

Full Length Research Paper

Geochemical assessment of toxic metals stocking in top-soil within the area of limestone quarry in Gombe of North-eastern Nigeria

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This work presents an assessment of geochemical toxic metal stocking in top-soil within the area of a limestone quarry in Gombe State. Samples of topsoil from the area of a limestone quarry in Gombe (North-eastern Nigeria) were collected to analyse levels of hazardous substances such as of Hg, Fe, Zn, Ni, Mn, Cu, Cr, Cd and Pb. A total of 24 topsoil samples were collected around the radius of 0.5 km from the blasting arena. Additionally, six background samples were also collected from an unexploited reserved area that was ~6 km far from the main sampling location. Two rocks of limestone samples from blasting area were also collected and analysed for heavy metals as a reference. All the samples were processed and extracted with nitrate acid solution and analysed using smart spectrophotometer methods. The results suggested varying organic contents in soil, sand, silt, clay and pH. All these parameters are correlated with those of unexploited samples. Limestone rocks samples displayed a high concentration of Fe and Mn improvement. Toxic metals concentrations (mg/kg) in top-soil with background levels were discovered in Hg, Fe, Mn, Ni, Zn, Cd, Cu, Cr and Pb. Residual phases exhibited the lowest enrichment for most metals possibly, because of high loamy sand content. The situated enrichment advocates influence from mining activities. The results especially geoaccumulation index assessment exhibit below detected limit to 0.20 mg/kg for Pb which is uncontaminated by Lead when compared with the USA threshold limit of particulate metal concentration. Conversely, the other hazardous metals ranged from 1 to 2, indicating the area is contaminated moderately. The exposure to dust containing high silica in quarry workers leads to deterioration of pulmonary function and hence suggesting a need for protective measures of the quarry workers.

Key words: Top-soil, heavy toxic metal, limestone quarry, air pollution.

INTRODUCTION

Limestone quarrying from subsurface deposits is an early technological activity that has been in place since the

ancient time (Gbadebo and Bankole 2007). The Romans and Egyptians present early examples of limestone used

in the construction of the large pyramids, monuments and temples. Quarrying activity is still common and 112800 metric tonnes is quarried annually according to Ashaka cement Plc annual report (unpublished). The company has the intention to increase its capacity by the end of 2017.

Quarrying activities also bring many adverse effects to ecosystems (Evans, 1989; NISA, 1997; Madhaven and Sanjay, 2005; Effiong and Gilbert, 2012; Abah et al., 2014) and to the health of human beings (Ugbogu et al., 2009; Morton et al., 2010; Ololade et al., 2015). For example, dust from quarrying affects the growth and flowering of crops because it settles down on the leave's surface and affects photosynthesis. Human exposure may occur directly by ingestion, inhalation, or dermal contact (Evans, 1989; Adewuyi and Osobamiro, 2016).

Silicosis is another dangerous disease in quarry miners that happens due to inhalation of silica containing dust material within 0.1 to 150 μm size range (Evans, 1989; Loska et al., 2003; Hamad et al., 2014). Skin diseases and other respiratory problems have also been reported in quarry workers (Ugbogu et al., 2009; Ololade et al., 2015). For example NISA (1997) and Safrudin et al. (2014) stated that inhaled limestone dust can increase the level of IL-8 serum of limestone mining workers after work. Toxic metals contamination of the locality from acid mine channel occurred from exposure to some minerals like sulphide minerals mostly arsenopyrite and pyrite in water and air of both abandoned and active mine areas. Zuhairi et al. (2009) found that, the concentration of some elements (Zn, Pb, Mn, Fe, Cu and As) in surface soil, water and mine tailings passed regulatory levels. Recently, a quarried limestone in the United State was discovered to contain exposure of hazardous limits of Hg metal (Safrudin et al., 2014; Adewuyi and Osobamiro, 2016).

According to Jibiri and Okorie (2006), because of the increase in demand for limestone as raw material in Nigeria, surface mining methods for limestone extraction have increased in recent times. For example, Gbadebo and Bankole (2007) reported a similar research in Shagamu, North-Western Nigeria, whose results generally show the elevated concentration of all the elements when compared with the USA threshold limit of particulate metal concentration, e.g., Pb (1.5g m^{-1}); Cd ($0.004 - 0.026\text{ g m}^{-3}$), in the surrounding air. These elements in the airborne dust may pose a great threat to the health of plants, animals and residents in and around the factory and also to workers and visitors to the factory (Gbadebo and Bankole, 2007; Ajala et al., 2014). Gamma radiation and radionuclides were also detected in selected quarries of limestone in Ibadan, Nigeria (Evans, 1989). In Nigeria, there is a dearth of research

information on the effect of quarrying limestone and some mineral explorations on the environment in regarding of toxic metals contaminations. There is serious need to carry out research on baseline levels of concentration of heavy metals in the quarry environment. With this, a database on pollution status would be produced of the heavy metals around the area of mining and used as reference material for research in future and comparison. Therefore, this work aims to quantify the concentration levels of hazardous substances such as Mercury (Hg), Iron (Fe), Zinc (Zn), Nickel (Ni), Manganese (Mn), Copper (Cu), Chromium (Cr), Cadmium (Cd) and Lead (Pb) in top-soil of a limestone quarry in Gombe, North-Eastern Nigeria.

