

In Vitro Bioaccessibility of Lead in Artisanal Mining Contaminated Soils and Sediments from the Anka Area, NW Nigeria

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Abstract

The gastric bioaccessibility of Pb was investigated in soils and sediments from five villages in the Anka area of north-western Nigeria which has been adversely affected by artisanal mining of gold from lead-rich ores. *In vitro* bioaccessibility experiments were used to determine the extractability of Pb in order to evaluate the human health risk, especially to children below the age of five. The concentration of Pb in the simulated gastric fluids ranges from ~ 198 to 41740 $\mu\text{g}\cdot\text{g}^{-1}$ (mean, 9732 $\mu\text{g}\cdot\text{g}^{-1}$), with corresponding human bioaccessible fraction between ~ 29 and 100% (mean, ~ 60%). Chemical daily intake (CDI, $\mu\text{g}/\text{Kg}/\text{Day}$) values of between 111 and 41587 are generally very high compared to the tolerable daily intake (TDI) of ~ 3.6 $\mu\text{g}\text{Pb}/\text{Kg}/\text{Day}$. The high bioaccessibility is a result of high total concentration of Pb and the presence of highly soluble carbonate and oxide minerals in the ores. These results point to the very adverse health effects likely to result from incidental hand-to-mouth ingestion of soils by children in the affected villages. The results further show that the low pH of gastric juices enhances the extraction of Pb. Given the likelihood of sub-nutrition in the affected communities, characterized by skipping of meals, which can result in lowering of the pH over extended periods, the risk of Pb poisoning is further increased. This study was based on a hand-to-mouth ingestion scenario alone, but as other exposure routes, such as eating improperly washed vegetables and inhalation of dust are possible, the risk might even be higher. This, along with the fate of extracted Pb in the intestinal environment may need to be evaluated in order to fully quantify the bioavailability of Pb in the area.

Keywords: artisanal mining, lead, *in vitro* bioaccessibility, contaminated soil

1. Introduction

Since the dawn of civilization, we have continually exploited minerals and rocks for the production of goods, energy and building materials (Hudson-Edwards et al., 2011) with its attendant environmental consequences. Mining results in a variety of wastes, ranging from host rock debris and its associated gangue minerals, to dusts from milling, to slag resulting from smelting operations. These, often potentially toxic element (PTE, Alloway, 1995) laden wastes serve as sources of contamination in the environment and provide pathways for human exposure. In many parts of the world, metalliferous mining activities have been shown to lead to heavy metal contamination of soils, sediments and water (Adriano, 1986; Thornton, 1996; Jung, 2001; Bird et al., 2003; Dolenc et al., 2007). In the Anka region of north-western Nigeria, exploitation of gold and associated sulfide minerals by artisans is a common practice and has led to severe contamination of soils and stream sediments. Environmental problems related to artisanal gold mining are widely reported in the developing world, for example, Ghana (Hilson, 2002; Babut et al., 2003); Ecuador (Appleton et al., 2001) and the Brazilian Amazon (Hinton et al., 2003). Artisanal mining and beneficiation methods are often very crude and under little or no regulation, leading to widespread improper disposal of mine wastes and contamination (Hilson, 2002).

As a result, elevated levels of the PTEs may be found in and around metalliferous mines due to the dispersion of mine wastes down slope by surface runoff, wind action and effluent drainage into nearby soils and open water systems (Jung, 2001). One implication of having excessive levels of these elements in soils is that crops may take them up and pass them through the food chain to human beings. Another route of transmission to humans, especially children, is hand to mouth ingestion, in addition to contamination of surface and groundwater resources and inhalation of dusts.

Little has so far been done to investigate the environmental impact of artisanal gold mining in general and soil heavy metal concentrations and bioaccessibility in this and other areas of Nigeria. As pointed out by Olade (1987), most studies on the biogeochemical cycling of heavy metals have been within temperate or sub-tropical ecosystems and therefore little is known about their behaviour in the semi-arid tropics, such as northern Nigeria. A recent outbreak of acute lead poisoning among rural dwellers of the Anka area, which killed hundreds of children (UNEP/OCHA, 2010) has been traced to artisanal mining and processing of gold from a mainly galena-chalcopyrite ore deposit. In fact, the work conducted by UNEP reported concentrations of up to 60,000 µg/g lead in the soil of some villages while the Blacksmith Institute (2011) reported soil lead concentrations in seven villages to be in excess of 100,000 µg/g, resulting in blood lead levels in children generally exceeding the internationally acceptable limit of 10 µg/dl. These results are similar those obtained in two villages in this area by Dooyema et al. (2012).

It is therefore vital to study the effect of these small-scale mines on the quality of the environment and the possible human health risks incident upon potentially toxic element contamination of soils and sediments in the area. To address this gap, the present work has investigated the geochemistry of soils and sediments from Anka in the north-western Nigeria schist belts, with particular focus on the relative *in vitro* bioaccessibility of lead.

