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Assessment of Cadmium and Lead Distribution in the Outcrop Rocks of Abakaliki Anticlinorium in the Southern Benue Trough, Nigeria

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Abstract This study investigates the distribution of cadmium and lead concentrations in the outcrop rock samples collected from Abakaliki anticlinorium in the Southern Benue Trough, Nigeria. The outcrop rock samples from seven sampling locations were air–dried for seventy–two hours, homogenized by grinding and pass through < 63 micron mesh sieve. The ground and homogenized rock samples were pulverized and analyzed for cadmium and lead using X-Ray Fluorescence Spectrometer. The concentrations of heavy metals in the outcrop rock samples ranged from < 0.10 – 7.95 mg kg^{-1} for cadmium (Cd) and < 1.00 – 4966.00 mg kg^{-1} for lead (Pb). Apart from an anomalous concentration measured in Afikpo Shale (Middle Segment), the results obtained revealed that rock samples from all the sampling locations yielded cadmium concentrations of < 0.10 mg kg^{-1} and the measured concentrations were below the average crustal abundance of 0.50 mg kg^{-1}. Although background concentration of <1.00 ± 0.02 mg kg^{-1} was measured in Abakaliki Shale, rock samples from all the sampling locations revealed anomalous lead concentrations above average crustal abundance of 30 mg kg^{-1}. The results obtained reveal important contributions towards understanding of heavy metal distribution patterns and provide baseline data that can be used for potential identification of areas at risk associated with natural sources of heavy metals contamination in the region. The use of outcrop rocks provides a cost–effective approach for monitoring regional heavy metal contamination associated with dissolution and/or weathering of rocks or parent materials. Evaluation of heavy metals may be effectively used in large scale regional pollution monitoring of soil, groundwater, atmospheric and marine environment. Therefore, monitoring of heavy metal concentrations in soils, groundwater and atmospheric environment is imperative in order to prevent bioaccumulation in various ecological receptors.

Keywords: *cadmium, lead, rock outcrop, mineralization, shale, contamination*

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1. Introduction

Cadmium and lead, which represent a coherent group of metals from the metallogenic viewpoint, are inorganic contaminants of environmental concern [1,2,3,4]. Some previous studies on the biogeochemical cycling of these metals have focused largely on the pathways from industrial sources and most commonly within either temperate or sub-tropical ecosystems [5,6,7,8]. However, there is a growing concern over lead and cadmium contamination in the Southern Benue Trough of Nigeria due to the fact that heavy metals are often released into the soils andgroundwater by erosion, dissolution and weathering of surface rocks. There are some reported cases of environmental contamination associated with mineralization of ore deposits and artisanal mining activities in Abakaliki formation in the Southern Benue Trough [9,10,11,12,13]. Notably, lead and cadmium are deleterious trace elements that could accumulate in animal and plant cells, leading to severe negative effects [14,15,16,17]. According to Peterson and Alloway [3], an assessment of the environmental impact of heavy metal contaminants can be effectively achieved if the main steps in their geochemical pathways within the various natural ecosystems are understood.

Although several researches have been published on tectonic evolution and origin of the basin [18-24], there are few studies on natural abundance and variability of the heavy metals in the rocks. Some of these studies are based on prospecting and exploration of mineral deposits in the area [25,26,27,28,29], chemical classification and/or petrogenic activities. Over the years, the Middle Benue Trough has been widely known for its substantial lead–zinc production derived mainly from hydrothermal veins restricted within the Asu River Group sediments as a result of the tertiary and recent volcanism within the trough. Despite the environmental consequences, artesanal mining of metals has become a major occupation of the rural mining communities in and around Abakalili especially during the dry season when the farming activity has ended [9]. There are reported cases of groundwater and land contamination associated with mining activities, abandoned mines and disposal of tailings with high concentrations of toxic metals [2,9,30,31]. Several studies have been reported on the distribution patterns and variability of heavy metals in the middle Benue Trough and determination of factors responsible for the overall pattern of surface soil variability using factor analysis [31].