METHODOLOGY

Study area

The studied stratigraphic succession in the study area (Ashaka area) begins with the Bima Sandstone, the Bima Sandstone is categorised in both the Dumbulwa-Bage High and Wuyo-Kaltungo High. It also occurs on the floor of the research area (Ashaka Cement Quarry section) and is divided from the overlying Pindiga Formation (Kanawa Member) by a thin ferruginous crust without the transitional Yolde Formation. The Yolde Formation is almost absent in the research area. According to Zarborski et al. (1998), the Yolde Formation wedges out in the western part of the Dumbulwa-Bage High where syn sedimentary uplift also resulted in the attenuation of the "Middle and Upper Bima Sandstones"; Carter et al. (1963) referred to the equivalents of the Pindiga Formation to the Gongila Formation and Fika Shales. Zaborski et al. (1998) subdivided the Pindiga Formation into Kanawa - Dumbulwa - Fika members in the area. Like the Yolde Formation, the overlying Kanawa Member has been eroded over the large part of the Ashaka area.

Ashaka cement limestone quarry was chosen as the research area. This is because it is the only active limestone quarry in the region of North-eastern Nigeria (Figure 1). The research area is located on $10^{\circ} 56' 10''\text{N}$ and $11^{\circ} 27' 20''\text{E}$. The stratigraphy and geologic setting of the research area which is part of the Benue trough evolved during the opening of the Atlantic which separated Africa and South America in the carboniferous as a result of continental rifting (Walkey and Black 1934). The Gongola Basin along with the Yola Basin forms the upper Benue trough, trending South West to North East for about 800 km and is about 150 km wide containing up to 6000 m of Cretaceous to Tertiary sediments that have been uplifted, faulted and folded.

Collection of samples and their chemical analysis

A total of 24 samples were systematically collected from the upper 0 to 10 cm depth within 0.5 km radius from the zone of blasting as shown in Figure 2. Another 4 top-soil samples were also collected around the quarry pit area and stand as samples at zero meters. Another 4 samples of the topsoil each were collected also within the radii of 100, 200, 300, 400 and 500 m distance from the blasting area as shown in Figure 2. All the above mentioned samples added

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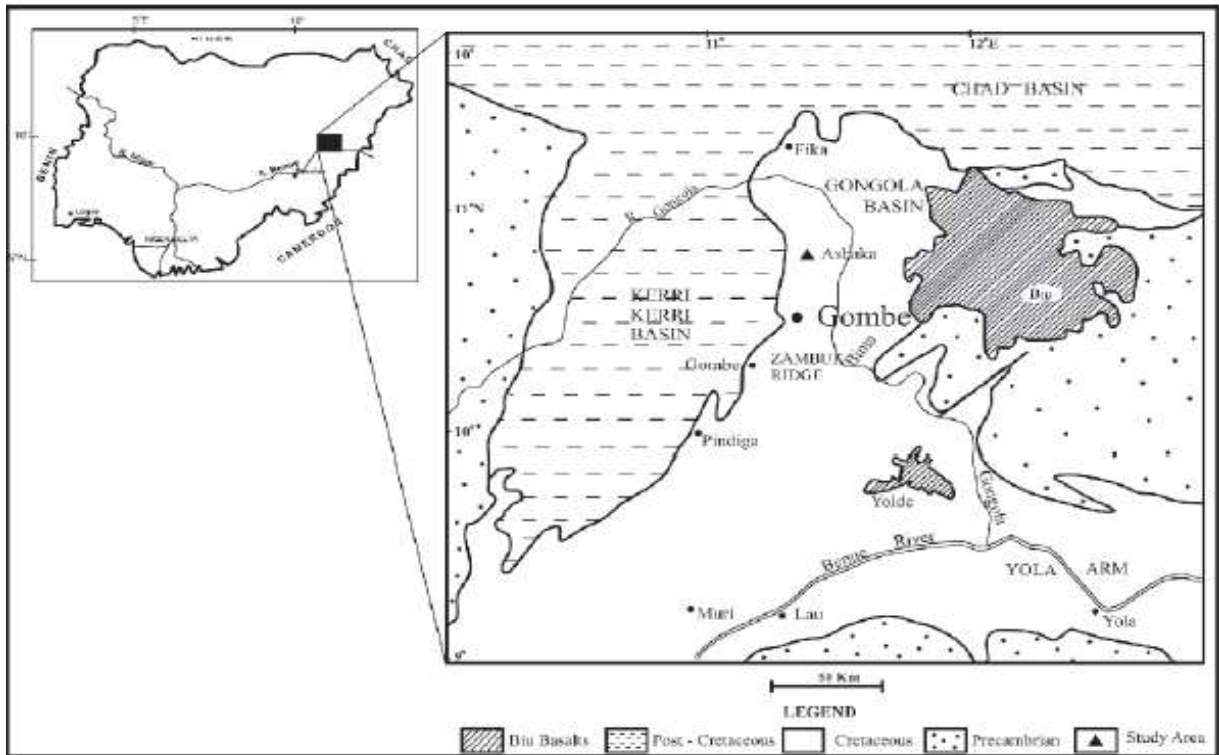