Knowledge of total metal concentration in environmental matrices alone is not enough in assessing bioavailability, mobilization and the human risk in an environment. Neither does the total concentration provide a good indication of the levels of metals potentially available to plants (Ullrich et al., 1999). *In vitro* bioaccessibility tests (IVBA) are inexpensive, physiologically-based extraction tests (PBET) designed to estimate the bioaccessibility of elements along exposure pathways (Morman et al., 2009). This is achieved by measuring the geochemical reactivity of the materials in simulated body fluids such as saliva, lung fluids and gastric juices or blood plasma. It is used as a proxy for the more complicated, expensive and often ethically constrained measurements of bioavailability using *in vivo* methods involving the use of animal or human subjects. Bioaccessibility in relation to human exposure by ingestion has been defined by Ruby et al. (1999) as the fraction of a potential toxicant in earth materials that becomes solubilised in the stomach or lungs, thus becoming available for absorption. For a given toxicant such as a potentially toxic element, the total concentration in an earth material is far more than the quantity eventually absorbed into the circulatory system of a subject (Plumlee & Ziegler, 2004). This means that, bioavailability < bioaccessibility < total concentration of a contaminant in an earth material.

Several methods of performing the *in vitro* studies have been reported in the geochemical literature. For example, Medlin (1997) used a fluid containing pepsin, admixed with citric, malic, lactic, acetic and hydrochloric acids. The method of Drexler and Brattin (2007) which was adopted by Morman et al. (2009) advances the combination of concentrated hydrochloric acid and glycine in deionised water. The approach of EPA (2008) involved combinations of sodium chloride, pepsin with hydrochloric acid and sodium bicarbonate, bile salts and pancreatin for the stomach and intestinal phases respectively. This two stage procedure earlier reported by Cave et al. (2006) was adopted by Button et al. (2009), while investigating the risk to humans at arsenic contaminated sites at a former mine at the Devon Great Consols, southwest England. However, the EPA (2008) in a subsequent study appeared to question the necessity of using the complex fluids. They argued that when the bioaccessibility of a series of test substances were compared using 0.4M glycine buffer at (pH 1.5) with and without the enzymes and metabolic acids, no significant difference was observed. They therefore concluded that the simplified buffer employed is appropriate, even though it lacked some constituents known to be present in gastric fluids: this is the method used in the present study.

2. The Study Area

The study area (Figure 1), which covers about 990 km², is in the Anka local government area of Zamfara State in the north-western part of Nigeria. It falls between latitude 11°51'N and 12°08'N, and longitude 5°51'E and 6°08'E and is characterized by generally gentle relief. The main surface water body in the area is the Anka River, which lies about a kilometre to the north of the town and numerous seasonal streams dissect the landscape, feeding into the main river. Many of these streams are used as sources of water for domestic use, irrigation and livestock watering, especially during the wet season. Vegetation in the entire region is generally sparse, and has been described by Russ (1957) as savannah forest together with scrubs, which thin out in a northerly direction, with semi-deciduous high forests along streams and depressions. Generally, the inhabitants of this area are farmers, who are engaged in the cultivation of a large number of cereal and vegetable crops.

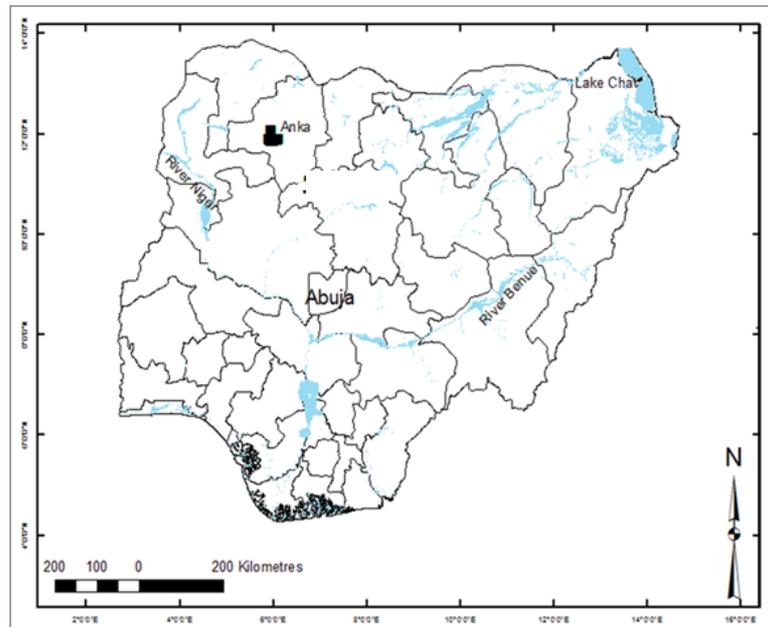


Figure 1. Outline map of Nigeria showing the location of the study area (modified from Waziri, 2012)

