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Assessment of some Essential Metals contents of limestone and soil samples from Ashaka cement factory, Funakaye Local Government Area, Gombe State, Nigeria

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Abstract- This research work aimed at assessing the level of the heavy metals, Cu, Mn, and Zn in soil and Limestone samples collected from Ashaka cement factory in Jalingo, Darumfa and Lariski Villages within the vicinity of company. Four different samples were collected at interval of five metres apart and the soil samples were collected at a depth of 5cm from the top. The collected samples were air dried and pulverized into fine powder and sieved with a 2mm sieve to obtain a powdered matrix of particles size < 75µm. The samples were subsequently pelletized using pressed machine. The heavy metals, Cu, Mn and Zn were analysed using Wavelength Dispersive X-ray Fluorescence (WDXRF). Zn was observed to show higher levels in all the soil samples; Cadmium was observed to show higher concentration in limestone samples; the results obtained shows that, of the entire element determined in this study, Mn have the highest concentrations in limestone. The value of the heavy metals suggests that activities are a major source of heavy metals.

Keywords: SS1=Limestone from Quarry, SS2=Soils from Darufa, SS3=Soil from Lariski, Limestone, WDXRF= Wavelength Dispersive X-ray Fluorescence, Heavy Metals

1. INTRODUCTION

Limestone quarrying from subsurface deposits is an early technological activity that has been in place since the ancient time [19]. 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activity is still common and 112800 metric tonnes is quarried annually according to Ashaka cement Plc annual report (unpublished).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

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by the end of 2017. Quarrying activities also bring many adverse effects to ecosystems [12]; [25]; [21]; [11]; [1] and to the health of human beings [29]; [23]; [26]. 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 [12]; [3]. 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 [12]; [20]; [16]. Skin diseases and other respiratory problems have also been reported in quarry workers [29]; [26]. For example [25] and [28] 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. [26] 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 [28]; [3]. According to [18] , 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 [19] 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 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 [19]; [5] Gamma radiation and radionuclides were also detected in selected quarries of limestone in Ibadan, Nigeria [12]. 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.

Soil quality determines the sustainability and productivity of agro-business of any nation. Soils are precious natural resources widely used as environmental indicators and their chemical analysis provide significant information on the assessment of anthropogenic activities of an area. They are important sinks for heavy metals and also play a significant role in the remobilization of contaminants under favorable conditions and interaction between soil and as well as water and sediments [15]. In recent years there have been increasing interests regarding heavy metal contaminations in soils, apparently due to their toxicity and perceived persistency within the aquatic systems and analysis of soil is a useful method of studying environmental pollution with heavy metals.

Developed a classification system that places primary emphasis on the detailed composition of grains and interstitial material in carbonate rocks. Based on composition, there are three main component: Allochems (grain), matrix (mostly micrite), and cement (sparites). The folk system uses two-part names; first refers to the grains and the second is the root. It is helpful to have a petrograhic microscope when using the folk scheme, because it is easier to determine the components present in the sample [13].

A. DUNHAM CLASSIFICATION

The Dunham scheme focuses on depositional textures. Each name is based upon the texture of the grains that make up the limestone. His efforts deal with question of wheather or not the grains were poriginally in mutual contact, and therefore self-supporting, or whether the rock is characterized by the presence of frame builders and algal mats. Unlike the Folk scheme, Dunham deals with the original porosity of the rock. The Dunham scheme is more useful for hand samples because it is based on texture, not the grains in the sample [10]

B. COMPOUND OF LIMESTONE

Limestone is a simple compound, familiar in many forms, made up of a doubly positive charge calcium ion bonded to carbon plus three oxygen ($CaCO_3$) it is a very common mineral, the substances of limestone, marble and chalk, where it usually take one of two crystalline structures, calcite and aragonite. Most calcium carbonate bearing rock is sedimentary, deposited millions of years ago from the shells of Dead sea creatures, then compacted under subsequent layers of sediment. Chalk and limestone are fairly similar materials, chalk being less compacted and so on softer. Marble takes lomger to form, starting with a raw material of chalk or limestone that then getstrans formed by heat and pressure, recystallisting to produce a significantly harder interlocking structure of crystals [10].

