Health Risks for a Rural Community in Bokkos, Plateau State, Nigeria Exposed to Potentially Toxic Elements from an Abandoned Tin Mine

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Abstract

The past mining activities in Bokkos Local Government Area (LGA) were performed in an uncontrolled way and gave rise to many abandoned ponds now serving as domestic and irrigation water sources. Past research focussed mainly on the environmental impact and we show for the first time what the human health risk through consumption of contaminated food crops is in these communities. This study was designed to determine the level of Potentially Toxic Elements (PTEs) contamination in pond water, soil, and food crops and assess the health risk of inhabitants in the abandoned tin mining community in Bokkos LGA. Samples of the mining pond water, soil, and selected food crops from farms irrigated with the pond water: bitter leaf *(Vernonia amygdalina*), pepper (*Piper nigrum*), okra (*Albelmoschus esculentu*s), maize (*Zea mays)*, sweet potato (*Ipomoea batatas)* and Irish potato (*Solanum tuberosum*) were analyzed for each of the eight PTEs (viz; Cu, Cr, Fe, Mn, Ni, Zn, Cd & Pb) using inductively coupled plasma optical emission spectrometry (ICP-OES). The results obtained showed that the levels of all the PTEs analysed in the soil, pond water, and selected food crops except for Fe and Mn in soil and Cd in sweet potato was greater than their corresponding background area values ($p<0.05$). Also, the mean concentrations of all the PTEs except for Cu in pond water were significantly ($p< 0.05$) higher than the WHO maximum permissible limit. With the exception of Fe, Ni, and Zn for pepper and okra, Cu and Fe for maize grains as well as Cu, Ni, and Zn for sweet and Irish potatoes and Fe and Cd for sweet potato, the mean concentrations of PTEs in the food crops were significantly higher than WHO maximum permissible limit. The EF values of Cd (0.39); Cu (3.59) and Ni (2.81); Cr (9.38) and Pb (17.84); and Mn (178.13) and Zn (83.22) classified the soil as minimally, moderately, significantly, and extremely highly enriched respectively. The PI values of all the PTEs in the soil studied were all greater than 5 indicating that the soils were severely contaminated. There was evidence that food crops significantly bioaccumulated PTEs either as a result of contaminated soil and/or irrigation water. The bioaccumulation was not uniform and was dominated by transfer from the polluted irrigation water. The bitter leaf, okra, and to some extent maize had the highest transfer of PTEs, and Mn, Cu, and Zn had the highest bioaccumulation in the food crops investigated. The Hazardous Index (HI) for the eight PTEs through the consumption of food crops was 107 for children and 33 for adults which greatly exceeded the recommended limit of 1, thus indicating that possible health risks exist for both local children and adults. For every PTE, the values of HI for children are many-fold higher than those for adults, which is of particular concern due to the high HI values for Pb found for maize consumption, a typical staple food. The cancer risk values for Cr and Ni for all the food crops were within 10^{-3} to 10^{-1} which is several fold higher than the permissible limits (10^{-6} and $< 10^{-4}$) indicating the high carcinogenic risk. It can be concluded based on the results and risk assessment provided by this study that human exposure to mining pond water and soil in farms around the mining pond through the food chain suggests the high vulnerability of the local community to PTE toxicity. Long-term preventive measures to safeguard the health of the residents need to be put in place.

Keywords Abandoned mine; Potentially toxic elements; Bioaccumulation; Contamination; Bokkos mining areas; Health risk

Introduction

Tin mining and processing were active on the Jos Plateau between 1904 when mining activities began and the 1970s when mining activities reached their climax. This constitutes an important source of PTEs contamination to the environment in Jos and Bokkos LGA (Musa and Jiya 2011; Ndace and Danladi 2012). Although productive mining has seized in the area, bad practice led to serious environmental contamination and left a legacy of polluted ponds and tailing dams in nearby villages. These ponds are used as an irrigation source for dry season farming activities and in some host communities, the mining ponds also serve as a domestic water source. Apart from farming activities, communities in Bokkos LGA also depend on hand-dug wells in addition to the mining ponds for irrigation purposes.

Studies have shown that soil-to-crop transfer of PTEs is the major route of human exposure to PTEs (Zhuang et al. 2009a; Emurotu and Onianwa 2017; Fan et al. 2017; Zhang et al. 2018). Uptake of PTEs by agricultural food crops grown in metal contaminated soil and irrigated with wastewater, including mining pond water and subsequent bioaccumulation is a potential threat to animal and human health through the food chain (Khan et al. 2015; Zhang et al. 2018; Liu et al. 2020a). Elsewhere, there are reports of adverse negative impacts of mining activities on environmental health due to exposure of human populations living in the mining area to heavy and trace metal pollutants through the food chain (Ngole-Jeme and Fantke 2017). Previous studies have associated human exposure to PTEs individually or collectively to various adverse health effects due to their persistence in the environment, bioaccumulation capacity, and non-biodegradable nature (Duruibe et al. 2007; Graber et al. 2010; Saha et al. 2017; Jiménez-Oyola et al. 2021). The PTEs such as lead (Pb), cadmium (Cd), arsenic (As), and mercury (Hg) are described as non essential elements because they have no known biological function in living systems and exert their toxicity in biological systems even at low levels (Alotaibi et al. 2021). For example, exposure to Pb has been shown to interfere with a variety of body processes affecting many organs and tissues in the body including the heart, bones, intestine, kidneys, reproductive organs, developing red blood cells, and nervous systems (Scinicariello et al. 2007; Flora et al. 2012; Offor et al. 2017). Clinical signs of lead toxicity generally manifest as neurotoxicity, altered blood enzyme levels or activity and anaemia (Kabeer et al. 2019). It interferes with the development of the nervous system in children resulting in decreased intelligence quotient (IQ) and memory, causing potentially permanent learning and behaviour disorders (Tsai et al. 2017; Offor et al. 2017). The lead induced anaemia results from reduced haemoglobin production and damage to erythrocytes because Pb is a potent inhibitor of enzymes of haem biosynthesis and erythropoesis (Scinicariello et al. 2007). Cd exposure can cause adverse health effects to many organs including damage to the lung, kidneys, liver, testicles, brain, bone, and blood system (Genchi et al. 2020; Liu et al. 2020b). Cadmium cause tissue damage due to its ability to generate free radicals by replacing iron and copper in various cytoplasmic and membrane proteins (Fortoul et al. 2015). Excessive amounts of these free radicals cause the stimulation and destruction of sensitive macromolecules and tissues leading to increased oxidative stress, membrane lipid peroxidation, DNA damage, inference with DNA repair mechanisms, and apoptosis contributing to many diseases such as cancer and stroke (Wang et al. 2014; Fortoul et al. 2015; Sharifi-Rad et al. 2020). Cd also exerts its toxic effect by blocking the mitochondrial electron-transfer chain by impairing electron flow through complex III which reduces oxidative phosphorylation and decreases the synthesis of ATP (Genchi et al. 2020). Cadmium also inhibits the activities of antioxidant enzymes which destroy free radicals which cause oxidative stress (Unsal et al. 2020; Genchi et al. 2020). It can accumulate for 10 to 20 years in the human body and is considered one of the most toxic PTEs (Liu et al. 2020a). Other PTEs such as Cu, Zn, and Fe amongst others are essential trace elements for human health because they mediate some vital biochemical reactions by acting as cofactors for many enzymes, as well as act as centres for stabilizing structures of enzymes and proteins while others control important biological processes by binding to molecules on the receptor site of cell membrane or by alternating the structure of membrane to prevent entry of specific molecules into the cell (Prashanth et al. 2015; Kortei et al. 2020). However, chronic and excessive intake of these essential elements may lead to damaging effects in human beings (Zheng et al. 2007; Zhang et al. 2022). High levels of Cu, Zn, and Fe can induce non-carcinogenic risks, such as neurologic involvement, headaches, liver and renal illness, and skin and respiratory system lesions (Zheng et al. 2007; Zhang et al. 2022). For instance, exposure to excess Cu and Zn might cause cellular injury via generation of reactive oxygen species, giving rise to enhanced lipid peroxidation, thiol oxidation, and DNA damage resulting in numerous diseases, including cancer, cardiovascular diseases, diabetes, atherosclerosis, neurological disorders (Alzheimer's disease and Parkinson's disease), chronic inflammation and others (Jomova and Valko 2011; Formigari et al. 2013).

An important aspect of public health protection is the prevention or reduction of exposure to environmental agents that contribute, either directly or indirectly, to increased rates of premature death, disease, discomfort, or disability(WHO 2000). PTEs such as Cd and Pb are toxic even at a very low level due to their persistence in the environment and the potential to accumulate to toxic levels in plants and humans (Ali et al. 2019). WHO, for example, estimates that about a quarter of the diseases facing mankind today occur due to prolonged exposure to environmental chemical pollutants, including potentially toxic elements (Pruss-Ustan and Corvalan 2006; Kimani 2007).

