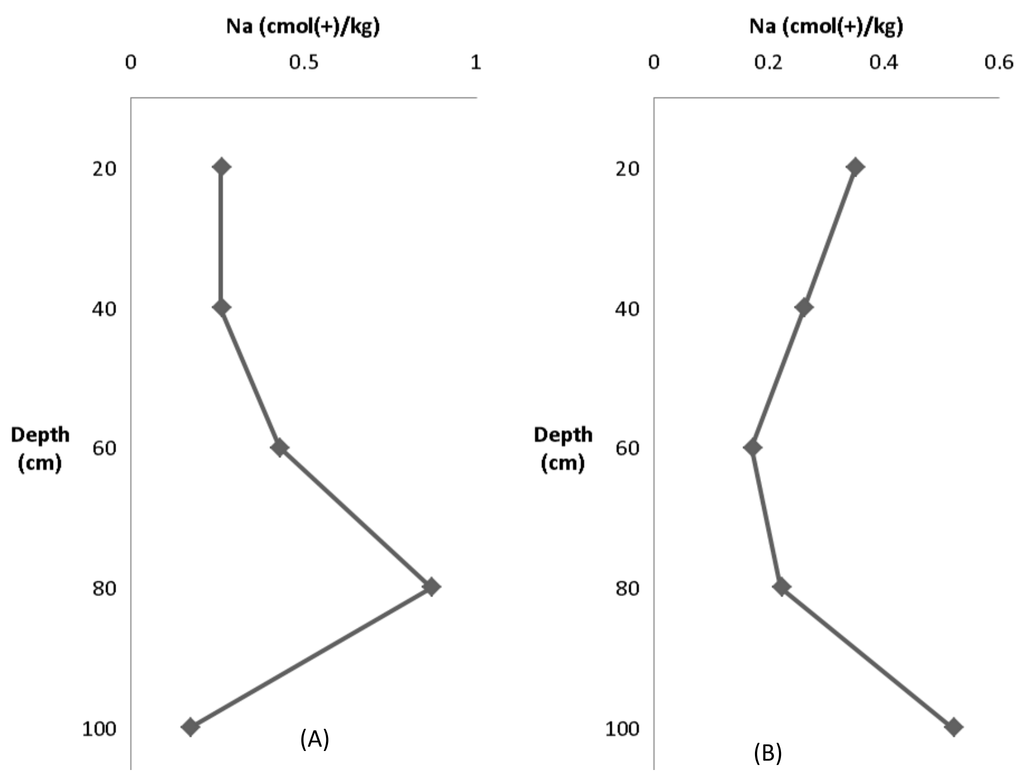

Figure 4. (a) Vertical Distribution of Na in Dareta North I, (b) Vertical Distribution of Na in Dareta North II.