The transport and fate of heavy metals within the soil environment is usually dependent on the chemical characteristics of the metal, the adsorptive capacity of the soil and physico-chemical factors, such as pH and redox potential [32,33,34], effects of organic matter, iron–manganese co–precipitation and formation of insoluble precipitates [34,35,36]. Cadmium tends to be fairly mobile during tropical weathering and it is redistributed within the soil profile. According to Olade [35], high pH and relatively high redox potential (Eh) values in freely drained humid tropical soils tend to promote formation and sorption of iron–manganese sesquioxide. In addition, R-Mode factor analysis suggests that cadmium, lead and copper are strongly associated with finely divided organic matter in carbonaceous shale parent rock. In soils overlying mineralized zones, cadmium shows a strong association with zinc and both metals are precipitated as secondary minerals [35,37]. Lead most often accumulates within the topsoil due to its relatively poor mobility, solubility, different interactions with the environment and strong tendency to form metallo-organic complexes. Lead forms secondary lead sulphates and carbonates in soils in areas underlain by rocks and in the mineralized areas [38]. It is widely known that the geochemical characteristics of the underlying rock and the nature of the weathering processes are major determinants of metal concentrations within the tropical soils like that of the Benue Trough in Nigeria [27].

There are great spatial variabilities in the sources of heavy metals among several regions due to different physical environment, geological, meteorological conditions, economic activities, stages of industrialization and urbanization [39]. The Southern Benue Trough of Nigeria has great stratigraphic and economic values due to its intensely folded belt and mineralized sediments [30]. However, there is high potential for heavy metal contamination of groundwater in Abakaliki Area in the Southeastern Nigeria due to the availability of sulfide ore minerals [12]. Apart from anthropogenic sources, lithogenic and geogenic effects increase the weathering rate of minerals or parent rocks thereby releasing the metals into soil and/or groundwater. Subsequent rainfalls leach these metals to the groundwater regime through permeable pathways in the sediments. Although few studies have been reported on the lead–zinc mineralization in the Southern Benue Trough [27,31,35,40,41], there is paucity of information on cadmium and lead distribution in the outcrop rocks of Southern Benue Trough of Nigeria. Therefore, monitoring and assessment of heavy metals concentrations in the environment contribute towards effective understanding of biogeochemical processes and gauging ecosystem health [42].

This study investigates the distribution of cadmium and lead concentrations in the outcrop rock samples collected from Abakaliki anticlinorium in the Southern Benue Trough, Nigeria. The concentrations of heavy metals in the outcrop rock samples were used to assess the degree of natural influence on geochemical effects and potential contamination of the soil environment and/or groundwater regime in the region.

2. The Geology of the Study Area

The Abakaliki anticlinorium (Figure 1), which is one of the depocentres in the Southern Benue Trough of Nigeria, contains approximately 3600 m thick sediments [18,43]. In addition, the Abakaliki anticlinorium consists of folded lead–zinc mineralized shales with lenses of sandstone and limestone, with one of the latter attaining a thickness of 30 metres [30,44]. The Asu River Group is represented in the study area by the 500 m thick seam of Abakaliki shale that occupies the core of the Abakaliki Anticlinorium. The Abakaliki Shale is locally rich in ammonite fauna and in some places, it is so abundant that fossils weathered out of the shales litter the terrain and fragments form part of the mounds in the yam farms [44]. The gently folded and fine-grained calcareous sandstones exposed along the Asu River are examples of Albian sediments which were deposited in a shallow marine environments and supply large quantities of fine sediments into a subsiding basin [30,44]. The Southern Benue Trough has been assigned the entire stratigraphic column encompassing the lower Cretaceous to Tertiary in Southeastern Nigeria (Figure 3). The Benue Trough, which is about 1000km long and 80 – 100 km wide[18],contains up to 5000 m thick of slightly deformed Cretaceous sedimentary and volcanic rocks. Detailed geological mapping of the study area shows that it is underlain dominantly by Cretaceous sediments comprising shales, sandstone, and limestone (Figure 4) [18,44,45].

3. Materials and Methods

3.1. Materials

Nitric acid (HNO_3) used for analyitical procedure was of supra pure quality (Merck, UK) and all the reagents used were of analytical grade (Analar grade). The PACS-2®Certified Reference Materials (CRM) were used for analytical quality control. Double deionised water was used for all analytical procedure (Milli-Q Millipore 18.2 MΩ cm^{-1} resistivity). All the plastic and glass wares were cleaned by soaking in dilute HNO_3 (10%) and were rinsed with distilled water prior to use [42].