Scientific studies have shown that abandoned mining sites on the Jos Plateau act as potential sources of PTEs and could be present in the human food chain causing subsequent exposure (Aliyu et al. 2015; Orisakwe et al. 2017). Recent studies focused mainly on environmental contamination of the Jos Plateau in the Northern, Southern, and Barkin-Ladi LGA regions (Gyang and Ashano 2010; Daniel et al. 2012). In particular, no evidence-based studies in Bokkos LGA have been conducted to evaluate the health impact of chronic exposure to these PTEs on communities living near the abandoned tin mines. While the focus of this paper is on a tin mine area in Nigeria, the implications for contamination from such a mine in terms of the surrounding land and water, as well as acid mine drainage often originating from such mines, are of global relevance and importance (Haddaway et al. 2019). This study aimed to determine the level and pattern of carryover of PTEs in tin mining ponds and contaminated mining soils in farm crops of the abandoned mining fields and to assess the potential health impact of exposure of the human host population to the observed levels of PTEs.

Materials and Methods

Study Area

The study area was Bokkos-LGA, one of the 17 LGAs in Plateau State, located in the North Central part of Nigeria (Fig, 1). It is 74 km south of Jos the capital and lies between latitudes 9° 24′ 17.9″N and longitude 008°55′ 01.8″E. Bokkos LGA was host to active tin mining activities in the 1970s, at Kuba and other villages. The combined population of the area is about 148, 345 people (Nigeria Census, 2006).

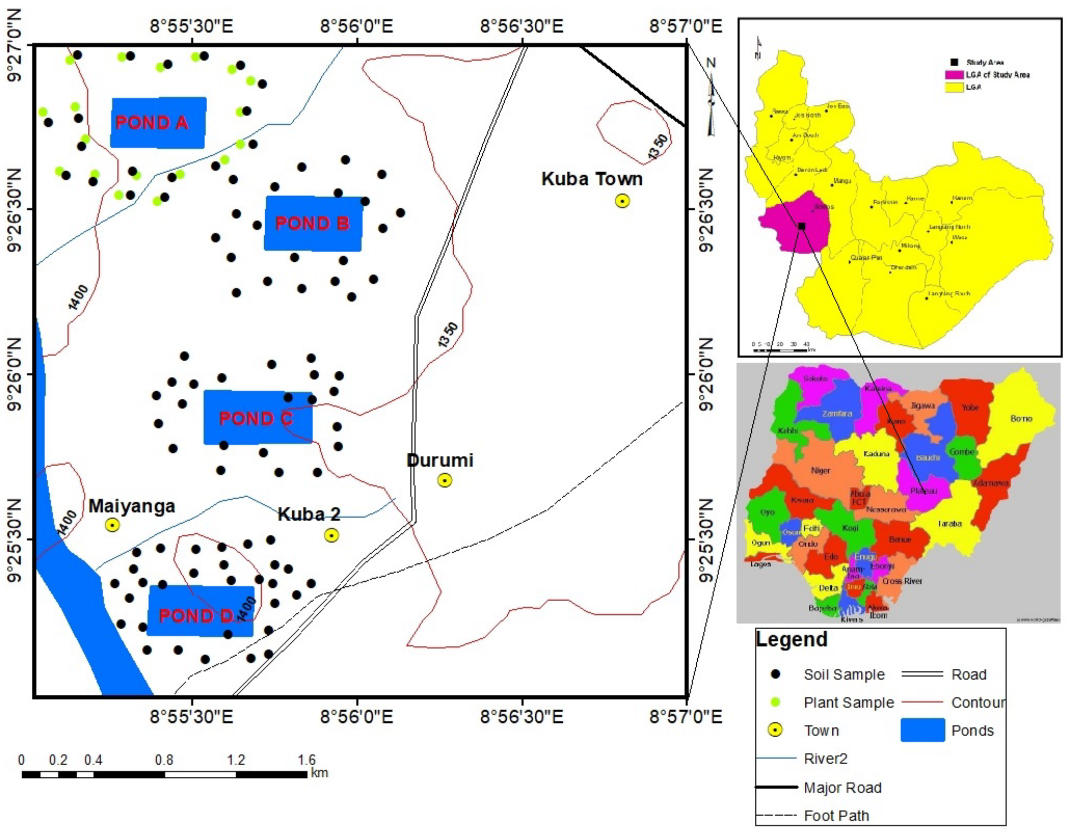

Fig.1 Sampling site in Bokkos LGA, Plateau State, Nigeria, indicating the position of ponds, soil, and food crops sampling site.

Sampling and Sample Preparation

Soil, pond water from the four major mining ponds (labeled A, B, C, and D), and crop plants (edible parts only) samples were collected during the dry season in March and April of 2016 from the study area (Illustrated in Fig. 1).

In farms around each specific pond, a representative soil sample for that particular area was taken in triplicate from a depth of 0-20 cm and then mixed thoroughly. This resulted in four groups of homogenised soils for the 4 contaminated pond areas investigated. Approximately one kg of each representative soil sample collected was stored in polythene bags for transport to the laboratory. Large soil clods were crushed to facilitate drying and were air-dried to constant weight at an average temperature of 25 °C for 2 weeks. The dried soil samples were pulverised and then stored in desiccators pending digestion and PTEs determination.

The pH was measured in a 1:2.5 soil/deionised H_2O suspension using a waterproof pH/ORP meter (Sparks 1996; Soon and Hendershot 2006). Total carbon (C) and nitrogen (N) concentrations were determined by combustion analysis at 950 °C using a LECO TruSpec CN Analyzer (Udawatta et al. 2008).

Water samples were taken from the four major mining ponds used for irrigation and domestic purposes into plastic sampling bottles that were pre-conditioned with 5% nitric acid 24 hours before the sampling was done. At each sampling site, the bottles were rinsed at least two times with deionised water before sampling was done. At each pond, samples were collected at the various withdrawal points and then combined into a single representative sample. The numbers of withdrawal points were 9, 3, 3, and 4 for ponds A to D, respectively. Approximately 250 ml of samples were taken at each withdrawal point by immersing the sampling bottles about 10 cm below the water surface. The samples were acidified with 2 ml of 10% nitric acid and then transported to the laboratory, where it was stored in the refrigerator at 4 °C pending digestion.

The crop plant samples collected were vegetables (*Vernonia amygdalina, Piper nigrum, and Albelmoschus esculentu*s) and staple crops (*Zea mays*, *Ipomoea batatas,* and *Solanum tuberosum*), donated by farmers. All the samples were handpicked using vinyl gloves, from farms located around pond A where soil samples were previously taken. They were collected three times and then mixed to form a composite sample for each plant. They were packed into polyethylene bags and then transported to the laboratory. Each sample, weighing approximately 200g, was thoroughly washed with deionized water to remove dust particles and then oven-dried to constant weight at 40°C. All dried samples were pulverised using pestle and mortar and sieved through a 1.5-mm sieve. The powdered samples were kept in clean polyethylene bags at room temperature awaiting analyses.

The soil, water, and crop samples used as the background were obtained from Gwande, another village in Bokkos LGA where there is no known past mining activity. This area is located 9 km away from the abandoned tin mines of the study area. All the samples were collected in triplicate and for each sample type collected; the sampling method was the same as that used in the abandoned mining area. They were prepared by the same method as the test samples and stored pending analysis.

The water samples were digested according to the method prescribed by the American Public Health Association (APHA 1998). Fifty (50) ml of each water sample was acidified with 5 ml of concentrated nitric acid and concentrated on a steam bath to approximately 5 ml. The concentrate was filtered through a Whatman (No.4) filter paper directly into a 50 ml volumetric flask and made up to mark with deionised water Milli Q 18 MΩ.

A CEM Mars Xpress (40 closed PFA vessels) microwave oven (Matthews, NC, USA) was used for the digestion of soil and plant samples. Approximately 0.25 ± 0.005 g pulverised soil samples, river clay sediment certified reference material, LGC 6139, plant samples and strawberry leaves certified reference material, LGC 7162 were weighed directly into the PTFE-TFM vessels. A mixture of 7.5 ml 65% HNO_3 and 2.5 ml 37% HCl was added to each soil sample and its corresponding certified reference material while 10 ml 65% HNO_3 was added to each plant sample and its corresponding certified reference material both were digested using the following heating programme: a ramp to 90 °C for 10 min, then 5 min holding time at 90 °C, a ramp to 170 °C for 10 min, followed by a 10 min holding time at 170 °C and finally a cooling period of 30 min at room temperature. The power applied was 1200W. The clear solutions obtained were quantitatively transferred to 50 cm^3 volumetric flasks then diluted to the mark with deionized water. All the samples were analysed in triplicate.

