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Determination of lead (Pb) levels and an assessment of environmental health risk from the vicinity of abandoned Pb mines

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ABSTRACT

Artisanal mining in Nigeria has caused lead (Pb) poisoning in 2010 and 2015 respectively. Available statistics revealed that in the two ugly scenarios over 500 children died and about 387 seriously sick. This study investigated 40 surface soil samples collected from the vicinity of 4 abandoned Pb mines in Ebonyi State, Nigeria. Mean concentration of Pb in the samples varied from 783 mg/kg to 1260 mg/kg. These values were compared with soil guideline values (SGVs) from 6 countries and the highest Pb content (1260) exceeded SGVs from 4 countries. To further evaluate the risk prevalent in these sites, we calculated the concentration of Pb from a sample that can be consumed by a child (representing the most vulnerable group) to reach the US EPA recommended value for Pb (3.6 µg kg-^{1}bw day-^{1}). These values were found to vary from 2.1 µg kg-^{1}bw day-^{1} to 3.7 µg kg-^{1}bw day-^{1}. On the basis of a soil ingestion rate of 50 mg d^{-1} for a child (<6 years), we also calculated the amount of soil that a child would need to ingest daily in order to exceed this guideline.

Keywords: Lead, abandoned mine, human health risk, soil, children.

INTRODUCTION

Mining is a temporary use of land, with the operating life of a mine lasting from a few years to several decades. In developing countries including Nigeria, it is a common practice for mining companies to leave mine sites in the excavated condition without following the appropriate practices in mine closure. Abandoned mines are sites where mining activities occurred, but acceptable mine closure and reclamation did not take place. Such mines could impact the environment negatively by contaminating air, water, soil, and wetland sediments from the scattered tailings, as well as pollution of groundwater by discharged leachate, unless the proper remediation is conducted. Thus, abandoned mines contribute to the legacy of environmental degradation left by historic mining activities and their health impact on residents, is a persistent social issue, and several studies [1-2] have identified health risks of residents living near abandoned mines. It has been reported [3] that artisanal lead (Pb) mining in Ebonyi state started in 1952 and has continued till date with more companies springing up and these activities have given rise to many abandoned Pb mines. This study observed that these mines are located near residential homes, schools and children's playground. It was also observed that some of these mines have been converted to either farmlands or water ponds. These practices could introduce Pb into the food chain. During the rainy season, children covert pond mine into a swimming pool (Figure 1) and during the dry seasons, ponds dry up and children use them as playground (Figure 2).

Figure 1: Children bathe in abandoned lead pond mine

In this scenario, the children are in constant touch with the environmental matrices (soil, dust and water) which could enter their bodies through the exposure pathways (oral ingestion, inhalation and dermal) [4-5]. Lead is an extremely useful metal but unfortunately has also proved to be a dangerous toxin. Lead exposure is particularly dangerous to young children because they absorb more lead from their environment than adult [6]. The toxic nature of lead has been recognized for millennia, with the earliest published reports dating back to 2000 BC [7]. However, the range of health effects that exposure to lead can cause and the low concentrations of lead in blood at which these effects can occur is only now being fully appreciated. It is now understood that lead is toxic, especially to children, at levels that were previously thought to be safe. Lead poisoning has been a menace to the environment and human health for decades

Figure 2: Children relaxing in abandoned Pb mine while searching for water

In addition to adverse health effects, a study [8] has shown that there is a very strong association between preschool blood Pb and the subsequent crime rate trends over several decades in the United States of America (USA) and some European countries. A recent report [9] has labelled Pb as ‘America’s real criminal element’. This is because high crime rates in the USA as well as other abnormal behavioural activities have been linked to high Pb content in children’s bodies. The report noted that when differences in atmospheric Pb density between big and small cities went away, so did the difference in murder rates.