3.2. Sampling and Analytical Procedure

This study was conducted in the vicinity of Abakaliki anticlinorium in the Southern Benue Trough of Nigeria (Figure 1). Seven fresh surface rock samples were collected from outcrops of all lithologic units from Abakaliki formation including Afikpo as shown in the map of the study area (Figure 1 and Figure 2). The lithological description and coordinates of the sampling locations are presented in Table 1. The outcrop rock samples were collected using plastic Auger, cleaned from mechanical impurities and stored in polyethylene bags. The air–dried rock samples were homogenized by grinding in agate mortars, pass through < 63 micron mesh sieve and stored in polyethylene bottles prior to elemental analysis.

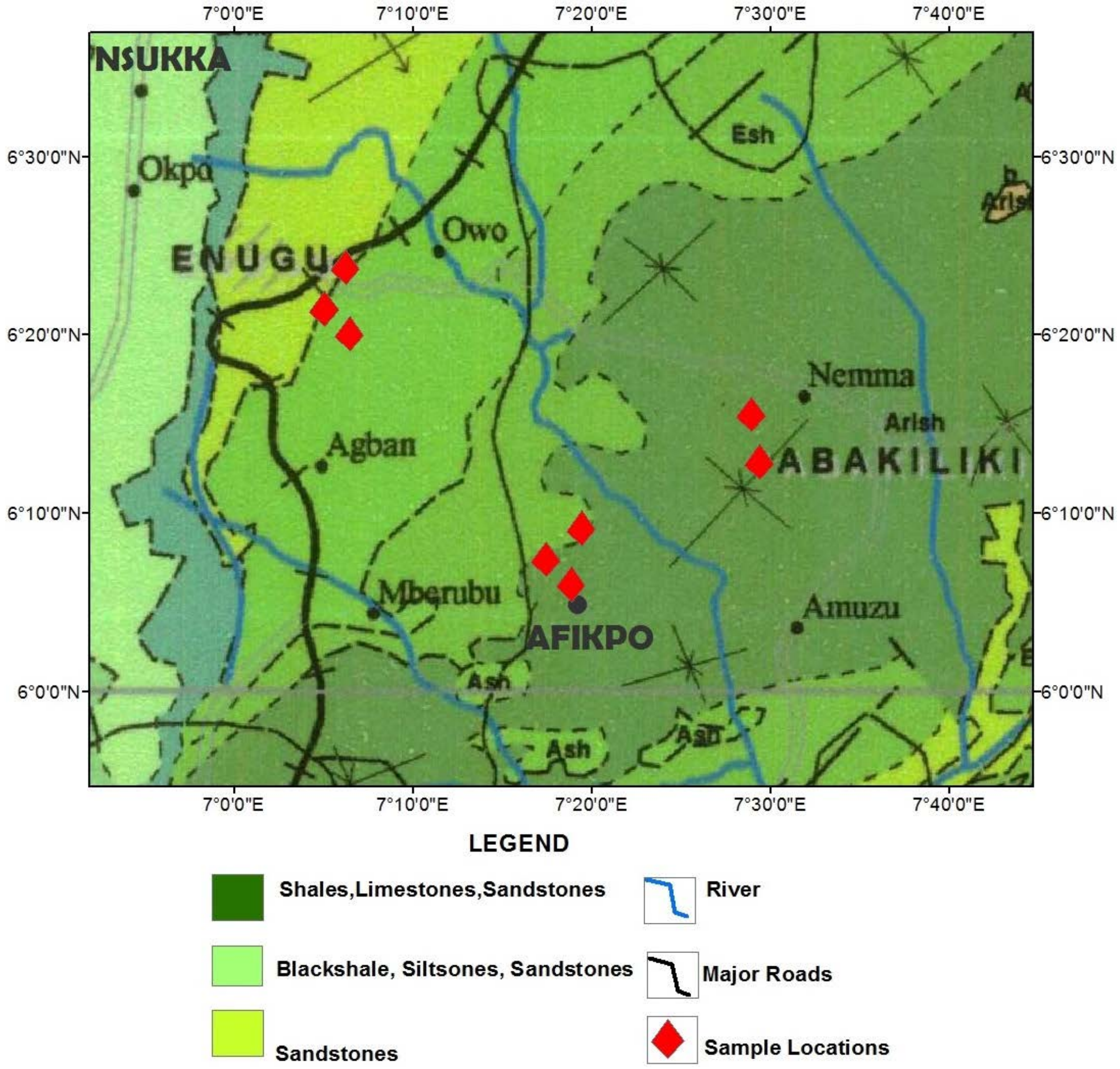

Figure 1. Geologic Map of the study area (Abakaliki anticlinorium in the Southern Benue Trough, Nigeria)showing sampling locations

Table 1. Sampling locations and co-ordinates.