The concentrations of the target potentially toxic elements in mining pond water samples were determined using a Buck Scientific 210/211 VGP atomic absorption spectrophotometer (AAS), while the target PTEs in plant and soil samples were determined using a Thermo Scientific iCAP 6000 series Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The operating parameters for the ICP-OES and wavelength selection were based on the most sensitive lines free of spectral interferences.

Quality Assurance and Quality Control

De-ionized water Milli Q 18 MΩ and reagents of analytical grade were used throughout the study. Reagent blanks were used to correct the instrument readings and standard natural matrix reference materials consisting of strawberry leaves LGC 7162 plant-based CRM and river clay sediment LGC 6139 soil-based CRM were employed to check the accuracy of analyses. The recovery rates of the target PTEs in the river clay sediment CRM varied from 85% to 102%, with the exception of Cd (123%) for the extractable elements (Cd, Cr, Cu, Ni, Pb, and Zn). The Fe and Mn certified values are only given as total concentration (our methodology only determined the acid extractable elemental profile) and the recovery of these two elements using the acid digestion procedure provided recoveries of 73 and 98%, respectively. In the case of the PTE concentrations in the plant CRM, recoveries varied generally from 82% to 100% with the exception of Cr for which a low recovery of 60% was obtained, and for Zn which yielded a 171 % recovery. The low Cr recovery may be due to the absence of peroxide in the digestion process and therefore incomplete oxidation.

Assessment of Metal Contamination

Bioaccumulation Factor (BAF)

The bioaccumulation factor (BAF) is also known as bioconcentration factor BCF (Maurya et al. 2019; Luo et al. 2020) is defined as the ratio of the total PTE concentration in the plant part to that in soil or mining pond water. This factor is commonly used to measure the ability of a plant to take up and transport potentially toxic elements to various parts (Ladislas et al. 2012; Cai et al. 2015; Zhou et al. 2016; Hu et al. 2017). The values were calculated according to equation 1.

$$BAF = \frac{[M]_{plant}}{[M]_{soil}} \qquad 1$$

$where [M]_{plant} = metal\ concentration\ in\ the\ plant$

$[M]_{soil} = metal\ concentration\ in\ the\ soil$

Enrichment Factor (EF)

Enrichment Factor is used to quantitatively assess the contributions of anthropogenic sources to the concentrations observed in the surface soils and to determine whether they were from natural or anthropogenic sources (Yongming et al. 2006; Lu et al. 2009; Khalilova and Mammadov 2016; Yang et al. 2016; Ávila et al. 2017). In this study, the enrichment factors of heavy metals in soil samples were calculated to assess the contribution of anthropogenic sources to the natural levels of heavy metals in the abandoned tin mine soils using equation 2:

$$\mathrm{EF} = \frac{(C_x/C_{ref})sample}{(C_x/C_{ref})background} \qquad 2$$

where EF is the enrichment factor of the heavy metal x while Cx is the concentration of heavy metal x and C_{ref} is the concentration of a reference heavy metal in study samples and background value. The reference heavy metal is usually a heavy metal mainly originated from soil parent material that are neither likely to be affected or suffered little contamination by anthropogenic activities nor correlated with heavy metal pollutants (Wu et al. 2015). Several studies have used iron (Fe) as the reference element in calculating the enrichment factor (EF) (Niencheski et al. 1994; Deely and Fergusson 1994; Candeias et al. 2015). In this study, Fe was selected as a reference element to calculate the EFs of the other elements because of its association with rock-forming minerals, and its abundance in soils is considered to be free from anthropogenic contribution. Also, Fe is negatively correlated with other potentially toxic elements. Five contamination categories are recognized based on the EFs and often used comparisons between degrees of metals enrichment in the soil pollution assessment: EF<2, minimal enrichment; 2≤EF<5, moderate enrichment; 5≤EF<20, significant enrichment; 20≤EF<40, very high enrichment; and EF≥40, extremely high enrichment (Sutherland 2000; Loska et al. 2004; Yongming et al. 2006; Lu et al. 2009; Yang et al. 2016; Ávila et al. 2017).

Pollution Index

The pollution index (PI) is generally used to assess the degree of metal contamination in the topsoil (Wu et al. 2015; Liu et al. 2016; Tong et al. 2020). In this study, the PI by a given PTE was calculated as the ratio between the metal concentration in a soil sample (C) and its reference value (S) using Equation 3:

$$\mathrm{PI} = \frac{C}{S} \qquad 3$$

where C represents the concentration of the measured heavy metal in the soil and S represents the corresponding metal reference value (S) which was based on WHO values of PTEs in soil samples. Contamination classes based on pollution index values have been defined as: (a) PI ≤ 1—no contamination; (b) 1 <PI ≤ 3—slight contamination; (c) 3 <PI ≤ 5—moderate contamination; and (d) PI >5—severe contamination (Wu et al. 2015; Ávila et al. 2017).

Human Health Risk Assessment

Human health risk assessment is a process used to estimate the health effects that might result from exposure to toxic and/or carcinogenic chemicals (USEPA 2015; Kamunda et al. 2016). These health risks posed by various contaminants that enter the body through various exposure pathways are usually classified as non-carcinogenic risk or carcinogenic risk (USEPA 2004; Liang et al. 2017; Alidadi et al. 2019). In this study, the human health risk posed by ingestion, dermal absorption, and inhalation of contaminated soil, as well as ingestion of food crops grown on contaminated soil and irrigated with mining pond water, were calculated as per the model developed by the USEPA and the values used for specific variables were adapted for Nigerian population statistics (Khan et al. 2013; USEPA 2015).

The estimated daily intake (EDI) of PTEs (mg/kg/day) was calculated using the mean concentration of each metal in soil and food crops, as well as the adults and children consumption rates (USEPA 2015; Kamunda et al. 2016). A daily dose of each PTE was used to calculate the EDI for each element via ingestion, dermal absorption, and inhalation pathways for contaminated soil and contaminated food crops, respectively using equations 4 to 8:

$$EDI_{Soil} Ingestion = \frac{CxIRxEDxEF}{BWxAT} \quad 4$$

$$EDI_{Soil} Inhalation = \frac{CxInhRxEDxEF}{PEFxBWxAT} \quad 5$$

$$EDI_{Soil} Dermal = \frac{CxSAxAFxABSxEDxEFxCF}{BWxAT} \quad 6$$

$$EDI_{Water} Ingestion = \frac{CxIRxEDxEF}{BWxAT} \quad 7$$

$$EDI_{Plant} Ingestion = \frac{CxIRxEDxEF}{BWxAT} \quad 8$$

Where EDI_{soil} Ingestion stands for estimated daily intake for soil ingestion, EDI_{soil} Inhalation is estimated daily intake through soil inhalation, EDI_{soil} Dermal is estimated daily intake through soil contact, EDI_{water} Ingestion is estimated daily intake for ingestion of water, EDI_{plant} Ingestion is estimated daily intake for ingestion of the food crops analysed, C is the concentration of the PTE in the samples, IR is the ingestion rate, ED is exposure duration, EF is exposure frequency, BW is body weight, AT is average time, InhR is inhalation rate, SA is skin surface area, FE is dermal exposure ratio, AF is soil adherence factor, ABS is dermal absorption factor, and PER is particulate emission factor, while the other terms in the equations and the values of the parameters used to calculate EDI for the different exposure pathways for soil and the ingestion of water and food crops during a specified period are summarized in supplementary material Table S1.The ingestion rate (IR) for average daily consumption of vegetables (bitter leaf, pepper, and okra) for adults and children was estimated to be 0.236 kg person^{-1} day^{-1} and 0.173 kg person^{-1} day^{-1} respectively, whereas the estimated average daily consumption of other food crops (maize grains, sweet potato, and Irish potato) for adults and children was considered to be 0.360 kg person^{-1} day^{-1} and 0.209 kg person^{-1} day^{-1} respectively (Wang et al. 2005; Ávila et al. 2017; Onyedikachi et al. 2018).

The non-carcinogenic risk associated with PTEs through exposure to soil, water, and food crops was estimated using the hazard quotient (HQ) and hazard index (HI) (Liang et al. 2017; Alidadi et al. 2019). HQ was calculated for individual PTEs by dividing the EDI of each PTE via the different exposure routes (oral, dermal, and inhalation) to their corresponding reference exposure dose (RfD)(USEPA 1989; Kumar et al. 2019) using equation 9:

$$HQ = \frac{EDI}{RfD} \quad 9$$

Where RfD is the reference dose of specified PTEs as can be seen in supplementary material Table S2.If HQ is less than 1, there is no significant risk from the substance over a lifetime exposure, while if HQ is higher than 1, the toxicant may produce an adverse effect. The higher the HQ value, the higher the probability of experiencing long-term toxic effects (Song et al. 2009).