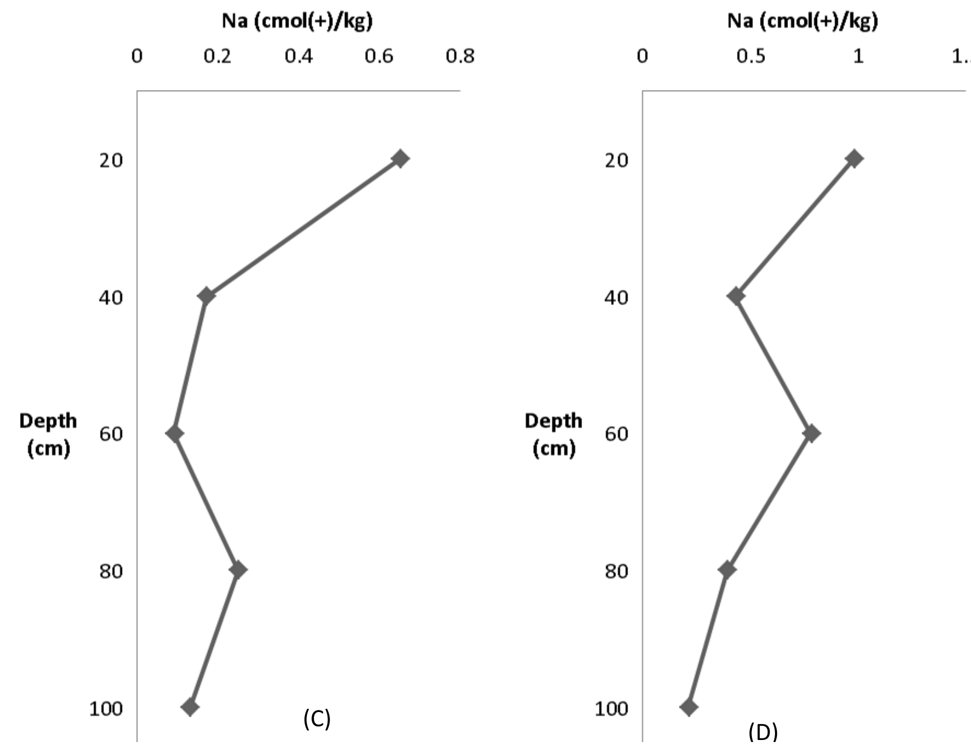

Figure 4. (c) Vertical Distribution of Na in Dareta South I, (d) Vertical Distribution of Na in Dareta South II.

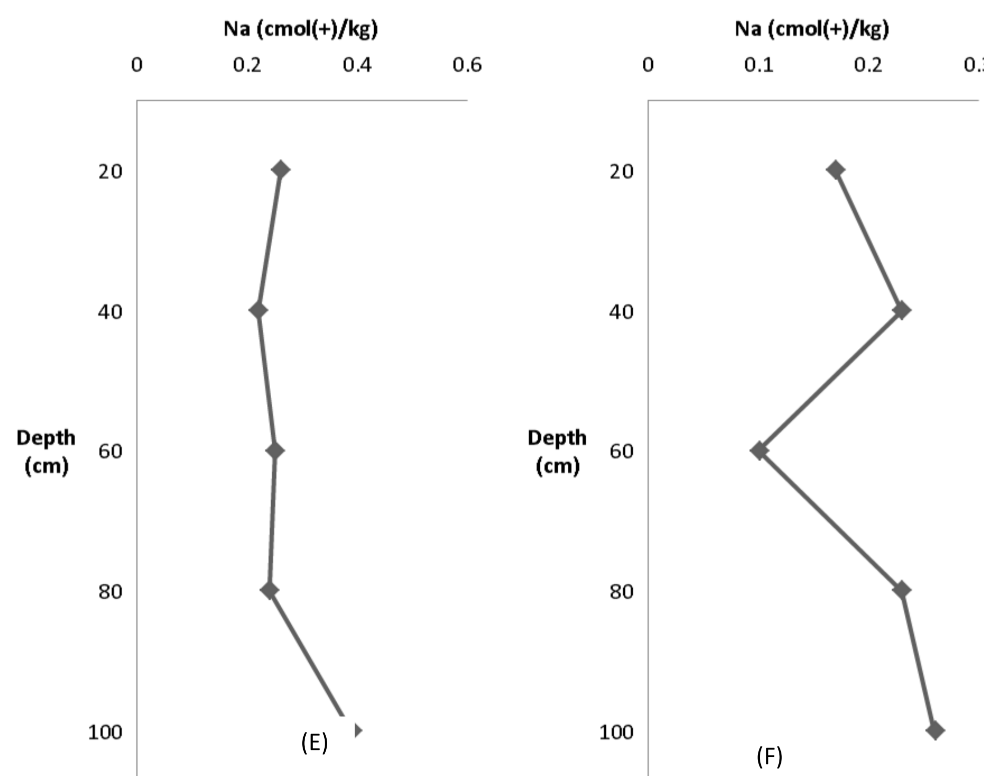

Figure 4. (e) Vertical Distribution of Na in Dareta East I, (f) Vertical Distribution of Na in Dareta East II.