Figure 1. Map of Nigeria showing the geological map of the study area location (Ashaka, Gombe state, North-eastern Nigeria).

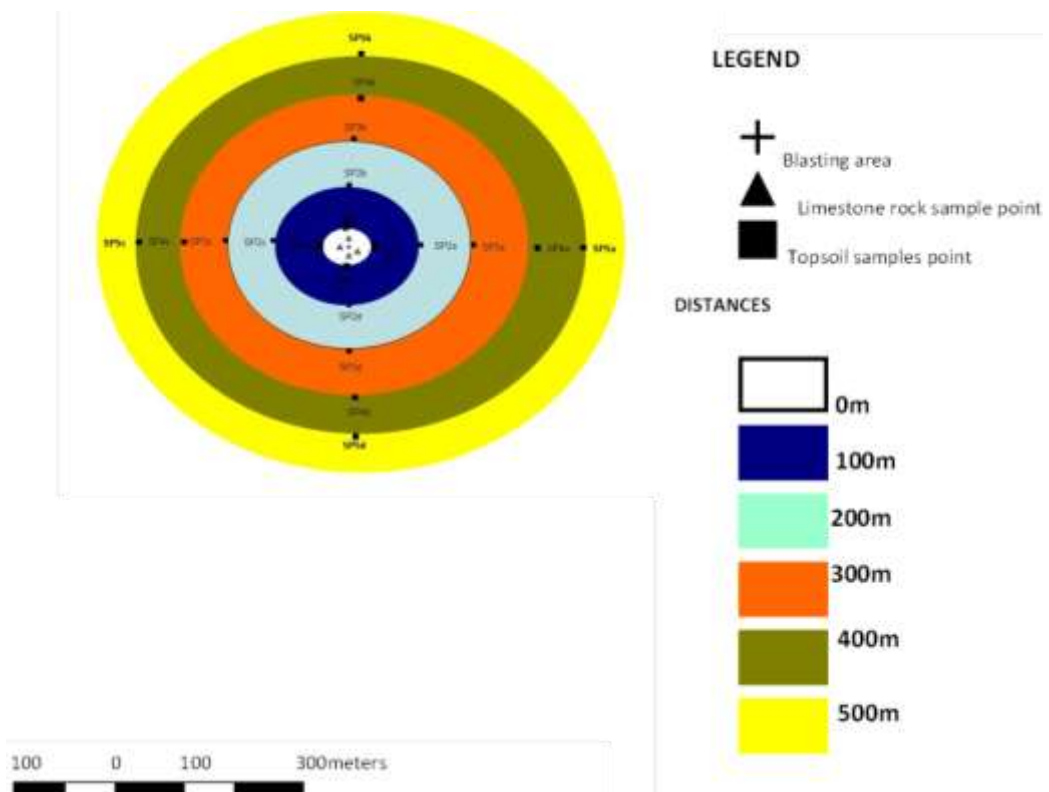


Figure 2. Top-soil sampling points at study area: Samples were collected up to half kilometre from blasting point at 100 m interval.

Table 1. Average concentration (mg/kg) of heavy metals in top-soil sample around the area of a limestone quarry pit.