The hazard index (HI) has been developed (USEPA 1989) to evaluate the potential risk to human health through more than one PTE. It is the sum of the hazard quotients for all the PTEs determined. It is calculated as follows (Li et al. 2015):

$$\mathrm{HI} = HI = \sum \mathrm{HQCu} + \mathrm{HQCr} + \mathrm{HQFe} + \mathrm{HQMn} + \mathrm{HQNi} + \mathrm{HQZn} + \mathrm{HQCd} + \mathrm{HQPb} \qquad 10$$

Where HQ_{Cu}, HQ_{Cr}, HQ_{Fe}, HQ_{Mn}, HQ_{Ni}, HQ_{Zn}, HQ_{Cd}, and HQ_{Pb} stands for the hazard quotients for Cu, Cr, Fe, Mn, Ni, Zn, Cd, and Pb respectively. If HI<1, there is no apparent health implications but HI > 1 indicates the possibility of an adverse health effect (Li et al. 2015).

Cancer health risk estimates represent the incremental probability that an individual will develop cancer over a lifetime as a result of a specific exposure to a carcinogenic chemical (USEPA 1989). The cancer risk of each of the carcinogenic elements was calculated by multiplying the EDI values for each exposure route by the cancer slope factor (CSF) for that metal and exposure route (USEPA 1989; Masri et al. 2021; Ashraf et al. 2021). This was calculated using equation 11:

$$\mathrm{CR} = EDI\ x\ CSF \qquad 11$$

where EDI = estimated daily intake averaged over 70 years (mg kg^{-1} day^{-1}) and CSF = Cancer slope factor (mg kg^{-1} day^{-1}) $^{-1}$. The cancer slope factors used for CR calculation were 0.5, 1.7, 0.0085, and 0.38 (mg kg^{-1} day^{-1}) $^{-1}$ for Cr, Ni, Cd, and Pb respectively (USEPA 2004; Masri et al. 2021; Ashraf et al. 2021). According to the New York State Department of Health (NYSDOH), CR values ≤ 10^{-6}, indicate low cancer-causing risks, between 10^{-5} and 10^{-4}, indicate moderate cancer-causing risks, and between 10^{-3} and 10^{-1} indicate high cancer-causing risks (Ashraf et al. 2021; Alsafran et al. 2021). The lifetime total cancer risk associated with exposure to multiple carcinogenic elements through the consumption of each food crop studied was calculated using equation 12:

$$TCR = \sum CRCr + CRNi + CRCd + CRPb \qquad 12$$

where TCR represents total cancer risk while CRCr, CRNi, CRCd, and CRPb are cancer risk for Cr, Ni, Cd, and Pb respectively (USEPA 2004; Masri et al. 2021; Ashraf et al. 2021).

Statistical Analysis

The results obtained were analyzed statistically using Microsoft Office Excel and the computing Statistical Package for Social Science (SPSS 23.0 for Windows, SPSS Inc., IL, U.S.A.). One-way analysis of variance (ANOVA) followed by Turkey-Kramer's Multiple Comparison was used to assess the variation in concentration of the PTEs in soil, pond water, and vegetable crops, separately. Probabilities less than ($p<0.05$) were considered statistically significant. Results were expressed as mean ± standard deviation.

Results and Discussion

PTE Concentrations in the Soil Samples

The characteristics of the soil and results of analysis of PTE concentrations in the soil samples from abandoned mining sites and the background area are summarized in Table 1. It was observed that the three samples analysed per soil gave an average % RSD less than 6 %, indicating good precision and successful homogenisation of the composite sample. The concentration profiles differed extensively between the four soils (Soil A: Mn>Zn>Cr>Pb>Cu>Ni>As>Fe>Cd; Soil B: Mn>Cr>Zn>Pb>Cu>Ni>As>Fe>Cd; Soil C: Zn>Cr>Pb>Cu>Mn=Ni>As>Fe>Cd; Soil D: Cr>Mn>Zn>Pb>Cu>Ni>Fe>As>Cd; Background soil: Mn>Zn>Pb>Cr>Cu>Ni>Fe>As>Cd).

Table 1 Some physicochemical parameters of soil samples collected in the proximity of the mining ponds, a background area, and the WHO recommended limit values.

	Concentration (mg kg^{-1})						
	Soil A	Soil B	Soil C	Soil D	Background soil	WHO standard	DPR Nigeria (1991)
Cd	0.90^{ab}	1.33^{ab}	0.24^{ab}	1.45^{ab}	0.01	0.003	0.8
Cr	60.7^{ab}	123.53^{ab}	41.57^{ab}	195.70^{ab}	3.00	0.1	100
Cu	19.7^{ab}	20.95^{ab}	27.61^{ab}	17.51^{ab}	1.15	0.1	36
Fe	3.04^{a}	4.83^{a}	0.32	5.37^{a}	0.65	50	
Mn	87.2^{ab}	148.15^{ab}	13.94^{b}	112.18^{ab}	57.00	2	
Ni	16.4^{ab}	15.91^{ab}	13.45^{ab}	15.40^{ab}	0.90	0.05	35
Pb	23.5^{ab}	28.81^{ab}	30.30^{ab}	19.15^{ab}	5.71	0.1	85
Zn	63.9^{ab}	54.75^{ab}	76.69^{ab}	43.00^{ab}	26.63	0.3	140
	Percentage N and C and pH of soils						
%N	0.06	0.03	0.14	0.03			
%C	1.58	0.57	5.53	0.20			
pH	4.18	4.86	3.26	4.31			

^{a}Values are significantly different from the background value ($p<0.05$)
^{b}Values are significantly different from WHO maximum permissible limit ($p<0.05$)
The WHO reference standard was based on WHO(Chiroma et al. 2014)Department of petroleum resources (DPR) Nigeria (1991) Target values.

It is observed that soils A and B followed nearly the same profile with Zn and Cr interchanging order, Mn always the highest concentration and Cd the lowest. However, soil C had a totally different profile, with Zn as the highest concentration followed by Cr, where the latter was only in fourth place in the other two soils. Soil D also followed a different profile with Cr as the highest concentration (and also the highest concentration overall for soils; 195.7 mg kg^{-1}), followed by the rest in nearly the same order as soils A and B. It could be hypothesized that the Cr in soil D and possibly also soil C, were not organically bound and therefore is easily acid extractable. These differences are also reflected by large %RSD values varying between 9 and 67%. The background soil had broadly the same profile as soils A and B and had the lowest concentration overall (Cd). Cd, Pb, and Ni levels are of concern due to their toxicity, even at very low levels, and rank among the priority metals that are of great public health significance (Järup 2003). Although Cu, Fe, Mn, Zn, and Cr are essential elements for the ecosystem and humans, their presence in high concentrations in food and feed plants is a concern because of their toxicity to humans and animals (Kabata-Pendias and Mukherjee 2007). The detected level of Cd (0.96 mg/kg) in this study is higher than those reported in Beijing, China (0.18 mg/kg;Liu et al. 2005), Finland (0.17 mg/kg; Salonen and Korkka-Niemi 2007), Romania (0.17 mg/kg;Harmanescu et al. 2011), and Korea (0.12 mg/kg; Rogan et al. 2009). The Pb levels were comparable with those in Romania and China, but much higher (8 and 5 times) than in India and Iran. Such high levels of PTEs, notably Pb and Cd, in agricultural soils in other countries have been associated with potential hazards to public health (Aelion et al. 2008; Su et al. 2014).

With the exception of Fe and Mn in soil C, the concentrations of PTEs analysed far exceeded the background soil values by factors varying from 1.5 times for Mn in soil A to 145 times for Cd in soil D. Also, the mean concentrations of all the PTEs except for Fe in all the soils were significantly ($p< 0.05$) higher than the WHO maximum permissible limit. Furthermore, with the exception of Cd in soil A, B, and D and Cr in soil B and D, the concentration of the PTEs did not exceed the DPR Nigeria target values (DPR, 1991). Fig. 2 provides an illustration of the variation of the levels across the four soils as a box plot. It is observed that the levels of Cu, Mn, and Zn varied across the different samples. It is also now clear that the background soil had significantly lower concentrations. This is in agreement with previous studies (Kang et al. 2020; Pan et al. 2020).