Geologically, the study area is in the Schist Belt of the Nigerian basement complex which is part of the Pan-African mobile belt, sandwiched between the West African Craton and the Congo Craton. It has been described by McCurry and Wright (1977) as a system of synclinal belts of low-grade metasediments, downfolded into high-grade gneisses and migmatites, the whole intruded by batholithic granites. Metamorphism in these belts is generally of low grade, falling within the green-schist facies and characterized mainly by schists, phyllites, banded iron formations, carbonate rocks and mafic metavolcanics which are now in the form of amphibolites and meta-conglomerates (Turner, 1983). These and the migmatite-gneiss basement have been cut by Pan-African granites.

Like many other similar geological belts in Nigeria and the entire West African region, the Anka area has been the focus of artisanal gold exploitation for several decades. Gold in this area is hosted by schists, phyllites and quartzites related to sub-regional structural elements subsidiary to the Anka fault (Garba, 2003) and metaconglomerates (Russ, 1957). The gold mineralizing fluids, based on $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ - $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ discrimination diagrams and inter-lithophile elements ratios are interpreted to be of metamorphic origin (Danbatta et al., 2009). The mineralized concordant veins are generally short, not exceeding half a kilometre of strike length and trace metal concentration in altered wall rock reported by Garba (2003) of 647–5410 ppm Cu; 7550–22600 ppm Pb; 1.5–8.6 ppm Ag and 123–6320 ppb Au show that the ores are very rich in lead and copper minerals, mostly galena which was observed during field work and identified in the contaminated soil using SEM (Figure 2) and also chalcocopyrite.

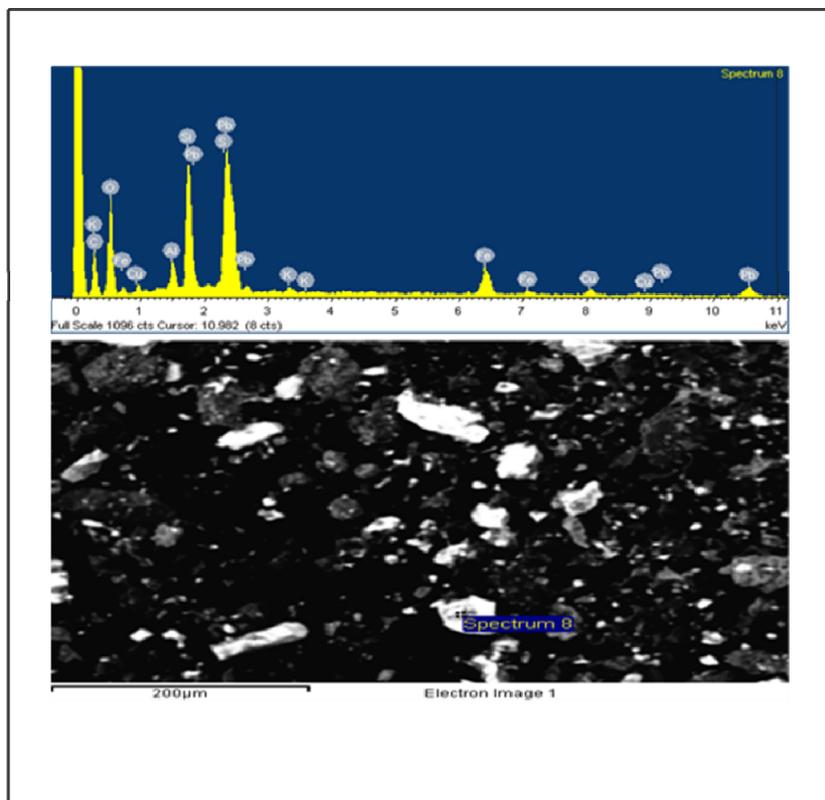


Figure 2. SEM micrograph and EDS spectra for a highly contaminated soil sample from Anka area, showing widespread lead minerals (light particles) in the sample. The particle sizes, generally less than 200 μm make them very amenable for hand-to-mouth ingestion and suspension as dusts

3. Methodology

3.1 Fieldwork

Top soil and sediment samples were taken from the vicinity of mines and within the villages where ore processing has taken place. Samples were collected from 0 to 15 cm depth using a plastic trowel and placed in plastic self-seal bags. At each sampling point, three samples were collected at the apices of a roughly equilateral triangle with sides one meter long and subsequently mixed together to make a composite sample. The location of each sample was indicated on a topographic base map of the area and geographic coordinates in the form of Latitude and Longitude were recorded using a hand held global position system (GPS). These were subsequently used to produce the sample location map (Figure 3) using Surfer Version 9.1.325 Surface Mapping System (Golden Software, Inc., 2009).