Sampling location/ Number	Sample Location	Co-ordinates
1	Enyigba Shale (Middle Segment)	6^{0} 11.772$^{'}$ N 8^{0} 08.269$^{'}$ E
2	Abakaliki Shale	6^{0} 20.995$^{'}$ N 8^{0} 03.587$^{'}$ E
3	Enyigba Shale (Upper Segment)	6^{0} 11.772$^{'}$ N 8^{0} 08.269$^{'}$ E
4	Enyigba Shale (Lower Segment)	6^{0} 11.772$^{'}$ N 8^{0} 08.269$^{'}$ E
5	Afikpo Shale (Middle Segment)	5^{0} 57.528$^{'}$ N 7^{0} 56.995$^{'}$ E
6	Afikpo Shale (Lower Segment)	5^{0} 57.528$^{'}$ N 7^{0} 56.995$^{'}$ E
7	Afkpo Sandstone (Upper Segment)	5^{0} 57.528$^{'}$ N 7^{0} 56.995$^{'}$ E

The ground and homogenized rock samples were pulverized [39,46,47,48,49] and analyzed for cadmium and lead using X-ray Fluorescence Spectrometer (Model XEPOS 03, STD – GAS). The x-ray counts were converted into concentrations using a computer program based on the matrix correction method. The instrument was calibrated using PACS-2® CRM (Marine Sediment Standards) in accordance with the operational instructions. The reference samples were analysed using the same procedure in order to ensure precision and accuracy of the analytical methods [42]. As part of the quality control procedures, PACS-2®Certified Reference Materials were run simultaneously with average crustal abundance (ACA) of 2 mg kg^{-1} [27]. The pH of the samples was determined using a pH meter (Thomas Scientific, TS 675), after mixing the ground and homogenized sample with deionised water in a 1:1 ratio. All measurements were triplicate determinations.