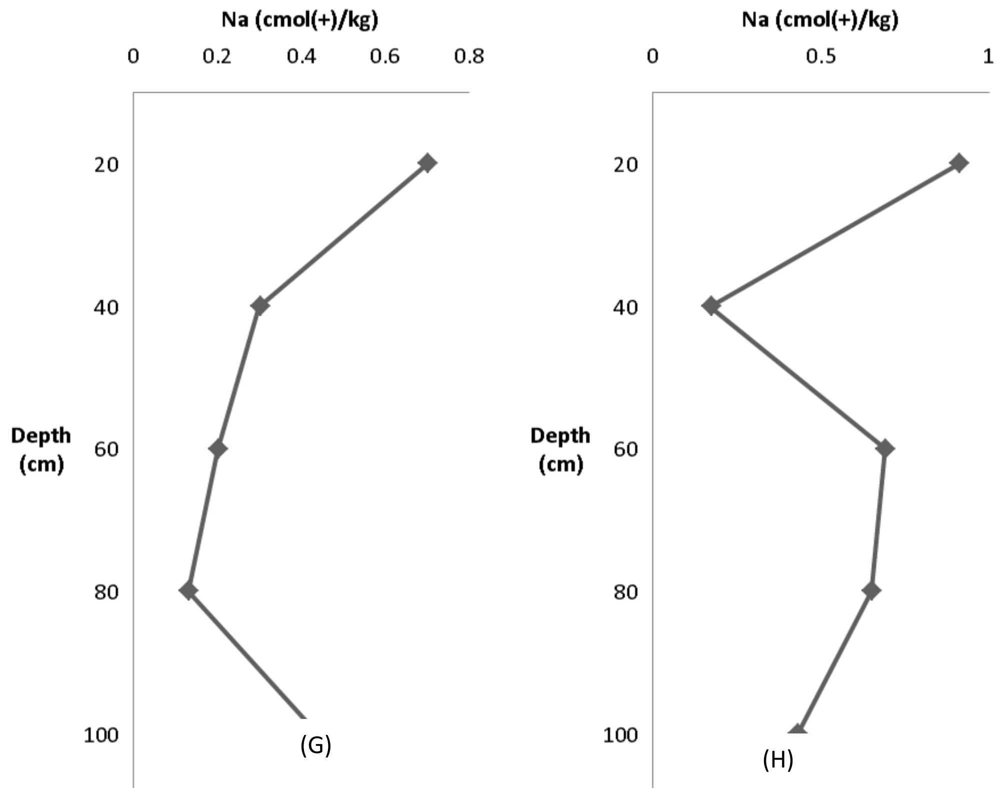

Figure 4. (g) Vertical Distribution of Na in Dareta West I,(h) Vertical Distribution of Na in Dareta West II.