3.2 *In vitro* Bioaccessibility Tests

The soil samples were air dried and sieved to $< 60 \mu\text{m}$. Gastric fluids were simulated by adding approximately 60 ml concentrated hydrochloric acid to 2 L of 0.4 M glycine solution. The glycine solution was prepared by adding 60.06g of glycine to 1.9 L of deionised water and the solution made up to 2 L. The solution was then warmed in an incubator to a temperature of $37 \text{ }^\circ\text{C}$ and its pH adjusted to 1.5 ± 0.05 by drop-wise addition of concentrated hydrochloric acid.

The test material (1 g of the $< 60 \mu\text{m}$ soil) and 50 ml of the extraction fluid were placed in high density, wide mouthed Nalgene bottles. The bottles were tightly closed and shaken well to ensure that there was no leakage and that no soil was caked at the bottom of the bottle. The bottles were then placed into a temperature controlled incubator ($37 \pm 2 \text{ }^\circ\text{C}$) and shaken side-to-side at 300 rpm for 1 hour. After 1 hour, the bottles were removed and placed upright on a bench top to allow the soil to settle to the bottom. A 15 ml aliquot of the supernatant was withdrawn using a syringe and filtered using a Luer-Lok attachment fitted with $0.45 \mu\text{m}$ cellulose acetate filter. The filtered solutions were stored in a fridge at $4 \text{ }^\circ\text{C}$ until they were analyzed.

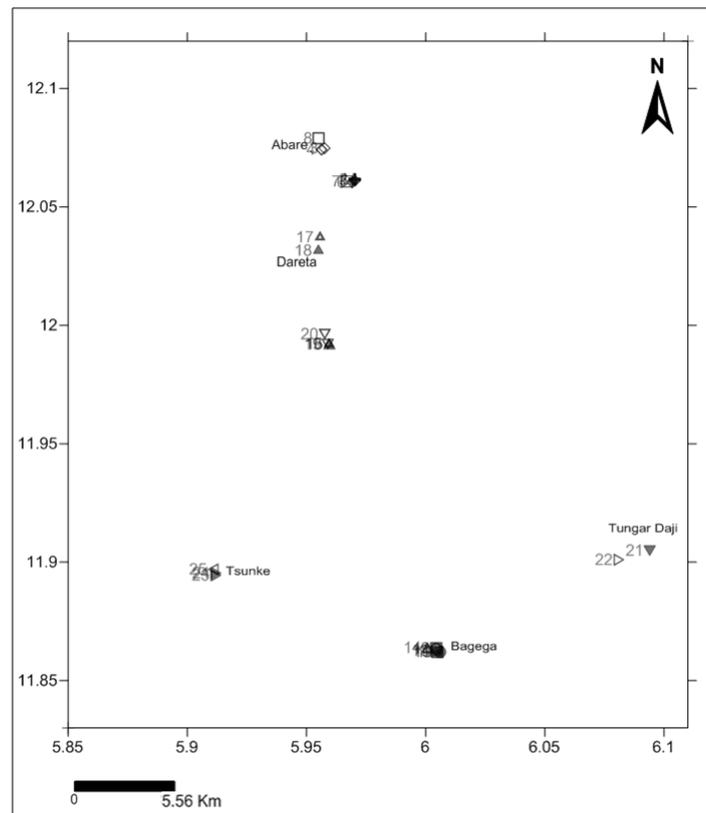


Figure 3. Map of the Anka area showing sampling sites and location of some artisanal mine pits. The location of this area in Nigeria is indicated in Figure 1

3.2.1 Effect of pH on *In vitro* Bioaccessibility

To test the effect of pH on lead bioaccessibility, the experiment was repeated at three pH values; 1.50, 2.20 and 2.90 which were achieved by successively reducing the volume of concentrated hydrochloric acid used (from 60 ml to 30 ml and 15 ml) while keeping weight of glycine and total solution volume constant. A set of fifteen samples was used in this study, where three equal aliquots of each sample were each extracted with the solutions of varying pH in an incubator for one hour at 37 °C with constant shaking.

3.2.2 Effect of Solid: Fluid Ratio on *In vitro* Bioaccessibility

To test the possibility that ratio of test material weight in the extraction bottle to volume of extraction fluid has an impact on contaminant solubilization, this experiment was conducted using three solid to fluid ratios. In addition to the 1:50 (1 g test material: 50 ml of extraction solution) adopted described above, extraction was also carried out on a sub-set ($n = 10$) of the samples at 0.5 g: 50 ml and 1 g: 25 ml test material to extraction solution respectively. The procedure involved placing three aliquots of the test material and adding the required volume of extraction solution. The set-up was then incubated for one hour at 37 °C with constant agitation: after this 10 ml aliquots of the supernatant were collected and filtered for analysis.