The association between low-level Pb exposure during early development and subsequent deficits in cognitive development and behaviour is widely studied and accepted [10-12]. A large and diverse literature in epidemiology, psychology, and neuroscience reaches the consensus that early childhood Pb exposure negatively affects cognitive development and behaviour in ways that increase the likelihood of aggressive and antisocial acts [13-14]. Furthermore, higher Pb levels have been associated with aggressive behaviour, impulsivity, hyperactivity, attention impairment, “minimal brain damage,” and attention deficit and hyperactivity disorder [15]. These effects are present for all Pb levels, for exposure from the prenatal period through early childhood, and for cognitive and behavioural performance of all age groups from infants to teenagers. It is generally agreed that early childhood exposure (less than 6) is most harmful to psychological development, and that these effects persist to a great degree [16].

Children have been the focus of human health risk studies with respect to high Pb content in environmental matrices because in the event of Pb poisoning, children are the most affected. For example, Pb poisoning which occurred in Zamfara State (North-West of Nigeria) in 2010 killed 400 children (less than 6 years) and made about 3,500 children seriously sick [17]. The epidemic which was described as the worst of such an occurrence in modern history occurred due to artisanal mining. In addition, on June 6, 2015, it was reported [18] that 28 children (less than 6) died and 37 seriously sick in Niger State (Central Nigeria). The devastating impact of this outbreak was associated with new mining sites which were found to contain high Pb ores which are often brought home for crushing and processing.

In line with this, there is increasing awareness [19-20] that abandoned industrial sites harbour contaminants and since some of these contaminants particularly Pb is immobile in soil, their accumulations occur over time which may result in elevated concentration. Such scenarios could be a potential threat to human health and the environment. Nigeria Pb poisoning and the lack of any information on the environmental pollution and health impact related to contamination of the abandoned Pb mines in Ebonyi State, (South-East Nigeria) drew the attention of the authors to the need for a community health study. Literature survey showed that no study has investigated Pb levels in the selected abandoned mines. Thus, this work has been designed to determine the total Pb content in soils within the vicinity of four abandoned Pb mines and also to explore the environmental and health implications via oral ingestion of soil.

EXPERIMENTAL SECTION

Study Area

Ebonyi State (South-East Nigeria) is rich in solid minerals including Pb. Mining and crushing is the main industrial activity prevalent in the State. Thus, artisanal Pb mining has been ongoing for over three decades and has given rise to many abandoned mine scattered across the three senatorial zones in the State. Four abandoned Pb mine (Mkpumaakpatakpa mine, Ohankwu Ikwo mine, Ishiagu Ihetutu mine and Achara Unuhu mine) covering the three zones of the State were selected for the study. The selection criteria was based on closeness to populated residential homes and children playground such as schools. Figure 3 shows the study locations.

Sample collection and preparation

Sampling was carried out during the dry season and surface soil samples were collected from the vicinity of four abandoned mining sites (not exceeding 500m from the mine). Surface samples (0 – 2 cm) were collected because it has been proven that surface material is most relevant for human health risk assessment via oral ingestion [21]. Ten samples were collected from Mkpumaakpatakpa mine (Ebonyi North) on February 19, 2015, ten samples were collected from Ohankwu Ikwo mine (Ebonyi Central) on February 28, 2015, ten samples were collected from Ishiagu Ihetutu mine (Ebonyi South) on March 8, 2015 and ten samples were collected from Achara Unuhu mine (Ebonyi North) on March 15, 2015. In total 40 samples were collected for the study. The samples were placed inside labelled bags and sealed and then transported to the laboratory. The samples needed no drying but were gently disaggregated before sieving. The soil samples were sieved using a < 125 µm nylon sieve to remove extraneous matter such as small pieces of brick, stones, and other debris. The >125 µm soil samples collected after sieving were weighed (their mass recorded) and stored in sealed plastic containers. All procedures of handling were carried out without contact with metal objects/utensils to avoid potential cross contamination of the samples. Finally, the < 125 µm soil samples were stored in plastic containers prior to digestion. All procedures were carried out without contact with metal objects / utensils to avoid potential cross-contamination of the samples.