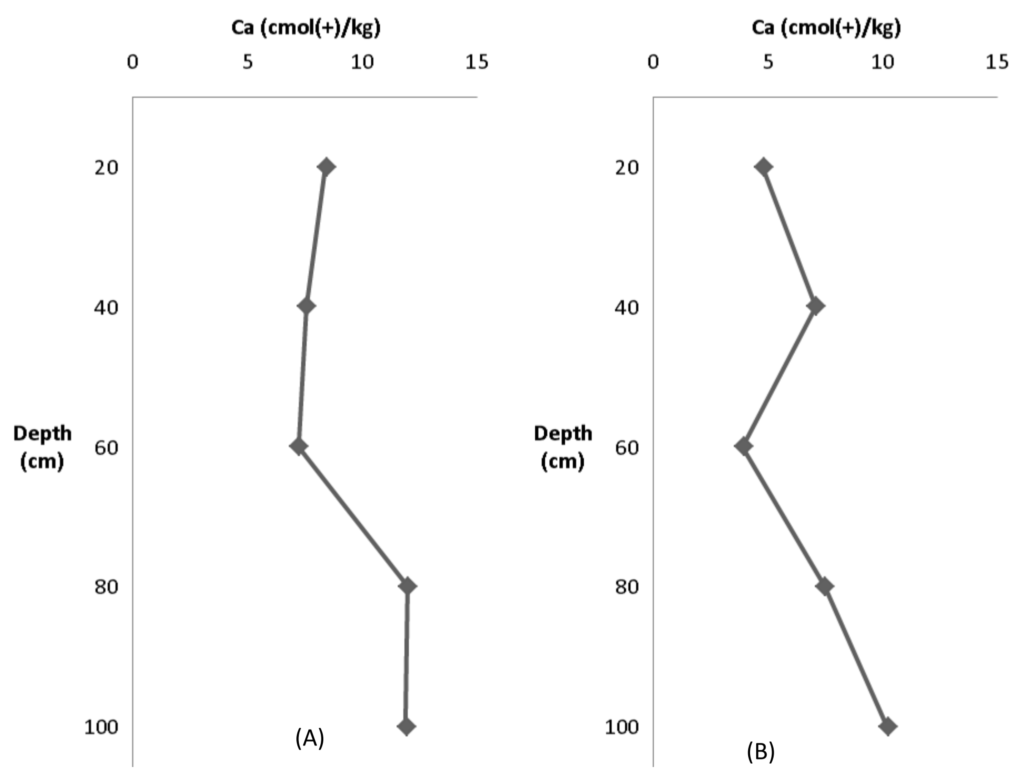

Figure 5. (a) Vertical Distribution of Ca in Dareta North I, (b) Vertical Distribution of Ca in Dareta North II.

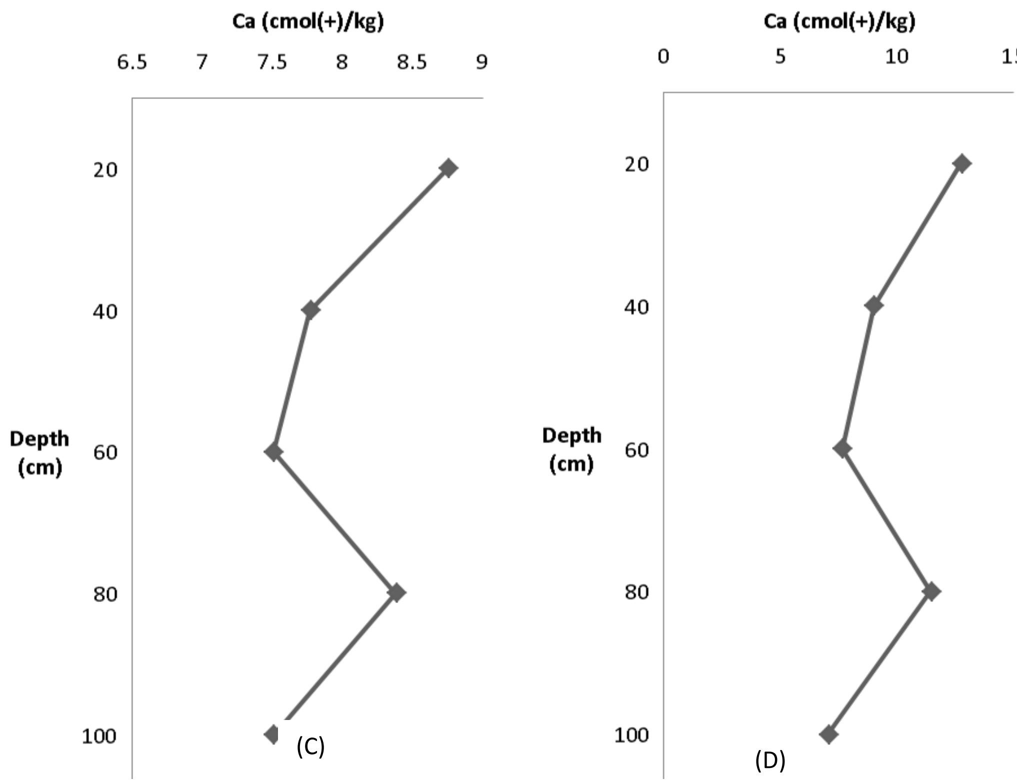

Figure 5. (c) Vertical Distribution of Ca in Dareta South I,(d) Vertical Distribution of Ca in Dareta South II.