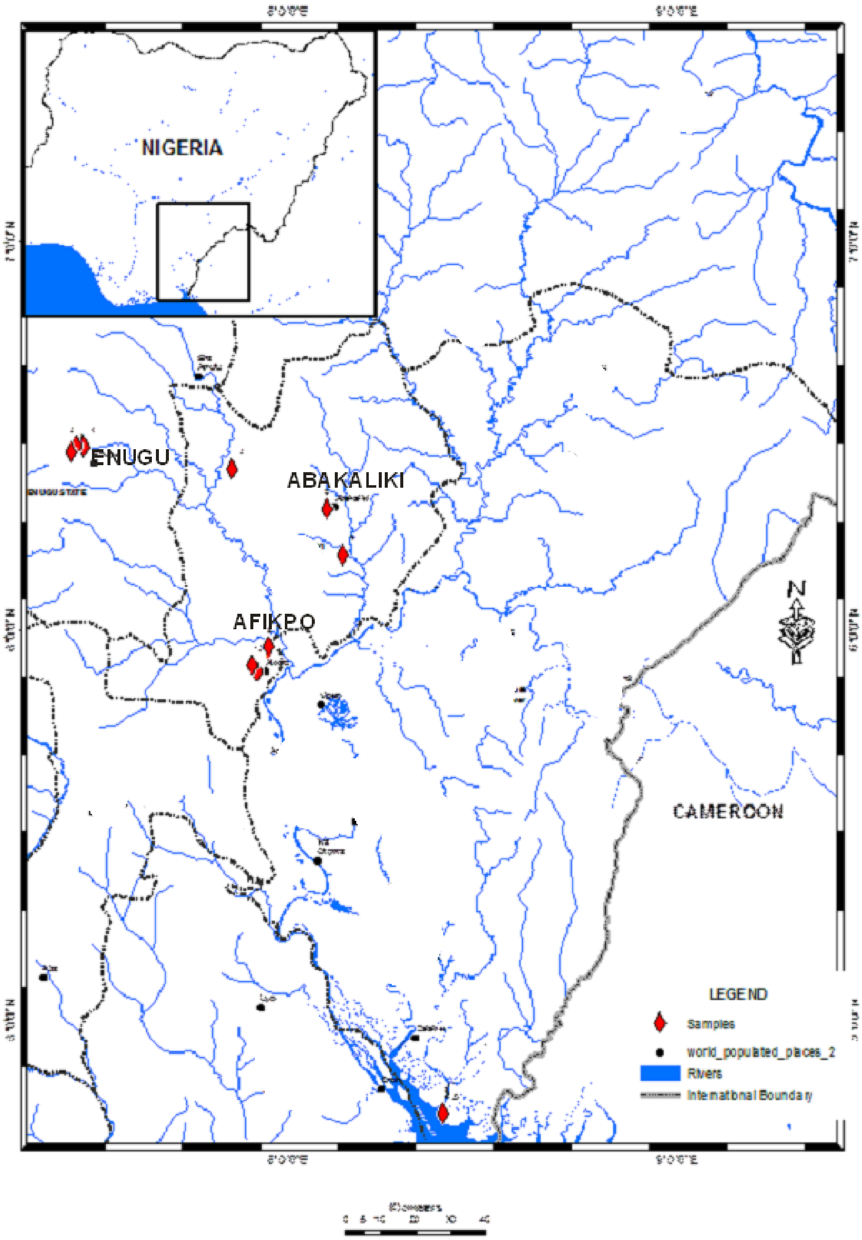

Figure 2. Geologic Map showing drainage system in Abakaliki anticlinorium in the Southern Benue Trough, Nigeria

Figure 3. Picture showing the stratigraphy of the rock units of the lead-zinc mineralization in Enyigba – Abakiliki in Ebonyi State

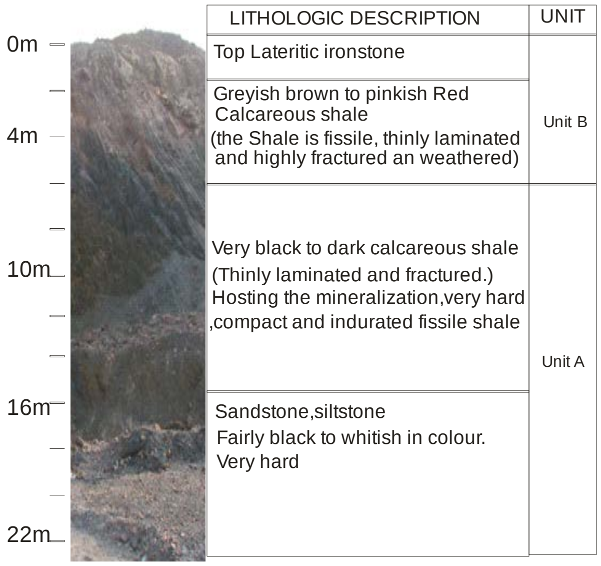

Figure 4. Lithostratigraphic description of the rock unit at the lead-zinc mineralization in Enyigba, Abakiliki in Ebonyi State

3.3. Statistical Analysis

The results obtained for the heavy metal concentrations in the outcrop rock samples were subjected to statistical analysis. Variance in the data set was tested for statistical significance through analysis of variance (ANOVA) using SigmaPlot® 12.5 (Systat Software Inc.).

4. Results and Discussion

The concentrations of cadmium and lead in the PACS-2® CRM (Table 2) reveal that there were no significant differences between measured values and certified values for the reference material ($P > 0.05$). The measure of good agreement between the results obtained and certified values of the reference material indicates high precision of the analytical methods and accuracy of the results. The concentrations of heavy metals and pH in outcrop rock samples at various sampling locations in the study area are presented in Table 3. The concentrations of heavy metals in the outcrop rock samples ranged from < 0.10 – 7.95 mg kg^{-1} for cadmium (Cd) and < 1.00 – 4966 mg kg^{-1} for lead (Pb).Apart from the anomalous cadmium concentration measured in Sample number 5 (Afikpo shale), there were no variations in the concentrations of cadmium between samples collected from different sampling locations ($P > 0.05$). However, there were variations in the concentrations of lead between samples collected from different sampling locations and the differences were statistically significant ($P < 0.01$). The concentrations of cadmium and lead in the outcrop rock samples obtained in this study (Table 3) were compared with the average crustal abundance of cadmium, lead and pH measured in remote or recently settled soils as presented in Table 4 [50].