Figure 3: Map of Ebonyi State, showing study locations

Legend: Mkpumaakpatakpa (Agbaja), Ohankwu (Ikwo), Ishiagu (Ihetutu), Achara Nuhu

Sample Digestion and Analysis

Reagent grade chemicals were used in all cases. Sample digestions were carried out using a hot-plate. Method 3050b [22] was adapted in sample digestion. 10 ml 1:1 nitric acid (HNO_3) was added to beakers containing 1g soil sample as well as beakers (triplicates) containing certified reference material (SRM 2711), covered with watch glass and heated for 15 minutes without boiling. Samples were cooled, 5 ml HNO_3 was added and heated for 30 minutes (brown fumes was given off). More 5 ml $HNO_3$was added and no brown fumes was given off. Solution was allowed to evaporate to < 5 ml and allowed to cool. 2 ml water and 3 ml 30% hydrogen Peroxide (H_2O_2) was added and heated for 2 hrs until effervesces ceased. Solution was reduced to 5ml via evaporation. 10 ml hydrochloric acid (HCl) was added and heated for 15 minutes without boiling. After cooling, the digested samples were filtered using a whatman filter paper (grade 41, pore size 20 µm) into 100 ml volumetric flask. The filtrate was diluted to the mark with ultrapure water of resistivity 18.2 MΩ-cm at 25^0C and ready for analysis using Flame atomic Absorption Spectrophotometer (FAAS). Each sample was digested in triplicates.

Flame Atomic Absorption Spectrophotometer (FAAS) protocol

Soil samples and the certified reference material to be analysed by FAAS were prepared in triplicates. Reagent blanks were included to check contamination whilst certified reference material was meant to check accuracy and reproducibility. Six calibration standards over the range 0-10 µgmL-1 (mgL-1) were prepared from 1000 µgmL-1 Pb stock solution; this was used to calibrate the instrument and also to plot the calibration graph and the regression coefficient (R^2) obtained was 0.999 (linear graph). Based on the excellent R^2 value, the samples were analysed.

RESULTS AND DISCUSSION

In order to check for the robustness of the analytical method, a certified reference material (SRM 271) was used. The certified value is 1162 ± 31 and 1153 ± 16 was obtained in this study. The percentage accuracy was calculated to be 99.2 certifying the robustness of the analytical protocols. The results from the different mines showed that Achara Unuhu mine had Pb concentrations that ranged from 431 mg/kg to 1305 mg/kg. In Ishiagu Ihetutu mine, Pb concentration was found to vary from 703 mg/kg to 2603 mg/kg. Lead concentration in Mkpumaakpatakpa mine ranged from 450 mg/kg to 2402 mg/kg while total Pb content in Ohankwu mine ranged from 402 mg/kg to 1980 mg/kg. A statistical software Minitab 16 was used in the result analysis. A boxplot (Figure 4) showing median, mean, box boundary (25th and 75th percentile) and whiskers (10th and 95th percentile) as well as statistical analysis (Table 1) showing minimum, maximum, median, mean and standard deviation (SD) have been used to show Pb concentrations across the four abandoned mines. It can be seen from the Table 1 that the highest concentration of (Pb 2603 mg/kg) was obtained from Ishiagu Ihetutu mine while the lowest Pb concentration (402 mg/kg) was observed from soil collected from Ohankwu mine. High Pb levels recorded these sites proofs that most Pb that is released to the environment came from accumulated deposit [23]. The primary processes influencing the fate of Pb in soil include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter. These processes limit the amount of Pb that can be transported into other environmental matrices. Moreover, studies [24-25] have shown that Pb is immobile in soil and accumulate over time which could lead to elevated concentrations. Studies on Pb levels in abandoned Pb mine is scarce, however, the result of this study competed favourably with the available ones. A study [26] that investigated Pb levels in abandoned Pb Mine at Frongoch in west Wales obtained Pb concentrations that ranged from 32 mg/kg to 4000 mg/kg. However, another study [27] that determined Pb concentration in a. former industrial Pb site in Newcastle upon Tyne, UK found Pb levels in the range of (188–60300 mg/kg), this finding exceeded maximum value obtained in this study. This is because the current study investigated Pb mines that are less than a decade whereas the study at Newcastle has existed for over eight decades. Since Pb is immobile and accumulates over time, higher Pb content is expected in the older site.