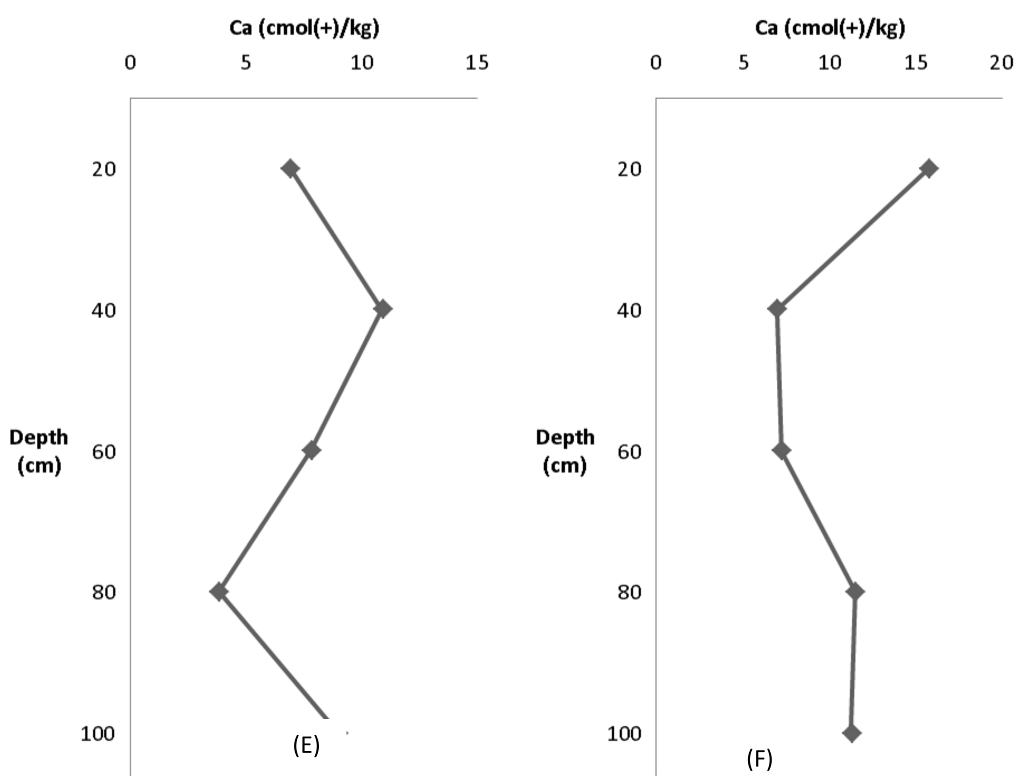

Figure 5. (e) Vertical Distribution of Ca in Dareta East I, (f) Vertical Distribution of Ca in Dareta East II.

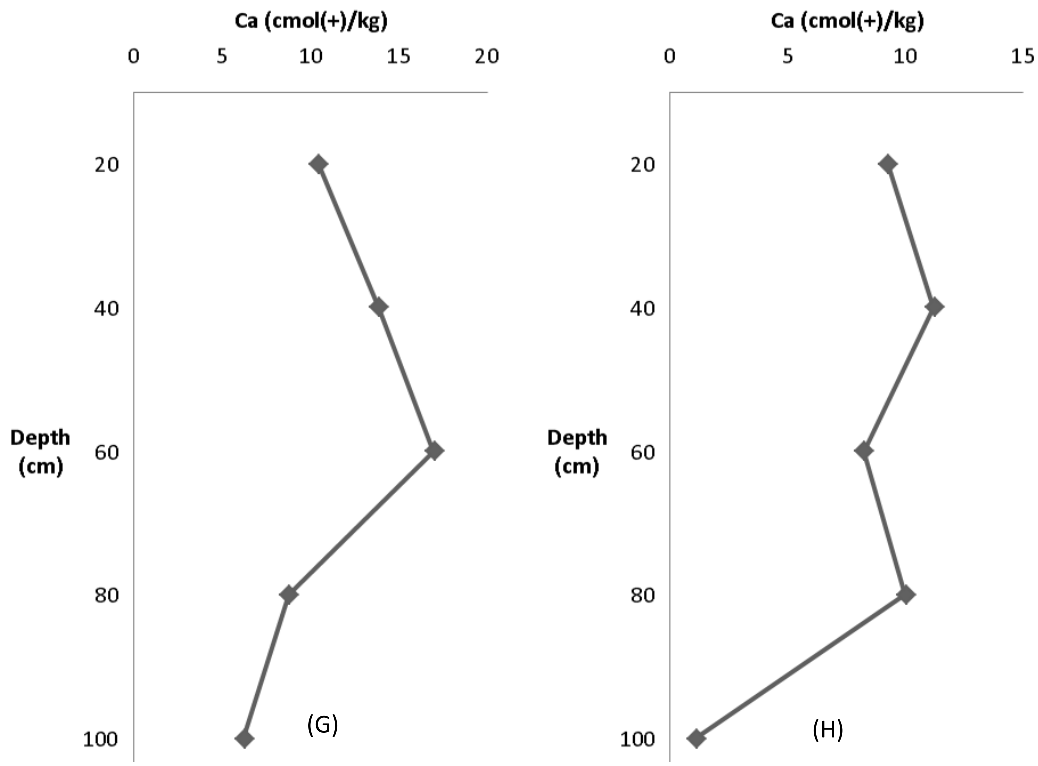

Figure 5. (g) Vertical Distribution of Ca in Dareta West I, (h) Vertical Distribution of Ca in Dareta West II.