Table 2. Results of the analysis of the PACS-2 certified reference material (CRM)

Element	Certified value	Measured	Recovery (%)
Cadmium	0.071±0.01	0.071±0.01	100
Lead	20.00 ± 13.00	20.00 ± 13.00	100

Table 3. Results of cadmium and lead levels in outcrops from Abakaliki formation

Sampling location	Cadmium (mg kg^{-1})	Lead (mg kg^{-1})	pH
1	< 0.10	4667± 39.00	4.26
2	< 0.10	< 1.00 ± 0.02	5.19
3	< 0.10	1488.00 ± 25.00	4.52
4	< 0.10	4966.00 ± 41.00	4.38
5	7.95 ± 0.21	978.00 ± 15.00	5.01
6	< 0.10	51.30 ± 7.00	5.66
7	< 0.10	39.10 ± 3.00	5.49

Table 4. Average Crustal Abundance of lead, cadmium and pH in Soil (source : Siegel [50])

Metal (mg/kg)	Mean (mg kg^{-1})	Range (mg kg^{-1})	Average Abundance(mg kg^{-1})
Lead	760.4	247 - 2100	1 – 30
Cadmium	68	26 - 210	0.1 – 0.5
pH	6.99	6.39 - 7.95	6.5 – 8.5

Cadmium concentrations in the rock samples ranged from 0.10 to 7.95 mg kg^{-1} (Table 3). Apart from an anomalous concentration of cadmium 7.95 ± 0.21mg kg^{-1}measured in Sample number 5 (Afikpo shale), cadmium concentration of < 0.1 mg kg^{-1} were measured in rock samples from six sampling locations. Several related studies have reported varying concentrations of cadmium in geological (lithogenic) samples. Examples of the concentrations of cadmium in geological (lithogenic) samples obtained from other studies ranged from0.10 to 1.00 mg kg^{-1} and < 240 mg kg^{-1} in black/oil shale [51,52,53,54]. Total concentrations of cadmium in topsoils ranged from < 0.20 to 40.90 mg kg^{-1} in United Kingdom [55], < 0.01 to 2.00 mg kg^{-1} in United State of America [56] and 0.20 to 0.33 mg kg^{-1} in China [57]. In this study, the anomalous concentration of cadmium measured in Afikpo shale could be attributed to rock type and changes in geological–geochemical processes within the Abakaliki Anticlinorium in the Southern Benue Trough, Nigeria. Typically, the highest cadmium concentrations are found in sedimentary rocks [58] and soils underlain by cadmium–rich Monterey shales in coastal regions of California contain some of the highest natural cadmium concentrations in the world [59]. With exception of Afikpo shale, the concentrations of cadmium measured in the rock samples were less than the average crustal abundance in soils which ranged from 0.10 to 0.50mg kg^{-1} (Table 5). Cadmium concentration in soil that exceeds 0.50mg kg^{-1} is an indication of soil pollution [60]and an average cadmium concentration in soil worldwide is reported to be 0.30mg kg^{-1} [61]. However, cadmium concentration of 2 mg kg^{-1}is accepted as the maximal permissible concentration by the Croatian Government [62]. In some soils, cadmium concentrations are high because of rock type (such as black shales), weathering of cadmium–rich parent materials or from mining contamination. The anomalous concentration measured in Afikpo shale is attributed to natural source and/or weathering of cadmium–containing parent materials. According to Alloway and Steinnes [36], the total concentration of cadmium in a soil comprises the contribution from the geological parent materials together with inputs from extraneous sources and in some cases, cadmium contamination of soil are associated with anthropogenic sources.

Table 5. Comparison of lead and cadmium levels from Abakaliki Formation with their average abundance in soils

Sampling location	**Cadmium (mg kg^{-1})**	**Lead (mg kg^{-1})**	**pH**
1	< 0.10	4667.00 ± 39.00	4.26
2	< 0.10	< 1.00 ± 0.02	5.19
3	< 0.10	1488.00 ± 25.00	4.52
4	< 0.10	4966.00 ± 41.00	4.38
5	7.95	978.00 ± 15.00	5.01
6	< 0.10	51.30 ± 7.00	5.66
7	< 0.10	39.10 ± 3.00	5.49
Average abundance	0.1 – 0.5	1 – 30	6.5 – 8.5