Sample Code	Distance from quarry(meter)	Hg	Fe	Mn	Ni	Zn	Cd	Cu	Cr	Pb
SP 1	0	0.05 ± 0.02	1.01 ± 0.02	2.93 ± 0.03	0.95 ± 0.05	0.13 ± 0.01	0.10 ± 0.01	0.77 ± 0.02	0.09 ± 0.01	0.2 ± 0.01
SP 2	100	0.09 ± 0.03	1.65 ± 0.01	1.19 ± 0.01	1.23 ± 0.01	0.07 ± 0.01	0.13 ± 0.01	0.77 ± 0.01	0.05 ± 0.00	nd
SP 3	200	0.16 ± 0.03	1.32 ± 0.02	1.00 ± 0.02	0.10 ± 0.01	0.18 ± 0.02	0.25 ± 0.01	0.90 ± 0.01	0.12 ± 0.01	nd
SP 4	300	0.04 ± 0.03	1.45 ± 0.02	0.66 ± 0.02	0.29 ± 0.02	0.06 ± 0.01	0.02 ± 0.01	0.92 ± 0.02	0.11 ± 0.01	nd
SP 5	400	0.07 ± 0.02	1.31 ± 0.02	0.40 ± 0.02	0.04 ± 0.01	0.12 ± 0.02	0.04 ± 0.01	0.56 ± 0.02	0.14 ± 0.01	nd
SP 6	500	0.17 ± 0.14	1.33 ± 0.01	0.53 ± 0.38	0.05 ± 0.01	0.09 ± 0.01	0.02 ± 0.00	1.03 ± 0.02	0.13 ± 0.01	nd
Background	Unexploited	0.02 ± 0.01	1.34 ± 0.02	0.46 ± 0.01	0.65 ± 0.02	0.04 ± 0.02	0.28 ± 0.01	0.91 ± 0.01	0.24 ± 0.01	nd
LR 1	-	0.15 ± 0.04	1.52 ± 0.02	0.60 ± 0.01	1.12 ± 0.03	0.04 ± 0.01	0.31 ± 0.02	0.74 ± 0.01	0.17 ± 0.01	nd
LR 2	-	0.16 ± 0.02	1.34 ± 0.01	1.90 ± 0.02	0.38 ± 0.02	0.02 ± 0.01	0.00 ± 0.00	0.72 ± 0.02	0.18 ± 0.01	nd

nd: not detected.

to a total of 32 samples. At each sampling points, samples were picked randomly and added up to produce composite samples. All the topsoil samples that were collected were labelled as SP₁ (0 m), SP₂ (100 m), SP₃ (200 m), SP₄ (300 m), SP₅ (400 m) and SP₆ (500 m). Four background samples from the unexploited area were also collected about 6 km from research area.

Four limestone samples were also collected from different sections of the quarry. There are two types of limestone deposits in the quarry based on their colour; brownish and greyish. A clean plastic trowel was used to spoon the samples and immediately they were preserved in clean polyethylene bags and conveyed to the geochemical laboratory for immediate pre-treatment and chemical analysis. Samples were safely conveyed to the geochemical laboratory and arranged on a pre-cleaned surface. During the sample preparations and analysis, sampling implements and other work surface were always thoroughly cleaned between samples. Soil samples were put in oven at room temperature for 24 h to air-dry, and grinded using agate mortar. All the samples for heavy metals analysis were sieved using hand sieve with 0.5 mm mesh size.

Geochemical analysis of heavy metal and soil properties determination

pH of soil samples was analysed by using the

potentiometric method. The method involved taking the pH of 1:2.5 (soil: deionised water) extracts using a calibrated pH meter. Organic content was analyzed in the soil samples using Walkley and Black wet oxidation method Walkey and Black (1934). The heavy metals were extracted by weighing 5.0 g of 2 mole of nitrate acid (HNO₃). The solution was covered in a conical flask and transferred to a hot plate at 30°C for 2 h. Agitation of all the samples solution after every 20 min was carried out to make sure all soil particles were exposed to complete leaching. All the samples were cooled for 2 h and Whatman No 1 filter papers were used for filtration, extracts from all the soil solution samples were kept in plastic bottles in the fridge.

For the determination of heavy metal, spectrophotometer (American model 2000) was used. The operation of smart spectro was controlled by a micro-processor; the micro-processor is programmed with menu driven software. Samples containing all reagents except the soil samples (blank samples) were carried through all methods, analyzed and subtracted from the sample, for the purpose reagent confirmation.

Risk determination

Geoaccumulation index (I_{geo}) was applied to assess the pollution level of heavy metals of the topsoil within the environment of the research area. Muller (1969) used the

I_{geo} as a tool to assess the level of toxic metal of the soil with regards to background concentration levels. The I_{geo} is mathematically expressed as:

$$I_{geo} = \log_2 [C_n / 1.5 \times B_n] \quad (1)$$

Where C_n and B_n are the average concentrations of heavy metals in the on-site soil and background location respectively, while 1.5 is an empirical coefficient.