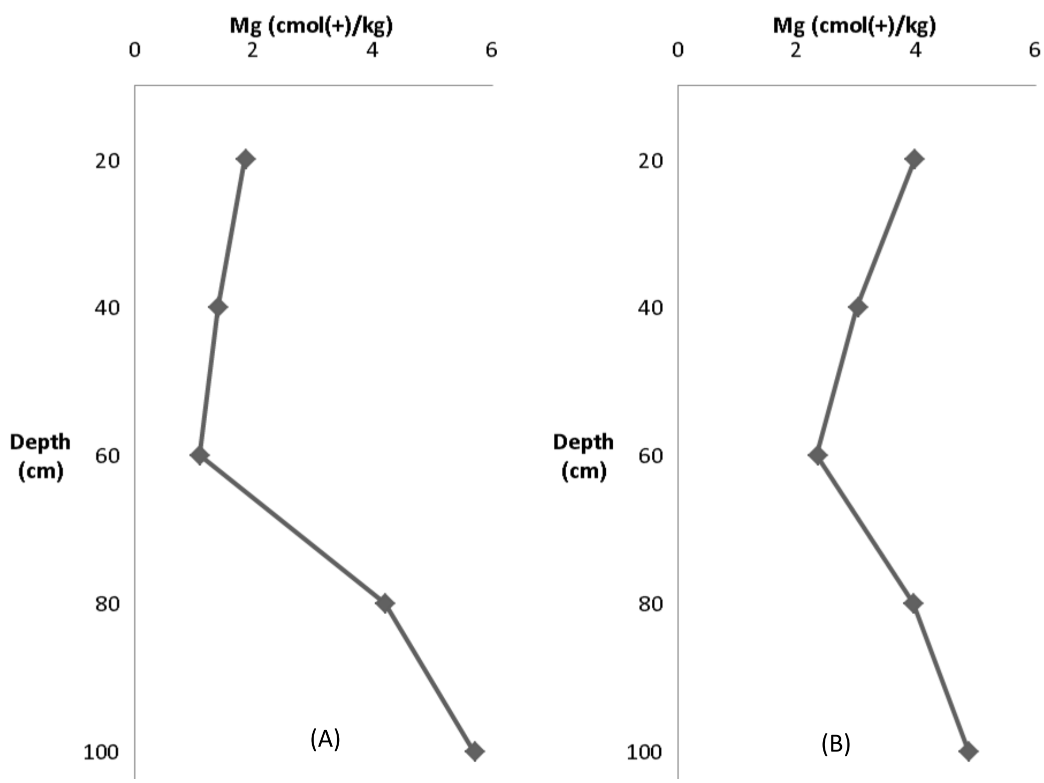

Figure 6. (a) Vertical Distribution of Mg in Dareta North I, 6(b) Vertical Distribution of Mg in Dareta North II.