3.2.3 Effect of Incubation Time on *In vitro* Bioaccessibility

In order to study the effect of incubation time on the *in vitro* bioaccessibility of contaminant elements, the extraction process was repeated at different time intervals. This was aimed at testing the impact of time of contact between the test material and extraction solution, within the stomach emptying time for a child. For this purpose, a sub-set ($n = 10$) of samples were incubated for one hour and two hours and finally left standing on the bench top for 17 hours. After the first hour, the bottles were removed and placed on the bench top as usual to cool and to allow solids to settle. A 10 ml aliquot was collected and filtered into sample vials before returning the remaining solution to the incubator for another hour with constant agitation: a second 10 ml aliquot was then collected for analysis. A third aliquot was collected after 17 hours standing time.

All in vitro bioaccessibility solutions were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Varian Vista Pro CCD Simultaneous spectrometer, equipped with a Varian Sample Preparation System (SPS-5). Calibration standards were prepared using commercially available analytical grade stock solutions from Fisher Scientific, UK. In order to check the quality of the analyses, an analytical spike was included within each batch of samples, coupled with at least three blank samples (milliQ water) in each case: replicate measurements were done on samples selected at random. The analytical blanks gave values generally very close to the LOD for all elements. The residual standard deviation (RSD) for the duplicate measurements on blanks and samples was generally within or slightly above the acceptable limit of 10% (Lu et al., 2011) or 15% (Smith et al., 2009), indicating good method precision.

3.3 X-ray Fluorescence Spectrometry

Total lead concentration in samples was measured using X-ray fluorescence spectrometry. Pressed powder pellets were prepared by mixing 7.5 g of the sieved, oven-dried sample with three cellulose tablets and grinding the mixture in an agate mill (Retsch RS 200) for 1 minute. The powder was then pressed into 25 mm pellets using a hydraulic press at a pressure of 20 tons. Analysis was carried out using a high performance sequential wavelength dispersive XRF spectrometer (S4 PIONEER, Bruker AXS, Germany), using the GEO-QUANT program for trace elements, and running on the SPECTRA^{plus} XRF software. However, for some samples with very high lead contents, beyond the upper calibration range of the GEOQUANT method (2500 µg/g Pb), a semi-quantitative method was used to estimate total concentrations. This involved preparation of glass beads and determining Pb as a major oxide. The quantification limit for this method is 0.02 % Pb. The set-up consists of a 75µm ultra-thin x-ray tube source and a LiF 220 high resolution analyzer crystal detector applicable for Ti or V K α to Mo K α which gives higher resolution and reduces spectrum overlap interferences. In order to check analytical accuracy, four certified reference materials (CRMs) were included among each batch of samples (n = 10). These were SDO-1, W2a, MESS-2 and STSD-2 for the trace elements and major elements and the measured concentrations show very good agreement with the certified values, therefore showing good measurement accuracy.

3.4 Statistical and Graphical Treatment of Data

The geochemical data was submitted to multivariate statistical analysis using SPSS (PASW 18) for Windows using methods described by Field (2009). Descriptive statistics (DS), correlation matrix (CM) and One-way repeat-measures ANOVA were performed on the data. While carrying out these tests, it was assumed that the data were normally distributed and therefore no normalization was done before statistical treatment. For the repeat-measures ANOVA, a correction for data sphericity was carried out using the Bonferroni method. A correlation matrix was used to obtain the Pearson relationship between parameters. Repeat-measures ANOVA were performed in order to assess the effect of pH, time and solid to fluid ratio on element bioaccessibility.

4. Results and Discussion

The bioaccessible concentration of lead in the samples is presented in Table 1, together with the total concentration and the human bioaccessible fraction. Lead concentration in the simulated gastric fluid lies between 197.5 and 41740 µg/g (mean, 9731.7 ± 12058 µg/g). The human bioaccessible fraction (HBA%) which is the proportion of lead that is extracted into the simulated gastric fluid as a percentage of the total concentration in the 25 soil and sediment samples was calculated by:

$$\%HBA = \frac{\text{Concentration in extraction solution } \mu\text{g/g}}{\text{Total concentration in sample } \mu\text{g/g}} \times 100 \quad (1)$$

The result is presented in Table 1 and shows that the bioaccessibility of lead ranges from 28.7 to 100.4% (mean 60.3%).