RESULTS AND DISCUSSION

Assessment of toxic metals

Table 1 presents the average concentrations of Hg, Fe, Mn, Ni, Zn, Cd, Cu, Cr and Pb in the top-soil of the Ashaka cement quarry samples. The concentration level of the various heavy metals exhibits a little range of alteration with fickle pattern in the order: Fe > Mn > Cu > Ni > Cd > Cr > Zn > Hg > Pb (Figure 3). Therefore, Fe is the most dominated toxic metal in the study area while Pb is the least represented. The major effect of Fe from a health perspective of the quarry worker is on pulmonary function (Madhavan and

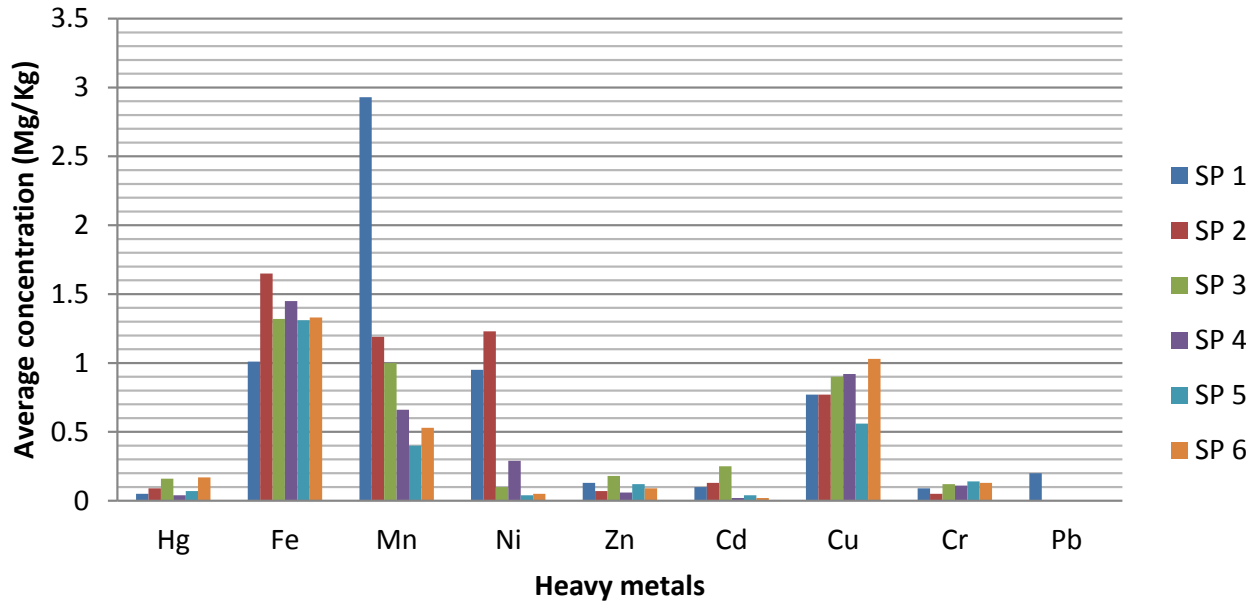


Figure 3. Average concentration of heavy metal in the topsoil samples of the study area.

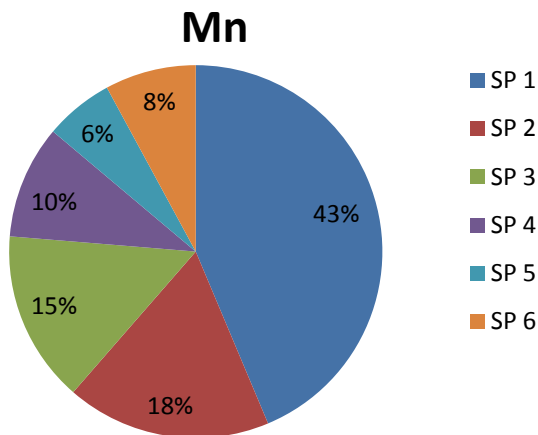


Figure 4. Concentrations level of manganese (Mn) in the study area topsoil samples.

Samjay, 2015). There is no specific pattern in variation for each heavy metal with an increase in distance from quarry blasting area as except for Mn and Zn as shown in Figure 3. This evidenced that the distribution of heavy metals from the origin could have been bulk by a wind which dispersed quarry dust containing heavy toxic metals in all corners at various time, space and magnitude.

Most of the samples between 0 and 200 m seem to display greater concentrations for most metals than samples from 300 to 500 m; this is because of the excavated overburden deposited in the locations and their proximity to the blasting area. Examination of the quarry limestone rocks (LR), which are classified as

Brownish and Greyish limestone chemically, displayed the conspicuously greater concentration of Fe as compared to other metals analyzed. The Fe concentration in top-soil samples analyzed up to 500 m (Table 1) away from the blasting area displayed a level almost similar to that of the unexploited area (background level), probably because of intense exposure of the limestone outcrop due to the erosion of the overburden in the area. Mn conspicuously showed high concentration at 0, 100 and 500 m from the blasting area, the high concentration of Mn at 500 m could be because of the excavated soil from the quarry pit which was dumped at 500 m distance, thus increasing the amount of soil containing Mn, this probably caused the high concentration of Mn compared to close sampling point at 400 m (Figure 4). It is believed that the origin of Mn in these three sampling locations is a non-point source. The soil properties, especially the sandy loam of the soil and organic content of topsoil samples in this research promote leaching, but pH values for all soil suggest that most heavy toxic metals might not be free in solution (Muller, 1969).