In order to assess the environmental health impact of high Pb content recorded in these sites, the values obtained were compared with the soil guideline values (SGVs) of other countries including South Africa as none exist for Nigeria. Table 2 gives the SGVs (industrial soil-use) of six countries while Table 1 shows Pb mean values obtained from this study. In comparison, it can be seen that 783 mg/kg obtained from Achara Unuhu mine, 1260 mg/kg from Ishiagu Ihetutu mine, 1252 mg/kg obtained from Mkpumaakpatakpa mine and 1034 mg/kg observed inOhankwu minewere found to be higher than SGVs from England, Australia, Netherlands and Canada, but lower than SGVs from South Africa and Germany.

Table 1: Statistical summary of Pb levels in the abandoned mines

Abandoned mines	Minimum	Maximum	Median	Mean	Standard deviation (SD)
Achara Unuhu	431	1305	724	783	281
Ishiagu Ihetutu	703	2603	1071	1260	601
Mkpumaakpatakpa	450	2402	1154	1252	626
Ohankwu	402	1980	771	1034	321

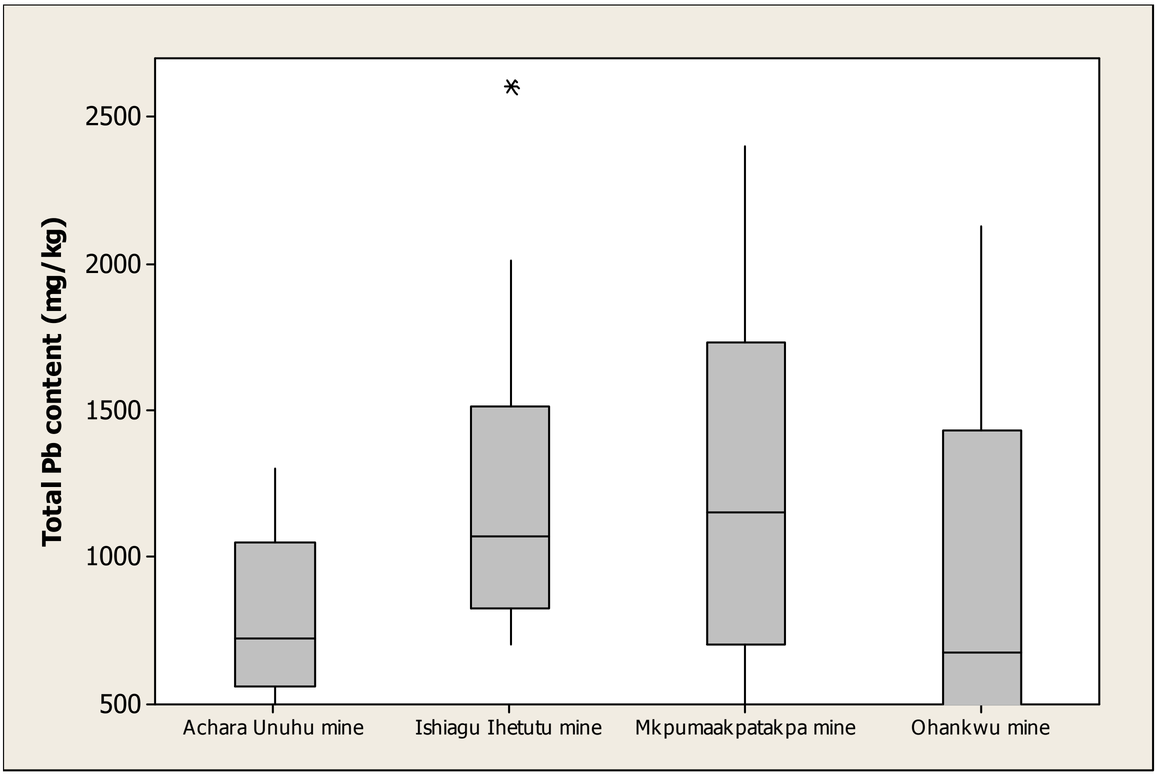

Figure 4: Boxplot of total Pb content in the four abandoned mine sites

Table 2: **Global Soil Guideline Values (industrial soil-use) for Pb**

S/N	Countries	Soil Guideline Values (SGVs) (Industrial) (mg/kg)
1	South Africa[28]	1,900
2	England[29]	750
3	Germany[30]	2,000
4	Australia[31]	500
5	Netherlands[32]	530
6	Canada[33]	600

When Pb levels are in excess of SGVs, it signifies the presence of risk to man and his environment, particularly children who continuously explore their environment. It is to be noted that since there no remediation plan either by site owners or government, Pb will continue to accumulate in these locations and when such sites are converted to farmland, Pb would inevitably be introduced into the food chain. Such scenario could lead to food poisoning.

Estimation of maximum potential daily Pb intake from the abandoned mines

Although, it has been established that there is some level of risks in the abandoned mines but the authors considered it necessary to calculate the potential daily Pb intake from the abandoned mines. This procedure determines the maximum potential daily intake from soil that any exposed child (representing the most vulnerable group) could possibility ingest in order to reach the tolerable daily intake (TDI) for Pb, which is 3.6 µg kg^{-1}bw day^{-1} [34]. Equation (1) below was employed to achieve this.