The high bioaccessibility of lead across all samples (Table 1) is in part a function of the higher total concentration of the element in the samples. However it is also influenced by the abundance of very labile residual lead oxide and lead carbonate minerals in the ores (Plumlee & Morman, 2011) and also confirmed by strong partitioning of lead into these phases seen during the SEPs experiments. Casteel et al. (2006) have shown that oral lead bioaccessibility in human children is highest in lead carbonates and lead associated with manganese oxides. According to them, lead phosphates and oxide minerals and lead associated with iron oxides show intermediate bioaccessibilities, while lead sulphides and silicates (residual phases) are the least bioaccessible. The mean lead bioaccessibility obtained in this work is very similar to that reported (64%) for mining contaminated soils in

Brazil and 75-80% for a certified reference soil, SRM 2710 by Bosso and Enzweiler (2008) using the PBET method. The mean lead bioaccessibility of 39.1% for urban soils in Guangzhou, China (Lu et al., 2011) is also within the range obtained here. Similarly, gastric bioaccessibility of between 23 and 69% obtained in lead-rich mine wastes by Jaggard (2012) are also broadly similar to the results of this work. However the results of this study are higher than median lead bioaccessibility of 23% for the < 2 mm and 18% for < 250 μm fractions respectively obtained by Morman et al. (2009) from uncontaminated background soils in the United States, which is perhaps a pointer to the important role mineralogy and total element concentration can play in its bioaccessibility.

Table 1. Total and *In vitro* bioaccessible concentration along with the human bioaccessible lead (HBA%) in soils and sediments from Anka area, NW Nigeria

Sample	Total Pb, $\mu\text{g g}^{-1}$	Bioaccessible Pb, $\mu\text{g g}^{-1}$	Human Bioaccessible Pb, %
A1	61700	17702	28.7
A2	378	247	65.3
A4	24300	14007	57.6
A5	2023	1226	60.6
A6	76000	26948	35.5
A7	10200	10239	100.4
A8	8500	5612	66.0
A10	327	223	68.1
B1	122800	41740	34.0
B2	59100	35470	60.0
B3	28300	16173	57.1
B4	1333	697	52.3
B5	403	238	59.0
B7	2771	1574	56.8
D1	3800	1869	49.2
D2	12100	8978	74.2
D4	1232	853	69.3
D5	2600	1705	65.6
D7	38200	23662	61.9
D9	858	566	66.0
TS3	357	249	69.8
TS4	49400	20464	41.4
TS5	327	198	60.4
TD6	15600	12312	78.9
TD10	497	243	69.0
Min	327	198	28.7
Max	122800	41740	100.4
Mean	17522	9732	60.3

4.1 Correlation Analysis

A Pearson correlation analysis was carried out (significant at $p = 0.01$) between total elemental concentration in the samples and the bioaccessible concentration. The results indicate that there is a very strong positive correlation between total concentration and bioaccessibility of lead, with a correlation coefficient of 0.94. In all

samples, there is a generally positive linear relationship between total lead and bioaccessible lead, except in samples with very high total lead concentration, where the relationship appears to be less linear. The strong relationships which appear to exist between the total and bioaccessible concentrations is a result of the introduction of lead into soils and sediments during the processing of ores, the higher bioaccessibilities occurring because the element had a relatively short time to bind to soil and sediment phases (Button et al., 2009).

4.2 Physicochemical Controls on Oral Bioaccessibility

The physicochemical parameters that are likely to affect the oral bioaccessibility of contaminants have been identified by previous workers (e.g. Drexler & Brattin, 2007) to include the pH of the extraction solution, extraction temperature, and length of extraction time; the feed or fast status of the individual and the ratio of the extraction fluid to the weight of test material.

4.2.1 Effect of pH

The bioaccessibility of lead was measured at three pH levels. This indicates that Pb extraction has a linear relationship with the pH of the extraction solution, generally decreasing as the pH of the solution increases, except in few samples, especially B2, where the bioaccessible concentration of Pb appears to rise with the rising of pH. Repeat Measures ANOVA was performed on this data in order to verify the observations made from the graphs. While the results of this statistical test could not identify the pH level that was more effective in extracting the elements, it does show that pH has a significant effect ($p < 0.05$) on the leaching of Pb. The link between the two data sets is not very clear, but shows that pH has had an effect on Pb solubilization.

According to Drexler and Brattin (2007) human gastric pH generally falls between 1 and 4 under fasted conditions, but may reach 5 for a few hours after the intake of food. The pH range used in this work therefore falls within the fasted range and in general, a reduction in pH is expected to result in an increase in the dissolution of contaminant elements from an earth material. The effect of gastric pH is important when assessing the risk associated with ingestion of soil borne toxic elements, especially in economically deprived areas (Bosso & Enzweiler, 2008). In such areas, irregular feeding habits, often exemplified by the skipping of meals, means stomach pH remains low enough over long periods of time to ensure effective dissolution of contaminants incidentally ingested by children. Turner (2011) points out, however, that the pH dependence of mobilization in the gastric environment is metal specific: co-variation of pH and chloride concentration in the human stomach allows the formation of very soluble metal chlorocomplexes. According to Plumlee and Ziegler (2004), within the acidic human stomach, most base metals, including Pb, Fe, Cu, Zn, Cd, Ni and Co are likely to be complexed chiefly by chloride. Turner (2011) reports that the accessibilities of Cr and Pb are more sensitive to pH, showing significant reduction in going from low to high pH, but Zn accessibility is comparatively less affected. This is similar to the results of this work, which show Pb accessibility decreasing with increasing pH.