Table 8 shows the EF values of the selected metals in soil. There was variation in the EF values of PTEs among the four soil samples (A-D) with the EF values of Cd in all the four soil samples and those of Cr, Cu, Ni, and Pb in soil A, B, and D were less than 2 indicating minimal enrichment while Mn and Zn in soil A, B, and D and Cr and Pb in soil sample C had their EF values greater than five but less than 20 indicating significant enrichment. However, the highest EF values for Mn (178.13) and Zn (83.22) in soil sample C were greater than 40 signifying that the PTEs were extremely enriched in the soil according to the enrichment classification criteria. In general, the EF values of Cu (3.59) and Ni (2.81); Cr (9.38) and Pb (17.84); and Mn (178.13) and Zn (83.22) classified the soil as moderately, significantly, and extremely highly enriched respectively whereas those of Cd classified the soil as minimally enriched. This finding is in agreement with the previous studies which reported moderately, significantly, and extremely enriched PTEs in soil (Yongming et al. 2006; Lu et al. 2009; Khalilova and Mammadov 2016; Yang et al. 2016; Ávila et al. 2017). This confirms that the soils around the ponds are enriched with the PTEs, and the Cu, Mn, and Zn values, and to a lesser extent Pb, are at particularly worryingly levels for human and animal health. What is more concerning is that a standard that is 30 years in existence is still used to determine if intervention is required, and in this case, the finding would be that it is not. Finally, the highest EF values of PTEs greater than 2, 5, and 40 as the case may indicate that these PTEs were predominantly from anthropogenic influence. This confirms that the soils around the ponds are significantly enriched with the PTEs, as was anticipated.

Table 1 also summarizes the pH in soils from the study area which shows pH values between 3.26 in soil C and 4.86 in soil B. According to the US Department of Agriculture (Ávila et al. 2017), soils A, B, C, and D collected from the abandoned mine are classified as acidic. This indicates that the soil is acidic and previous studies have shown that the pH of the soil has a significant impact on soil activities and plant nutrient availability, and is thus regarded as a master variable in soils because it regulates a variety of chemical reactions and controls the chemical forms of nutrients, all of which have a direct impact on plant nutrient availability (Mccauley 2009; Ávila et al. 2017). It has also been reported that at lower pH metals are less bound to the soil which makes them more available for uptake by plants which can cause potential metal toxicities for food crops in acidic soils (Mccauley 2009; Ávila et al. 2017).

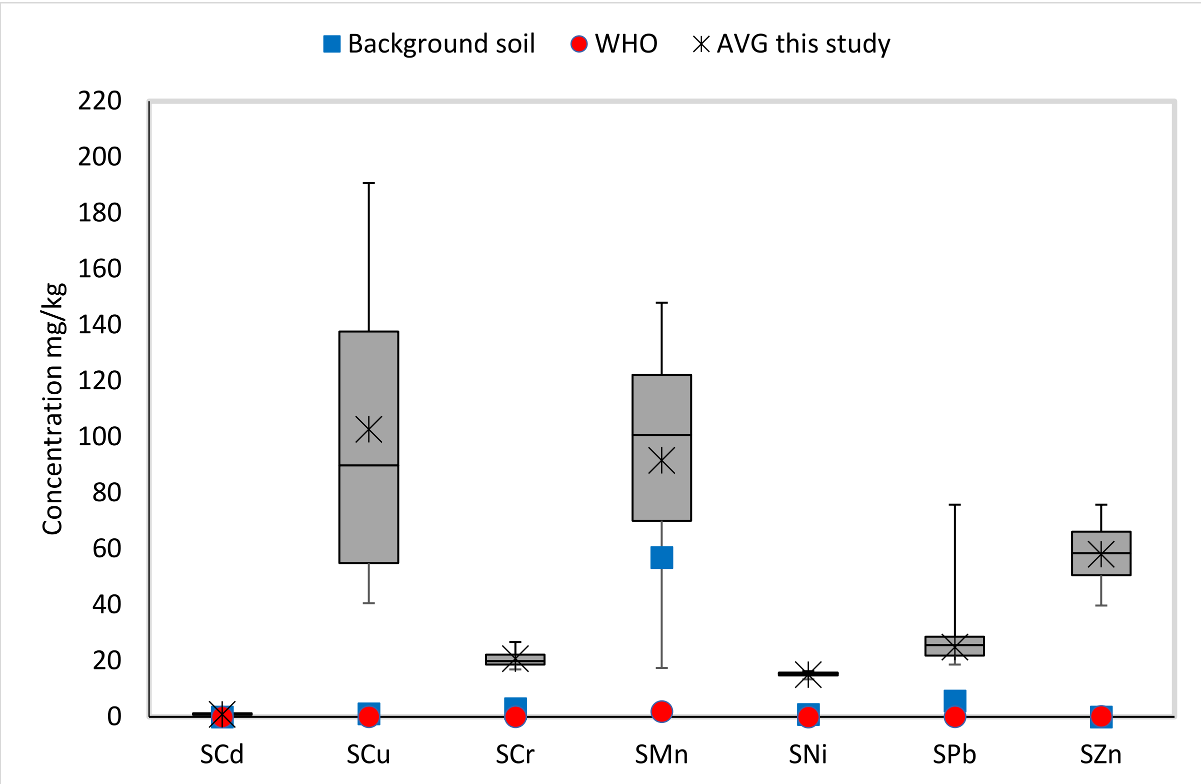

Fig. 2 Box plots of the various PTEs in the soil around the different mining plots were investigated, compared to the WHO reference standard and the background values.

The PI of PTEs in soil was calculated in this study based on WHO quality standards for agricultural soils and the results are presented in Table 8. The PI values of all the PTEs in the soil samples studied were all greater than 5 indicating that the soils were severely contaminated based on the PI classification criterion (Wu et al. 2015). The degree of contamination of the soils in the majority of the samples was high. A similar degree of contamination of soils with PTEs has been reported by previous researchers (Yongming et al. 2006; Lu et al. 2009; Khalilova and Mammadov 2016; Yang et al. 2016; Ávila et al. 2017). This confirms that the soil around the abandoned tin mine in terms of agricultural use is highly polluted with PTEs.

PTEs Concentrations in Mining Pond Water Used for Irrigation

The results of the analysis of potentially toxic element concentrations in mining pond water and the background area water are summarized in Table 2. The results showed that the mean concentration of all the potentially toxic elements determined was significantly ($p<0.05$) higher than their corresponding background area values. Also, the mean concentrations of all but Cu were significantly ($p< 0.05$) higher than WHO (Beyene and Berhe 2016) maximum permissible limit, as well as the Nigerian drinking water standard(NSDWQ 2015). Furthermore, the mean concentration of the potentially toxic elements Cd and Pb in mining pond water was several-fold higher than the background area value, WHO, and Nigerian maximum permissible limits for drinking water. In terms of the water used for irrigation purposes, all samples exceeded the permissible levels set by the FAO (Ayers and Westcot 1994) for all elements analysed, except for Fe for which the level was well below the 5 mg L^{-1} target value.

Table 2 Mean concentrations of the four pond samples (mg L^{-1}) of selected potentially toxic elements in pond water used for irrigation in study area

Potentially toxic element	Mean	Background area value	WHO Ref Std	FAO Water Irrigation Std	Nigerian Drinking Water Std
Cu	0.41±0.20^{a}	0.05±0.31	2	0.2	1.0
Cr	6.77±1.05^{ab}	0.95±0.01	0.05	0.1	0.05
Fe	1.16±0.82^{ab}	0.69±0.40	0.3	5.0	0.3
Mn	1.30±0.12^{ab}	0.32±0.47	0.1	0.2	0.2
Ni	0.88±0.49^{ab}	0.53±0.86	0.2	0.2	0.02
Zn	3.57±2.20^{ab}	0.49±0.10	3	2	3.0
Cd	6.68±2.21^{ab}	0.31±0.21	0.02	0.01	0.003
Pb	18.30±6.36^{ab}	0.02±0.31	0.01	5.0	0.01

[a]Values are significantly different from background value ($p<0.05$)
[b]Values are significantly different from WHO maximum permissible limit ($p<0.05$)
Reference standard (Ref Std) were based on WHO (Beyene and Berhe 2016); Nigerian drinking water (NSDWQ 2015) and FAO irrigation water(Ayers and Westcot 1994).

The results of the individual pond water were compared as illustrated in Fig. 3 below. The data indicated that pond A is the most enriched in PTEs and the main concern. Especially the Cr, Cd, and Pb levels are significantly higher at this pond.