DI= [EC x SIR] / BW …………..(1) [35].

Where DI = daily intake (µg kg bw-1 day-1) as determined in < 125 µm fraction of the soil sample with the highest concentration; EC = Exposure concentration of the PTEs in < 125 µm (µg/g); SIR = soil ingestion rate (0.05 g day-1) [36]; and BW = body weight (18.6 kg for a 3-6 year old child) [37].

It can be seen from Table 3 that maximum Pb estimated daily intake exceeded recommended daily intake slightly (3.7 µg kg^{-1}bw day^{-1}) in soils collected from Ishiagu Ihetutu and

Table 3: Maximum Pb estimated daily oral intake from sampled soils

Abandoned mines	Maximum estimated daily intake (μg kg^{-1}bw day^{-1}) based on 50 mg/day ingestion	Amount of soil that could be consumed by a child in order to exceed the guidelines (mg/day)
Achara Unuhu	2.1	85.7
Ishiagu Ihetutu	3.7	48.6
Mkpumaakpatakpa	3.7	48.6
Ohankwu	2.8	64.3
Recommended daily intake	**3.6**	**50**

Mkpumaakpatakpa mines respectively while soil samples from Achara Unuhu and Ohankwu mines had maximum Pb estimated daily intake below recommended value. On the basis of a soil ingestion rate of 50 mg d^{-1} for a child(less than 6 years), to exceed the guidelines (TDI) a child would need to consume, per day, the following amounts of soil: 85.7 mg/kg, 48.6 mg/kg. 64.3 mg/kg. Obviously, these calculations have helped to estimate the potential risk from the studied sites via oral ingestion of soil but plans are on the way to further investigate the environmental health risk by applying the oral bioaccessiblity protocol as recommended by Bioaccessibilty Research Group Europe (BARGE).

CONCLUSION

We conclude that high Pb content recorded across the sites has demonstrated that Pb mines are media through which Pb could leach into the neighbouring environment particularly water bodies which could lead to contamination and poisoning. Based on these findings, we conclude that it is not advisable, however, to convert these abandoned mines into farmlands or playgrounds (schools or recreation parks) as this would increase the exposure risk to humans. We also suggest that the appropriate practices in mine closure after excavation should be adopted.

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