4.2.2 Effect of Incubation Time

Three sample incubation times were used to assess the effect of extraction time on accessibilities of elements in soils against the background of the reported half-time of stomach emptying time in human beings of about 1 hour (Washington et al., 2001). The results presented in Figure 4 show that the accessibility of Pb remained unchanged over the entire period and repeated Measures ANOVA analysis ($p < 0.05$) indicates the length of extraction time was not a significant factor affecting Pb solubilization. Stomach emptying rate or residence time is said to be a complex function of the degree of smooth muscle stimulation, humoral signalling in the gut, food composition if present, time of day and other physiological factors (Drexler & Brattin, 2007). Whatever the factors controlling stomach emptying, it does appear that longer extraction time does not enhance the accessibility of lead. This is consistent with the results of Drexler and Brattin (2007) and USEPA (2008) who found no significant difference in the *In vitro* bioaccessibility of Pb when the time was varied from 1 to 4 hours.

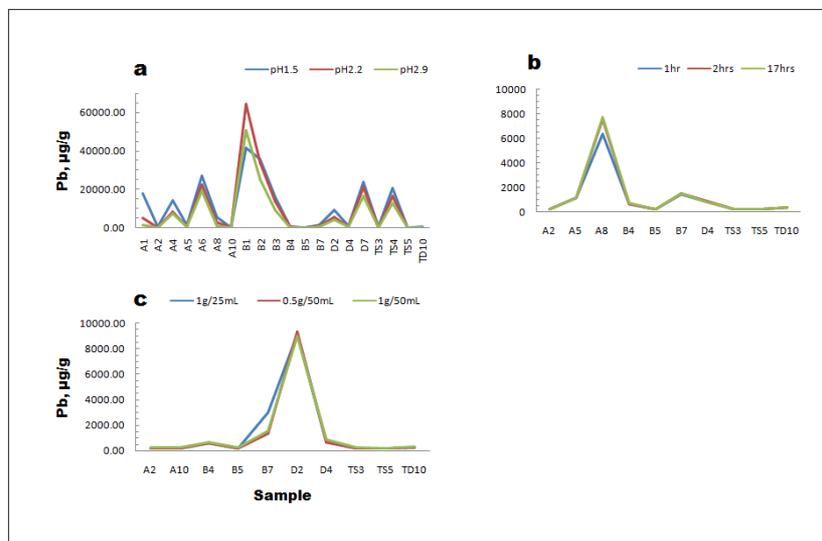


Figure 4. Effects of physicochemical parameters on the *In vitro* bioaccessibility of lead in contaminated soils

4.2.3 Effect of Solid: Fluid Ratio

The ratio of fluids to solid in the human stomach varies depending on feeding status and the amount of contaminated earth material ingested. The effect of solid/fluid ratio on the accessibility of lead was investigated using three combinations of the test material to the extraction fluid. The results (Figure 4) show that mobilization of Pb did not appear to change with variation in the ratio of solid sample to extraction fluid volume. Results of One-way Repeat Measures ANOVA support this [$F(1.12, 10.06) = 0.65, p > 0.05$].

A wide range of ratios have been reported in the literature, ranging from 1: 100 to 1: 500 (Turner, 2011) and as high as 1: 1000 (Wragg et al., 2011). Drexler and Brattin (2007) performed tests on a variety of standard reference materials and reported no significant variation in the *in vitro* bioaccessibility with soil masses as low as 0.2 g per 100 ml of extraction fluid (1:500). Because actual test materials may not be as homogenous as reference materials and because of weighing errors, they proposed a ratio of no less than 0.4 g test material per 100 ml of fluid to reduce possible variability in bioaccessibility. However, Wragg et al. (2011) have reported the use of a ratio of 1: 1000 in order to eliminate poor reproducibility occasioned by high. As concentration in soils contaminated with mine wastes and slag, although they too acknowledged the possible effects of sample inhomogeneity. The use of ratios of between 1: 25 to 1: 100 (Figure 4) in this work did not result in a significant difference in lead bioaccessibility. The comparatively lower total Pb concentration in samples used for this experiment may have helped to avoid the problem of extraction fluid saturation and lead chloride precipitation (Drexler & Brattin, 2007; USEPA, 2008) reflected in samples with highly soluble Pb minerals such as lead acetate, lead oxide and lead carbonates. Even when a ratio of 1 g in 25 ml fluid was used, no significant difference was observed despite of the presence of more sample mass and surface area. Unless one is dealing with highly contaminated samples exceeding the 50,000 µg Pb/g limit set by previous workers, it appears that the ratios used in this work are acceptable when there is limited sample supply.