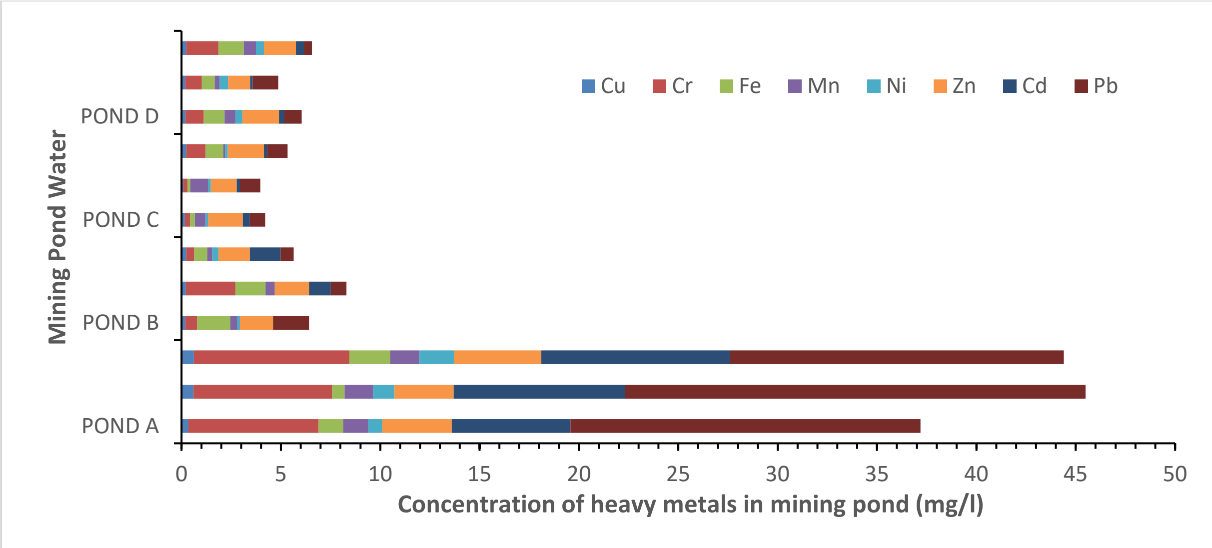

Fig. 3 Bar chart of the various PTEs in the individual mining ponds water investigated, in the study area showing pond A as the most polluted.

Water pollution affects both developing and developed countries and exposure to PTEs through drinking water remains a threat to human health (Bird et al. 2009; Ghannam et al. 2014). The levels reported in this study, especially for Pb and Cd, are comparable to those reported by Rooney et al. (2007), Flores-Magdaleno et al. (2011), Kobayashi (1978), and Sharaf and Shehata (2015), which had serious public health implications in those countries. Concentrations of 0.95 mg/l of Pb and 0.521 mg/l of Cd have been reported to cause health effects in the Suez Canal in Egypt (Sharaf and Shehata 2015), and in the cadmium-polluted Jinzu River basin in Japan, cadmium was associated with the incidence of diseases (Kobayashi 1978; Besante et al. 2011). Pb and Cd are considered potential carcinogens that are associated with the etiology of a number of diseases, especially cardiovascular, kidney, nervous system, blood as well as bone diseases (Järup 2003). The presence of these metals in drinking water even in very low concentrations has been shown to cause toxicity due to the fact that they have no known biological function and their potential to bioaccumulate (Caggiano et al. 2005; Akoto et al. 2014). This study has indicated that bioaccumulation of certain PTEs from the irrigation water via the direct use of water for domestic purposes or the indirect use via the food chain is significant (Roychowdhury et al. 2005; Aelion et al. 2008; Su et al. 2014; A et al. 2015; Bhattacharya et al. 2021; Chen et al. 2022).

PTEs in Some Selected Food Crops Harvested From Farms Irrigated With Mining Pond Water

The results of the analysis of potentially toxic elements in some selected food crops grown and irrigated with pond water in the vicinity of the abandoned mining area in Bokkos LGA are summarized in Table 3. As could be seen from the table, the PTEs of concern were detected in all the analysed food crops (bitter leaf, pepper, okra, maize grains, sweet and Irish potatoes). In each case, the mean concentrations of all the PTEs detected in all the food crops except Cd for sweet potato were significantly ($p<0.05$) higher than their corresponding values from the background non-mining area. With the exception of Fe, Ni, and Zn for pepper and okra, Cu and Fe for maize grains as well as Cu, Ni, and Zn for sweet and Irish potatoes and Fe and Cd for sweet potato, the mean concentrations of metals in the food crops were significantly higher than WHO maximum permissible limit.

In comparison with other mining areas, the highest concentration of Cd (0.69 mg/kg) recorded in bitter leaf in this study was 4.6 times higher than concentrations reported for Cd in an Au-Ag-Pb-Zn mining area in Korea (0.15 mg/kg,) (Lee et al. 2001; Ji et al. 2013). However, it was comparable with the level reported for Cd in rice grains in Japan (0.63 mg/kg) (Inaba et al. 2005) and China (0.8 mg/kg) (Liu et al. 2005). The highest Pb concentrations (2.68 mg/kg) recorded in okra in this study was 3.35 times higher than those reported for a Pb and Zn mining area from China (0.8 mg/kg) (Liu et al. 2005), and those reported for an abandoned metal mine from Korea (Ji et al. 2013). Rice has been identified as a major source of Cd intake, which caused the *itai-itai* disease in Japan in the mid-20th century (Besante et al. 2011). The *itai-itai* disease was a combination of osteomalacia and osteoporosis which was caused by Cd contaminated water used for irrigation of local rice fields (Järup 2003).

Table 3 PTEs concentrations in some selected food crops grown in the study area

Vegetable		Metal concentration(mg/kg)							
		Cu	Cr	Fe	Mn	Ni	Zn	**Cd**	**Pb**
Bitter leaf	Mining area	18.54±5.48^{ab}	2.60±0.01^{ab}	0.03±0.01^{a}	356.00±3.90^{ab}	3.35±0.29^{ab}	89.00±4.41^{ab}	0.69±0.29^{ab}	0.60±0.29^{ab}
	Background area	0.84±0.10	0.42±0.20	0.02±0.00	19.82±2.35	0.50±0.51	16.10±1.10	0.01±0.21	0.09±0.30
Pepper	Mining area	11.92±0.72^{ab}	2.85±0.17^{ab}	0.03±0.01^{a}	29.50±0.58^{ab}	1.55±0.40^{ab}	19.10±2.77^{ab}	0.09±0.02^{ab}	0.28±0.06^{ab}
	Background area	0.35±1.21	0.26±0.35	0.02±0.30	5.00±1.52	0.38±0.41	8.20±1.05	0.01±0.31	0.09±0.11
Okra	Mining area	11.19±1.50^{ab}	16.10±1.10^{ab}	1.28±0.05^{ab}	107.00±1.40^{ab}	3.40±1.30^{ab}	45.60±1.20^{ab}	0.13±0.10^{ab}	2.68±1.51^{ab}
	Background area	0.42±1.20	0.90±1.32	0.02±1.00	26.00±1.50	0.39±0.10	15.40±1.50	0.01±0.10	0.09±0.20
Maize Grains	Mining area	5.95±0.75^{a}	3.15±0.40^{ab}	0.003±0.02^{a}	26.50±0.58^{ab}	0.65±0.06^{a}	80.95±2.71^{ab}	0.03±0.01^{ab}	1.86±0.27^{ab}
	Background area	1.50±0.15	0.25±0.10	0.001±0.10	6.26±0.50	0.09±0.14	5.04±2.02	0.01±0.05	0.01±0.10
Sweet potato	Mining area	3.96±0.75^{a}	2.70±0.00^{ab}	0.009±0.002^{a}	10.25±2.50^{ab}	0.33±0.05^{a}	7.98±2.31^{a}	0.01±0.00	0.13±0.06^{ab}
	Background area	1.10±0.21	0.26±1.20	0.001±0.10	2.20±1.05	0.02±0.34	1.50±0.35	0.01±0.05	0.01±0.32
Irish potato	Mining area	4.62±0.08	1.70±0.05	48.20±4.58	9.39±0.30	0.41±0.03	18.08±1.37	0.11±0.02	0.15±0.12
	Background area	4.03±0.21	0.12±0.04	31.89±3.03	5.94±0.46	0.23±0.19	15.86±2.46	0.06±0.01	0.06±0.04
WHO Ref Std		10	1.3	20	0.1	10	50	0.02	0.01

^{a}Values are significantly different from the corresponding background area values ($p<0.05$) ^{b}Values are significantly different from WHO maximum permissible limit ($p<0.05$). The reference standard (Ref Std) was based on WHO (Naser et al. 2012; Shah et al. 2013; Ogundele et al. 2015).

PTEs Distribution among Water, Soils, and Plants

From the values summarized in Tables 1, 2, and 3 giving the distribution of selected potentially toxic elements in the soil, mining pond water, and selected food crops in the study area, large variations were observed in the patterns of distribution. Compared to the mining pond water and food crops, the mean concentration of Cu was highest in the soil samples and least in mining pond water. The level in the food crops varied with the food crop according to the following order: bitter leaf > pepper > Okra > maize grains > sweet potato > Irish potato. Cr had its highest concentration in the soil sample followed by okra while the lowest concentration was in mining pond water. The concentration of Fe in Irish potato was several folds higher than those of soil sample, mining pond water, and other food crops investigated. In the case of Mn, bitter leaf had the highest concentration followed by the soil sample and okra with the lowest concentration in mining pond water. Ni concentration was highest in the soil sample while Zn had its highest concentration in bitter leaf and lowest in mining pond water. Compared to the soil sample and food crops, the concentration of the toxic metals Cd and Pb were several folds higher in mining pond water.