Properties of the top-soil

The outcome of the result analysis of soil properties within the vicinity of an Ashaka limestone quarry in North-eastern Nigeria is presented in Table 2. The pH ranged from 5.28 to 6.03 for the top-soil samples within the corners of half a kilometre away from blasting pit. The average pH of unexploited area (background) soil was 5.69 ± 0.62 , while that of the quarried limestone

Table 2. Soil properties of top-soil samples around the area of limestone quarry pit.

Sample code	Percentage			Organic content	pH in H ₂ O	EC
	Sand	Clay	Silt		1:2.5	dscm ⁻¹
SP 1	57.10 ± 4.5	10.40 ± 7.9	32.50 ± 5.1	0.72 ± 0.22	5.81 ± 0.70	0.69 ± 0.18
SP 2	56.87 ± 10.3	9.87 ± 5.2	32.49 ± 3.2	0.60 ± 0.14	5.70 ± 0.38	0.75 ± 0.02
SP 3	59.60 ± 19.5	7.90 ± 3.50	32.50 ± 6.4	0.49 ± 0.25	5.63 ± 0.52	1.06 ± 0.05
SP 4	64.60 ± 1.78	5.40 ± 2.5	30.00 ± 23.1	0.64 ± 0.19	6.03 ± 0.82	0.87 ± 0.17
SP 5	57.10 ± 23.2	10.40 ± 6.5	32.50 ± 3.9	0.60 ± 0.30	5.55 ± 1.0	0.55 ± 0.03
SP 6	59.60 ± 15.1	12.90 ± 9.50	27.50 ± 23.1	0.51 ± 0.02	5.28 ± 0.44	0.71 ± 0.23
Background	69.60 ± 5.3	12.90 ± 7.23	17.50 ± 5.5	0.43 ± 0.44	5.69 ± 0.62	0.36 ± 0.11
LR 1	N/A	N/A	N/A	N/A	6.80 ± 0.49	N/A
LR 2	N/A	N/A	N/A	N/A	6.64 ± 0.52	N/A

N/A: No answer; LR, limestone rock.

displayed as LR 1 and 2 in Table 2, was 6.80 ± 0.49 for the brownish limestone and 6.64 ± 0.52 for the greyish limestone, respectively. The pH value slightly reduced from 0 to 300 m while there is significant increase at 400 m probably because of dumping of top soils and shales associated with limestone bed by the quarry excavators at that distance. pH results of the soil samples were similar to that of the limestone rocks, where the pH of all the soil sample with the exception of sample at 400 m were more moderately acidic. This shows the influence from limestone rocks which are slightly acidic in nature. The similarity of pH values of limestone quarry's topsoil samples with pH value of background sample which is 6 km from the study are because of too much exposure of limestone rocks on the surface of the area which the leaching of some metals from the topsoil (background) affected.

Organic content of topsoil samples are presented in Table 2, which show a range from 0.49 to 0.72% compared with the average of $0.43 \pm 0.44\%$ for background samples. Determination of organic matter helps to estimate the nitrogen which will be released by bacteria activity for the next season depending on the climatic conditions, soil aeration, pH, type of organic material, and other factors. Soil organic matter is usually rich in humic materials with multiple functional groups. These functional groups have the ability to complex metals thereby absorbing them in the soil (Evans, 1989; Jibiri and Okorie, 2006; Effiong and Gilbert, 2012); therefore, the greater the soil organic content, the greater the ability of that soil to absorb or retain metals within it. The organic content in sandy loam soil samples were found to be absolutely low as presented in Table 2.

Particle size analysis of all top-soil samples showed 56.87 - 59.60, 27.50 - 32.50 and 5.40 - 10.40% for sand, silt and clay, respectively. All the samples compared with the unexploited background samples confirmed that they were from the same geographical region; these samples also displayed no or little interference from the activities of exploration.

Risk assessment

Table 3 shows the risk assessment based on geoaccumulation index (I_{geo}) rating. Here a factor of 1.5 is multiplied in each of the background samples in order to find the natural fluctuations of a given heavy metal in small anthropogenic influences and as well as the environment (ENS, 2007; Abah et al., 2014; Hamad et al., 2014). Rating of I_{geo} showed for all the top-soil from Ashaka limestone quarry ranged from uncontaminated (< 0) to moderately contaminated (1 - 2). All the toxic metals displayed a significant enrichment from the limestone quarrying activities except that Pb input in the soil is related to the parent material that formed the soil or small anthropogenic non-point sources or other natural sources. Morton et al. (2010) reported that a slightly low spatial distribution of Ni in topsoil within an industrial area in Mexico has been studied to have contributed to the input from parental rocks in the area.