4.3 Contaminant Daily Intake

The chemical or contaminant daily intake is used to assess the exposure of humans, especially children to contaminant elements through ingestion of contaminated soil. For a child 2 to 6 years old, weighing 17.8 kg (USEPA, 1997), the daily chemical intake (CDI, µg kg⁻¹ day⁻¹) is calculated using the following formula:

$$CDI = \frac{CS \times IR \times BA \times EF}{BW} \times CF \quad (2)$$

where CS is the total concentration of the contaminant element in the sample (µg/g), IR is the ingestion rate set at (USEPA, 2002) 200 mg soil per day, BA is the mean bioaccessibility of the element in the test materials, EF represent the exposure frequency, in this case 0.5 (182 days per year, Hemond & Solo-Gabriele, 2004), BW denotes body weight and CF is the unit conversion factor (10⁻³).

The CDI estimates show that children exposed to these soils are likely to ingest between 110 to 41,585 $\mu\text{g Pb/kg}$ per day with a mean of 7,086 $\mu\text{g Pb/kg}$ of body weight daily. These figures grossly exceed the tolerable daily intake (TDI) of $\sim 3.6 \mu\text{g/kg/day}$ for lead calculated from a provisional tolerable weekly intake (PTWI) of 25 $\mu\text{g/kg}$ body weight (DEFRA, 2002). The results show that at all the sample sites, the tolerable daily intake of Pb is far exceeded. This may explain the excessively high blood lead levels reported by the Blacksmith Institute (2010) in children of the affected villages leading to high levels of childhood mortalities. This is brought about by a combination of high total lead concentration in the soils, especially within living compounds and sediments of the area and the abundance of highly soluble secondary lead carbonate and lead oxide minerals within the ores (Plumlee & Morman, 2011).

This estimate is based on an assumption that the only way of transmission is through the ingestion of fine particles which stick to the hands of children. But the daily ingestion of soil in these villages may be higher than the conservative figure of 200 mg of soil per day used in this work, due to the possibility of other routes of exposure, such as eating poorly washed vegetables and the deliberate ingestion of soil. Where poor people live in contaminated areas, sub-nutrition and direct contact with wastes and soils are common (Bosso & Enzweiler, 2008). This may result in the ingestion of up to 10 g of soil in a single day (USEPA, 2002) leading to much higher contaminant uptake. If the latter scenario is taken into account, the health risks posed by the ingestion of these soils will be much higher than this data indicates, considering especially the very high levels of bioaccessible lead.

5. Conclusions

In vitro bioaccessibility measurements based on hand-to-mouth ingestion of soils in the contaminated Anka villages has shown high Pb concentrations. The higher concentration obtained *in vitro* is a function of the lower pH of the simulated gastric fluids, and in nature, bioaccessibility may be further enhanced by the near anoxic condition of the human stomach. The chemical daily intake (CDI), computed for children in the Anka area based on hand-to-mouth ingestion of contaminated soil shows that the tolerable daily limit for Pb has been exceeded. The mean CDI for Pb was found to be nearly 2000 times the tolerable daily intake for a 2–6 year child weighing 17.8 kg; the minimum value being about 31 times the limit. These results highlight the severity of the contamination of soils in the affected villages. Hand-to-mouth ingestion is the only exposure scenario investigated in this study. However, given the poor socioeconomic status of the residents of this study area, children and even adults can be exposed to lethal doses of lead and other PTEs through consumption of improperly washed vegetables, inhalation of indoor and outdoor dusts and drinking contaminated surface water. Similarly, factors such as low body weights due to sub-nutrition together with poor sanitation, which may increase the exposure frequency, are likely to increase the risks. While high blood lead levels have been reported in children in these villages by a combined team from the UNEP/OCHA, Blacksmiths Institute and other organizations, it will be interesting to study adult subjects, especially those actively involved with ore processing in order to assess possible chronic Pb and other PTE toxicity.

The results underscore the need to study more closely, the effects of artisanal mining and processing of ores on the quality of the environment and the attendant human health consequences. Determining the spatial distribution of mining related potentially toxic elements relative to baseline concentrations, together with an assessment of their geochemical partitioning and *in vitro* bioaccessibility would be useful for artisanal mining areas in Nigeria and other parts of the developing world. The knowledge gained can guide remediation efforts and help to mitigate the harm to resident populations of contaminated areas.

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