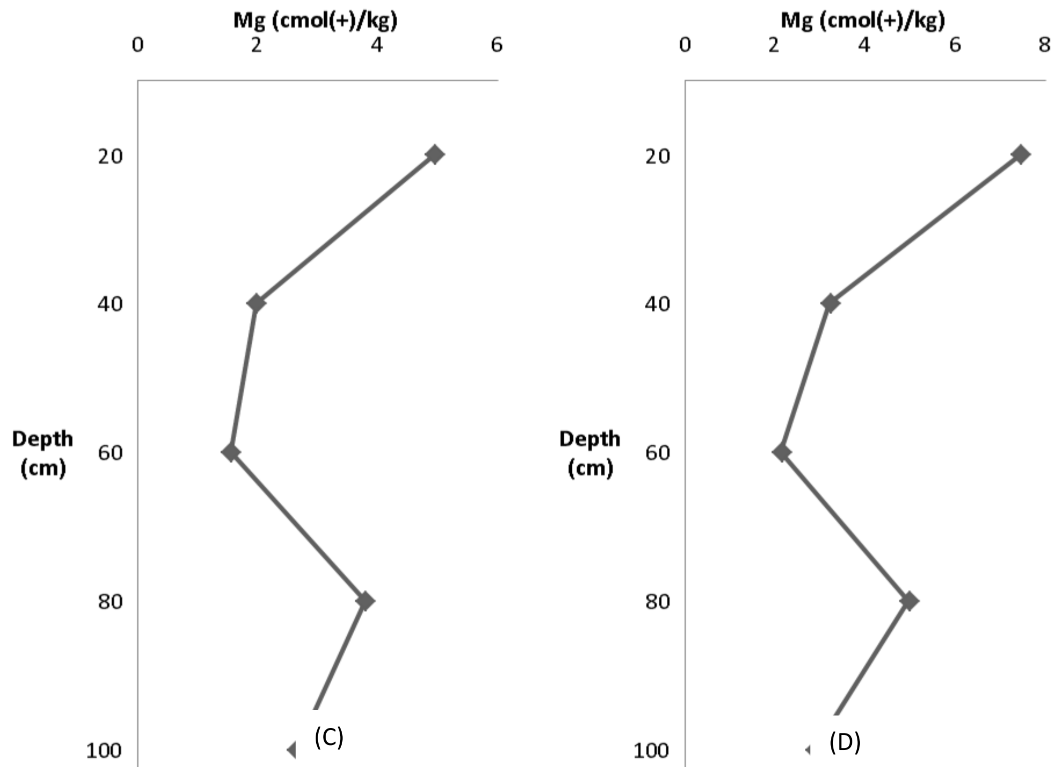

Figure 6. (c) Vertical Distribution of Mg in Dareta South I, 6 (d) Vertical Distribution of Mg in Dareta South II.

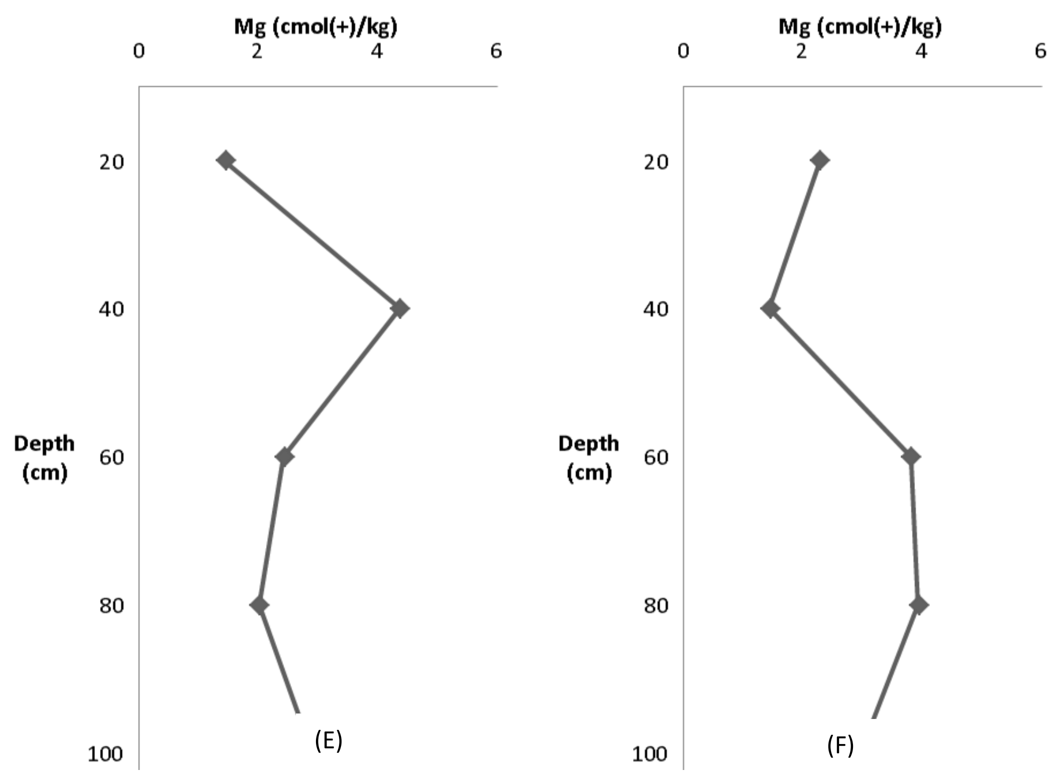

Figure 6. (e) Vertical Distribution of Mg in Dareta East I, (f) Vertical Distribution of Mg in Dareta East II.