There is no similar research in this study area, but Effiong and Gilbert (2012) conducted similar work on risk assessment of topsoil samples at Ratcon limestone quarry in Oluyole, South-western Nigeria. The I_{geo} of these samples were compared with those estimated in our work this (Table 4). The I_{geo} rating results displayed that all samples of topsoil of Ratcon limestone quarry of Mn are < 0 , implying that the topsoil samples were clearly uncontaminated by Mn. However, I_{geo} of Mn is greater than zero for all the samples compared with Ratcon limestone quarry (Figure 5); suggesting moderate contamination by Mn of slightly high concentration level from 0 m while reducing as distance increases from the blasting point.

Criteria for soil quality

The average level for the soil sample heavy metals studied was within the limits provided by some countries and the European Union, except for Pb which is not

Table 3. Geoaccumulation index (I_{geo}) of heavy metals in top-soil samples around a limestone quarry.

Sample code	Hg	Fe	Mn	Ni	Zn	Cd	Cu	Cr	Pb
SP 1	0.50	0.15	1.28	0.29	0.65	0.07	0.17	0.08	-0.20
SP 2	0.90	0.25	0.52	0.38	0.35	0.09	0.17	0.04	Nd
SP 3	1.61	0.10	0.44	0.03	0.90	0.18	0.20	0.10	Nd
SP 4	0.40	0.22	0.29	0.09	0.30	0.01	0.20	0.09	Nd
SP 5	0.70	0.20	0.17	0.01	0.60	0.03	0.12	0.11	Nd
SP 6	1.71	0.20	0.23	0.02	0.14	0.01	0.23	0.11	Nd

Nd: Not detected.

Table 4. Comparative research findings of geoaccumulation index (I_{geo}) of Heavy metals in topsoil samples between Ashaka (NE, Nigeria) and Oluyole (SW, Nigeria) limestone quarry.

Present study										
Sample code	Hg	Fe	Mn	Ni	Zn	Cd	Cu	Cr	Pb	Co
SP 1	0.50	0.15	1.28	0.29	0.65	0.07	0.17	0.08	-0.20	-
SP 2	0.90	0.25	0.52	0.38	0.35	0.09	0.17	0.04	Nd	-
SP 3	1.61	0.10	0.44	0.03	0.90	0.18	0.20	0.10	Nd	-
SP 4	0.40	0.22	0.29	0.09	0.30	0.01	0.20	0.09	Nd	-
SP 5	0.70	0.20	0.17	0.01	0.60	0.03	0.12	0.11	Nd	-
SP 6	1.71	0.20	0.23	0.02	0.14	0.01	0.23	0.11	Nd	-
Similar research findings (Effiong and Gilbert, 2012)										
SL 1	-	0.97	-0.43	0.57	0.20	-0.64	1.31	1.08	0.31	0.50
SL 2	-	1.10	-1.89	0.26	0.16	-0.40	0.41	0.16	-0.42	-0.76
SL 3	-	1.38	-0.79	0.93	0.76	-1.32	3.28	1.06	-0.22	-0.36
SL 4	-	-0.01	-0.54	-0.54	-0.03	-1.56	1.12	-0.04	-0.22	-0.29
SL 5	-	-0.06	-1.09	-0.43	0.10	1.24	0.73	-0.25	-0.40	-0.89
SL 6	-	0.23	-1.09	0.20	0.01	1.94	0.19	0.56	0.45	-0.54

detected. The concentration of metals showed no potential toxicity associated with the mining of limestone in Ashaka quarry. However, other attributes such as more acidity, weathering of the rock, and pH, showed the possibility of the high infiltration potential of these toxic metals from the surface soil into subsurface soil and gradually into

groundwater. The slightly moderate contamination of top-soil represented by I_{geo} rating as displayed in Table 3 is a direct confirmation that the blasting and other exploration activities promote some level of heavy metals onto the soil. These findings clearly suggest that continuous monitoring of the top and sub-soils is important to assess level of

toxic metals.