Bioaccumulation of Potentially Toxic Elements from Soil and Pond Water into Food Crops

The results of BAFs for the PTEs transfers from soils to plants and pond water to plants via irrigation were used to quantify the metal concentrations in plants (Tables 4 and 5). The soil to crop transfer (Table 4) varied greatly across the different food crops. Only Fe in Irish potato and Mn in bitter leaf seem to accumulate to a significant extent, despite the fact that the soil was enriched in all of the PTEs investigated. This is in contrast to a study by Avila et al. (2017) where transfer from soil to potato tubers was not observed. Despite the fact the BAFs for Cd and Cu were lower than one, it is still slightly higher than what Luo et al. (2019) reported for rice, corn, and sweet potato crops in China.

Table 5 represents the BAFs for irrigation to crop absorption. Both Cd and Pb do not bioaccumulate significantly in any of the crops, and neither does Cr except for the okra plant (BAF = 2.4). For Ni, the bioaccumulation is moderate for bitter leave (3.8), pepper (1.8), and okra (3.9). Fe accumulates in Irish potatoes, similar to the soil absorption data although the Fe enrichment in the water is only doubles that of the background value. This is indicative of Fe being present in a bioavailable form in the water. Cu, Mn, and Zn BAF values were all well above one in all the crops, with a maximum BAF value of 274 for Mn in bitter leave, even though the Mn enrichment is only a factor of four. It is evident that the two plant crops, bitter leave, and okra, are extraordinary bioaccumulators of Mn, Zn, and Cu. This is in agreement with previous studies which showed that plants have higher levels of PTEs due to accumulation (Gupta et al. 2010). Dietary intake of many PTEs through consumption of plants has long-term detrimental effects on human health (Sharma and Agrawal 2005; Ezeabara et al. 2014). Even when toxic elements such as Cd and Pb are present in low concentrations, long-term exposure to these metals may result in bioaccumulation and thus harmful effects on the population (Ali et al. 2019).

Table 4 Bioaccumulation factors of eight PTEs in some selected food crops grown on soil around mining pond A in the study area

	Potentially toxic elements							
Food crop	Cu	Cr	Fe	Mn	Ni	Zn	Cd	Pb
Bitter leaf	*0.89*	0.03	0.01	***3.88***	0.22	***1.53***	*0.72*	0.02
Pepper	*0.57*	0.03	0.01	0.32	0.10	0.33	0.09	0.01
Okra	*0.53*	0.16	0.31	***1.17***	0.22	*0.78*	0.14	0.11
Maize Grains	0.28	0.03	0.00	0.29	0.04	***1.39***	0.03	0.07
Sweet potato	0.19	0.03	0.00	0.11	0.02	0.14	0.01	0.01
Irish potato	0.22	0.02	***11.59***	0.10	0.03	0.31	0.11	0.01

Table 5 Bioaccumulation factors of eight ptes in some selected food crops irrigated with mining pond Awater

	Potentially toxic elements							
Food crop	Cu	Cr	Fe	Mn	Ni	Zn	Cd	Pb
Bitter leaf	***45.22***	0.38	0.03	***273.85***	***3.81***	***24.93***	0.10	0.03
Pepper	***29.07***	0.42	0.03	***22.69***	***1.76***	***5.35***	0.01	0.02
Okra	***27.29***	***2.38***	***1.10***	***82.31***	***3.86***	***12.77***	0.02	0.15
Maize Grains	***14.51***	0.47	0.00	***20.38***	*0.74*	***22.68***	0.00	0.10
Sweet potato	***9.66***	0.40	0.01	***7.88***	0.38	***2.24***	0.00	0.01
Irish potato	***11.27***	0.25	***41.55***	***7.22***	0.47	***5.06***	0.02	0.01

Health risk assessment

The results of the HQ of potentially toxic elements through exposure to soil and consumption of food crops for both adults and children living in communities around the study area are summarized in Tables S4 and 6 respectively. The soil ingestion, inhalation, and dermal HQ values for adults and children were less than one and therefore seem to be of low risk for any of the exposure routes. Previous researchers reported similar findings where the HQs and their corresponding HIs of the studied PTEs in soil were less than 1 indicating that there was little adverse health impact from soil exposure (Hu et al. 2017; Chonokhuu et al. 2019; Luo et al. 2020). Furthermore, children had higher HQ and HI values than adults indicating that they are more likely to suffer from non-carcinogenic risks of exposure to PTEs in the studied soil. Children's hand-to-mouth activities have been reported by previous researchers as an additional pathway for exposure to soil PTEs in children (Rasmussen et al. 2001; Chen et al. 2015; Wang et al. 2019). Some previous studies have explained that the low HQ values for the soil pathway are a reflection of low transport risk, but still indicated that the extent of contamination will influence crop content and hence still forms a major component of the exposure scenario (Wang et al. 2019; Luo et al. 2020).

In contrast, the HQ and HI values for ingestion of the PTEs investigated in food crops are given in Table 6. It is clear from these values that toxicity risks are significantly higher than exposure to soil and are mostly above one. These findings are in agreement with previous studies which reported HQ values greater than one in various food crops (Zhuang et al. 2009b; Giri and Singh 2017; Bhatti et al. 2020; Edogbo et al. 2020;Ogunkunle et al. 2016). Children are clearly more at risk than adults, with a total HI of 48 for bitter leave as the highest value and 3.5 for sweet potato as the lowest. This indicates that intake of some of these PTEs through consumption of the varieties of food crops investigated, constitute a considerable risk. This is particularly the case for bitter leave, okra, and to lesser extent maize. It is also noted that the risk for bitter leave and okra is dominated by Mn, but for maize, Pb contributes the most to the HI. This correlates well with the earlier observation that bitter leave and okra had BAFs for Mn higher than 1 for both soil and water transfer. However, the BAF values for Pb were always well below one but the Pb levels are such that it still poses a significant risk in both age groups for okra and maize.

The cancer risks for four elements, Cr, Ni, Pb, and Cd, were calculated for all the food crops investigated in this study via ingestion, and the results are summarized in Table 9. The CR values for Cr and Ni for all the food crops were within 10^{-3} to 10^{-1}, indicating the high carcinogenic risk when compared to the New York State Department of Health (NYSDOH) cancer risk classification. However, the CR values of Cd and Pb in all the food crops, with the exception of Cd in bitter leaf for children, were within the range of 10^{-5} to 10^{-4}, indicating that they are associated with a moderate cancer risk. As it was with the noncarcinogenic risk, so also it is with the CR where the children had higher CR values than adults indicating that they are more likely to suffer from carcinogenic risks of exposure to PTEs in the studied food crops. This finding is similar to those reported by previous studies (Liu et al. 2013; Alidadi et al. 2019; Ashraf et al. 2021; Bayissa and Gebeyehu 2021). Adults and children had much higher Cr and Ni CR values than Cd and Pb, indicating that Cr and Ni make a significant contribution to the carcinogenic risk of the local population through consumption of the studied food crops. This indicates that intake of these carcinogenic elements through consumption of the varieties of food crops investigated, constitute a considerable risk. This is particularly the case for okra which has the highest CR value that is dominated by Cr for children. Previous studies have also reported similar CR values in food crops (Ametepey et al. 2018; Ashraf et al. 2021; Bayissa and Gebeyehu 2021). The total CR values for the carcinogenic PTEs in all the food crops studied were several fold higher than the permissible limits (10^{-6} and < 10^{-4}). This is in agreement with the previous studies (Tepanosyan et al. 2017; Ashraf et al. 2021; Alsafran et al. 2021).

Pearson rank correlation coefficient was calculated to find the relationship and possible sources of heavy metal contamination in the samples of food crops used in the study area. The result of the correlation between all the eight heavy metals (Cu, Cr, Fe, Mn, Ni, Zn, Cd, and Pb) in the food crops samples is summarized in Table 7. Significant positive correlation was observed between Cu-Mn (r = 0.88, $p< .01$), Cu-Ni (r = 0.87, $p< .01$), Cu-Zn (r = 0.56, $p< .01$), Cu-Cd (r = 0.85, $p< .01$), Cr-Ni (r = 0.62, $p< .01$), Cr-Pb (r = 0.82,$p<.01$), Mn-Ni (r = 0.78, $p< .01$), Mn–Zn (r = 0.69, $p< .01$), Mn–Cd (r = 0.98, $p< .01$), Ni-Zn (r = 0.50, $p< .01$), Ni-Cd (r = 0.68, $p< .01$), and Zn-Cd (r = 0.62,$p< .01$) respectively. This significant and positive correlation observed between most of the PTEs in the studied food crops is indicative of a heavy anthropogenic source of these materials in the environment. Previous studies have also reported that a high correlation coefficient between metals is indicative of the common source and nearly or similar metal accumulation in food crops (Hosna Ara et al. 2018; Zhuang and Lu 2020; Ashraf et al. 2021). However, across all the studied food crops, insignificant negative correlations observed between Fe and the other PTEs indicate that Fe concentration has less anthropogenic influence in the plants.