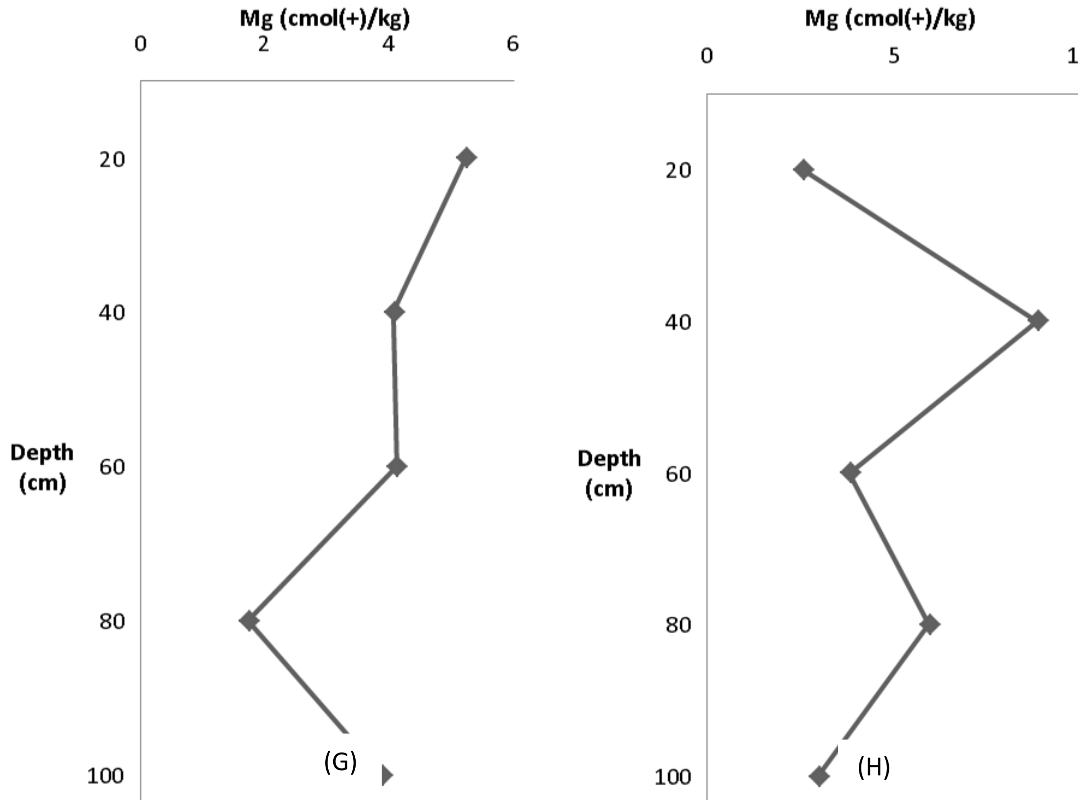

Figure 6. (g) Vertical Distribution of Mg in Dareta West I, (h) Vertical Distribution of Mg in Dareta West II.

Conclusion

Results from this study can be use to conclude that the deadly outbreak of Pb poisoning in Dareta village northern Nigeria highly contaminated the soils beyond the threshold level set by the United State Environmental Protection Agency (USEPA, 2004). Although acute lead poisoning of young children has been the most immediate and severe consequence, older children, adult workers, pregnant women and their unborn children, and breastfeeding infants are also at risk. Therefore it is recommended that strict legislation be made by the government to restrict artisanal gold mining in order to limit heavy metal discharges especially around human habitations. Further work should aim at carrying remediation practices such as those that will render Pb to become unavailable or bio-accumulated is suggested.

Conflict of interest

The authors have not declared any conflict of interest.

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