Lead concentrations in the rock samples ranged from < 1.00 to 4966 mg kg^{-1} (Table 3). Apart from the background concentration of lead < 1.00 mg kg^{-1}measured in Sample number 2 (Abakaliki shale), anomalous concentrations of lead were measured in all the outcrop rock samples collected from different sampling locations. Several related studies have reported varying concentrations of lead in geological (lithogenic) samples. Examples of the concentrations of cadmium in geological (lithogenic) samples obtained from other studies ranged from 0.05 to 20 mg kg^{-1} and < 100 mg kg^{-1} in black/oil shale [51,52,53,54]. Total concentrations of lead in topsoils ranged from < 3.00 to 16,338 mg kg^{-1} in United Kingdom [55], < 7.50 to 135.00 mg kg^{-1} in United State of America [56] and 9.95 to 56.00 mg kg^{-1} in China [57]. In this study, the measured concentrations of lead were significantly higher($P < 0.01$) than the average crustal abundance of 1 – 30 mg kg^{-1}in soils except Abakalikishale (Table 5). The high concentrations of lead measured in the outcrop rock samples from sampling locations 1, 3, 4, 5, 6 and 7 could be attributed to mineralization of ore deposits and/or weathering of lead–containing parent materials. The results obtained in this study agrees with findings from other studies on lead–zinc mineralization in the Benue Trough [27,31,35,41]. Apart from Abakaliki Shale, the lead concentrations measured in this present study were statistically higher than values reported in previous study [63] and also, higher than maximal permissible concentration of lead (150 mg kg^{-1}) set by the Croatian government [38]. In a previous study conducted in the Middle Benue Trough of Nigeria, Nganje [13] reported that the concentrations of heavy metals in soils in cultivated farmlands close to the mine and in unmineralized areas are not significantly different with the mean values of 40 and 52 mg kg^{-1}for lead. The concentrations in the control site are close to world average contents of 30 mg kg^{-1}for lead over unmineralized soil [50]. The elevated concentrations of lead reported in the present study are mainly attributed to natural sources associated with geological parent materials.

In this study, the pH values measured in the outcrop rock samples of Abakaliki anticlinorium ranged from 4.22 – 5.66 and the measured pH values were below the range of 6.5 – 8.5 reported for world sediments [38]. At near neutral pH, solubility of chemical elements from their solid hosts generally increases with higher temperature [34].In studies on the influence of pH on mobility of cadmium and zinc in loamy soils, Scokart *et al*. [64] found that a pH < 6 increases mobility of cadmium while pH value < 5 increases mobility of zinc. According to Nganje [13], soil samples from cultivated farmlands close to mine dumps and unmineralized rural soil are characterized by neutral pH (≥6.7≤7.5). The implication of these pH values is that the weathering of these rocks may likely contribute to adverse increased acidity of the receiving soils, sediments and groundwater in the Abakaliki Anticlinorium. The groundwater of the Abakaliki area is generally contaminated with heavy metals such as manganese, mercury and cadmium while iron, lead and nickel are environmental contaminant of concern in some locations [12].According to Siegel [34], the order of environmental concern about health impact on ecological receptors depends on lead and cadmium concentrations in environmental media at the sampling site being investigated. Therefore, the release and transport of heavy metals in soil as well as bioavailability could be affected to varying degree by acid–neutralization processes. The amount of heavy metals accumulation in a soil associated with natural sources of environmental pollution depends on the scale of chemical dissolution, rate of weathering, the transport of the metal from the source to the site and the retention of the metal once it has reached the soil.

5. Conclusion

This study has shown the variations in the concentrations of heavy metals in the outcrop rocks samples and the distribution of the cadmium and lead has further reveal that distribution patterns are mainly dominated by local natural (lithogenic and geogenic) sources peculiar in the studied area. Considering the anomalous concentrations of cadmium and lead measured in the outcrop rock samples at some of the sampling locations, there is the likelihood that mining activities may contribute toward contamination of soil, groundwater and subsequent bioaccumulation in plants. Apart from anthropogenic sources, soils in areas underlain by rocks with anomalously high contents of heavy metals will also have become enriched through natural geomorphological and pedogenic processes over a longer timescale. Depending on speciation and bioavailability, long–term exposure to elevated concentrations of heavy metals may pose a threat to the environment and possible health risk to humans through the plant uptake-dietaryroute. This study has made important contributions toward the understanding of metal distribution patterns in the geological (lithogenic) sources and the obtained baseline data can be used for identification of spatial and temporal changes in the distribution of heavy metals in the soil and/or groundwater in the studied area. This study suggest that effective understanding of the factors controlling the geochemistry of heavy metals in soil within the mining districts could play a key role in planning of environmental management, protection and sustainable development. Therefore, monitoring of heavy metal concentrations in soils, groundwater and atmospheric environmentis imperative in order to prevent bioaccumulation in various ecological receptors.

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