Table 6HQ and HI values of eight PTEs through consumption of selected food crops from abandoned tin mines in the study area for adults and children

Variety	Age group	Cu	Cr	Fe	Mn	Ni	Zn	Cd	Pb	*HI*
Bitter leaf	Child	***5.13***	0.07	0	***28.12***	***1.85***	***3.28***	***7.63***	***1.66***	***47.74***
Pepper	Child	***3.3***	0.08	0	***2.33***	***1.17***	*0.7*	***1***	*0.77*	***9.04***
Okra	Child	***3.09***	0.45	0.02	***8.45***	***1.88***	***1.68***	***1.44***	*7.41*	***24.42***
Maize Grains	Child	***1.99***	0.11	0	***2.53***	0.43	***3.61***	0.4	***6.21***	***15.27***
Sweet potato	Child	***1.32***	0.09	0	***1.01***	0.22	0.36	0.13	0.43	***3.53***
Irish potato	Child	***1.54***	0.06	***1.02***	*0.9*	0.27	*0.81*	***1.47***	0.5	***6.57***
Bitter leaf	Adult	***1.5***	0.02	0	***8.22***	*0.54*	*0.96*	***2.23***	0.48	***13.96***

Pepper	Adult	*0.96*	0.02	0	*0.68*	0.25	0.21	0.29	0.23	***2.64***
Okra	Adult	0.9	0.13	0.01	***2.47***	0.55	0.49	0.42	***2.17***	***7.14***
Maize Grains	Adult	*0.73*	0.04	0	*0.93*	0.16	***1.33***	0.15	***2.29***	***5.64***
Sweet potato	Adult	0.49	0.03	0	0.36	0.08	0.13	0.05	0.16	***1.3***
Irish potato	Adult	*0.57*	0.02	0.34	0.33	0.1	0.3	0.54	0.18	***2.39***

Table 7 Pearson rank correlation coefficient of selected heavy metals in food crops samples in the study area

	Cu	Cr	Fe	Mn	Ni	Zn	Cd	Pb
Cu	1							
Cr	0.17	1						
Fe	-0.41	-0.25	1					
Mn	0.88	0.07	-0.29	1				
Ni	0.87*	0.62	-0.40	0.78	1			
Zn	0.56	0.07	-0.36	0.69	0.50	1		
Cd	0.85	-0.10	-0.13	0.976**	0.68	0.62	1	
Pb	0.11	0.82*	-0.35	0.07	0.48	0.47	-0.11	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table 8 Enrichment factor and pollution index values of heavy metals in soil samples

	EF				PI			
PTE	Soil A	Soil B	Soil C	Soil D	Soil A	Soil B	Soil C	Soil D
Cd	0.00	0.00	0.03	0.00	300	443	80	483
Cr	0.99	0.62	9.38	0.56	607	1235	416	1957
Cu	0.38	0.24	3.59	0.21	197	210	276	175
Mn	18.75	11.80	178.13	10.61	44	74	7	56
Ni	0.30	0.19	2.81	0.17	328	318	269	308
Pb	1.88	1.18	17.84	1.06	235	288	303	192
Zn	8.76	5.51	83.22	4.96	213	183	256	143

Table 9 CR values of four PTEs through consumption of selected food crops from abandoned tin mines in the study area for adults and children

Food crop	Age Group	Cr	Ni	Cd	Pb	TCR
Bitter leaf	child	1.96x 10^{-2}	8.59x 10^{-2}	3.96x 10^{-3}	7.69x 10^{-5}	1.09x 10^{-1}
Pepper	child	2.15x 10^{-2}	3.98x 10^{-2}	5.16x 10^{-4}	3.59x 10^{-5}	6.18 x 10^{-2}
Okra	child	1.22x 10^{-1}	8.72x 10^{-2}	7.45x 10^{-4}	3.44x 10^{-4}	2.09 x 10^{-1}
Maize Grains	child	3.63x 10^{-3}	2.54x 10^{-2}	2.62x 10^{-4}	3.68x 10^{-4}	6.23 x 10^{-2}
Sweet potato	child	3.11x 10^{-2}	1.29x 10^{-2}	8.75x 10^{-5}	2.54x 10^{-5}	4.41 x 10^{-2}
Irish potato	child	1.96x 10^{-2}	1.60x 10^{-2}	9.62x 10^{-4}	2.94x 10^{-5}	3.66 x 10^{-2}

Bitter leaf	Adult	4.20 x 10^{-3}	1.84x 10^{-2}	847x 10^{-4}	1.65x 10^{-5}	2.35 x 10^{-2}
Pepper	Adult	4.6x 10^{-3}	8.52x 10^{-3}	1.11x 10^{-4}	7.69x 10^{-6}	1.32 x 10^{-2}
Okra	Adult	2.60x 10^{-2}	1.87x 10^{-2}	1.59x 10^{-4}	7.36x 10^{-5}	4.49 x 10^{-2}
Maize Grains	Adult	7.76x 10^{-3}	5.45x 10^{-3}	5.62x 10^{-5}	7.79x 10^{-5}	1.34 x 10^{-2}
Sweet potato	Adult	6.65x 10^{-3}	2.77x 10^{-3}	1.87x 10^{-5}	5.45x 10^{-6}	9.45 x 10^{-3}
Irish potato	Adult	4.19x 10^{-3}	3.44x 10^{-3}	2.06x 10^{-4}	6.28x 10^{-6}	7.84 x 10^{-3}

Limitation of the study

Due to insecurity in some parts of Nigeria, including Plateau State, it is currently difficult to return to the original sampling sites to generate new data from some of the sites where samples were collected in 2016. The authors acknowledged that the study's presentation of data from 2016 is indeed a limitation of this study, and that more work is required to collect and analyze more recent samples from the study area. We believe that this can only be accomplished in the near future, once the insecurity has decreased. However, as far as the authors are aware, no reclamation work in the area has been done, and the data set presented and discussed here should still be largely relevant or useful.

Conclusions

Based on the results of this study, it can be concluded that the mining pond water in farms surrounding the mining ponds contains different concentrations of potentially toxic elements, which are well above all guideline values. This makes the consumption of pond water as a drinking water resource, highly undesirable and unsafe. Although the levels of PTEs in soil were well below the DPR (Nigerian) target values, it was significantly higher than the WHO guideline values for arable land. In addition, the use of the pond water as an irrigation source and the surrounding soil as arable land are also not advisable. There is evidence that these PTEs are absorbed by crops (either as a result of contaminated soil or irrigation water or both) in significant amounts. The bioaccumulation is also not uniform and it was shown that bitter leave and okra are two crops that have high PTE accumulation potential. The HQ and their corresponding HI values for adults and children in all the routes of soil exposure (ingestion, inhalation, and dermal) were less than one indicating low noncarcinogenic risks from exposure to the soil for the studied PTEs individually and their combination. However, the results of non-carcinogenic risk of exposure to PTEs from crops reveal HQ values greater than 1, and total risk values as high as 48 were found for bitter leaf. Specifically, bitter leaf, okra, and maize pose significant risks upon consumption. What is more, the risk for children is 3.5 times higher than for adults. Of major concern is the fact that Pb dominates the total risk for maize, as it is probably a staple crop. The CR values for Cr and Ni for all the food crops via the ingestion route for both children and adults indicated high carcinogenic risk. This research could inform policymaking, but also crucially could provide data for further research on the mental development of children in the area. Furthermore, the data can be used by the local community in taking protective measures and providing evidence to the government to take action in alleviating heavy metal pollution in mining areas. Since the data presented in this study is from 2016 we recommend that additional work should be done to collect and analyze recent samples.

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Conflict of interest

The authors declare that they have no conflict of interest.

Data availability

On reasonable request, the corresponding author will make the datasets used or analysed during the current study available.

Compliance with ethical standards

Animal research

'Not applicable'

Consent to participate and consent to publish

'Not applicable'

Authors Contribution

"All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by [Simon Gabriel Mafulul]. The first draft of the manuscript was written by [Simon Gabriel Mafulul] and [Sanja Potgieter-Vermaak] with input from [Zebulon S.C. Okoye], [Ishaya Yohanna Longdet], and [J.H. Potgieter]. All authors read and approved the final manuscript."

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