CONCLUSIONS

The concentration of Fe, Zn, Ni, Mn, Hg, Cu, Cr, Cd and Pb in top-soil samples within the area of

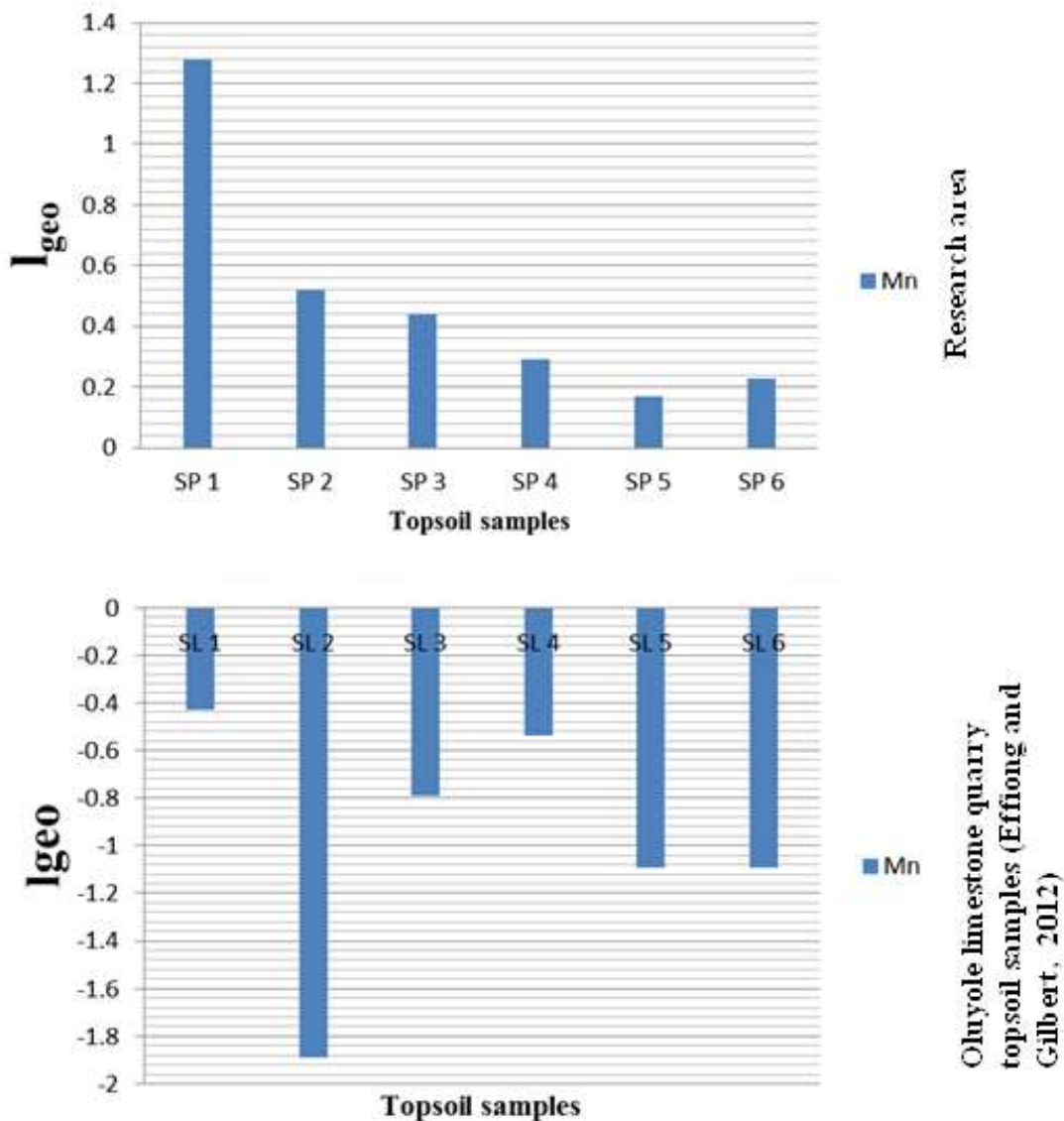


Figure 5. Comparative research findings for geoaccumulation index (I_{geo}) of Mn in topsoil samples between Ashaka (NE, Nigeria) and Oluyole (SW, Nigeria) limestone quarry in their topsoil samples.

Ashaka limestone quarry was analyzed. The acidity (pH) of the soil heavy metals falls between the range of moderately acidic. Properties of the organic content of soil and size of the particles freight support leaching of heavy metals from the top-soil. The organic content of Ashaka soils were found to be in low concentration. Pollution levels for all heavy metals according to I_{geo} rating ranged from uncontaminated to moderately contaminate. It is believed that Pb is related with parent material of topsoil as confirmed by I_{geo} for samples with a rating of <0 from 100 to 500 m indicating practically uncontaminated soil. All the heavy metals were found to be in line with the regulatory ranges, except the Pb that had the level far below the detecting limits when compared with other countries. Constant control of dust

and study of the limestone quarrying operations are significant to quantify the toxic level of hazardous substance, which could promote threat with active piling up of quarry dust on the soil and leaching by acid rain.

Conflict of Interests

The authors have not declared any conflict of interests.

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