C. PROPERTIES OF LIMESTONE

The properties of limestone are divided into two; physical and chemical properties.

Physical properties

1. It is quite impervious
2. Its hardness is 3 to 4 on Moh´s scale
3. It is fine, to a very fine grained Calcareous rocks of sedimentary nature
4. It has less than one percent (1%) water absorption
5. It has a density of 2.5 to 2.3kg/cm^3
6. It has comprehensive strength of 60-170N/mm^2

Chemical properties

In chemical properties, they are calcareous rocks principally of calcic minerals with minor amounts of alumind (Al_2O_3) 2-5% Ferric and Alkaline oxides [15].**USES**

Limestone is commonly used in architecture, especially in Europe and other parts of the world, below are other uses of limestone.

1. It is the raw material for the manufacture of quicklime (calcium oxide), slaked lime (calcium hydroxide), cement and mortar.
2. Pulverized limestone is used as a soil condition to neutralize acidic soils.
3. It is crushed for use as aggregate—the solid base for many roads
4. Geological formations of limestone are among the best petroleum reservoirs
5. It is a reagent in flue-gas desulfurization; it reacts with sulphur dioxide for pollution control
6. It is used in glass making.

D. EFFECT OF LIMESTONE

Limestone affects the environment as it produces highly alkaline dusts which are air pollutants. It also has effects on health, in particular for those with respiratory problems. The dust also has physical effects on the surrounding plants, like it blocks and damages their internal structures and abrasion of leaves and cuticles, as wellas chemical effects which may affect long-term survival. [17].

E. AIM

The aim of this research is to assess the potential of Soil from Darumfa and Lariski village within which industry is located, and Limestone within the industry.

F. OBJECTIVES OFTHE STUDY

The objectives of the study include:

1. Determination of the heavy metals; Lead (Pb), Cadmiun (Cd), Copper (Cu), Nickel (Ni), Zinc (Zn), and Manganese (Mn), in the soil and limestone samples.
2. To map out the distribution pertain of the heavy metals determined.

2. LITERATURE REVIEW

Evaluate the assessment of geochemical toxic metal stocking in top-soil within the area of a limestone quarry in Gombe State [30]. 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 [27]. 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 [31] [22].

[8], study the Utility of Pollution Indices in Assessment of Soil Quality around Madaga Gold Mining Site, Niger State, North-Central Nigeria, using Environmental Pollution Indices. Geological mapping of the study area indicated that the area was dominated by schist and granite. The static water level measurement revealed a westward groundwater flow direction which also coincides with the regional structural trend of the area. Laboratory analyses of soil and stream sediment were carried out in National Geosciences Research Laboratory Kaduna. The results of the soil analyses revealed high concentrations of mercury, cadmium, lead and arsenic. The results of the laboratory analysis were further elucidated using pollution indices such as geo-accumulation index, contamination factor, [14] degree of contamination, elemental contamination index and metal pollution index. These environmental indices revealed that the soil is seriously polluted with mercury, cadmium and lead, moderately polluted with arsenic,[9] lightly polluted with iron and copper and very lightly polluted with manganese, zinc, nickel and cobalt in the order of: Hg > Cd >Pb> As > Fe > Cu > Mn > Zn > Ni > Co. The mean concentrations of the first four metals (Hg, Cd, Pb and As) exceeds their average crustal abundance, which is an indication of possible pollution. The concentrations map of the analyzed heavy metals indicated a westward decrease in concentration away from the mine sites. This was in agreement with the flow direction and the possible reduction in pollution intensity away from the mine sites could be attributed to the natural attenuation mechanism of soil in the course of groundwater migration as well as hydrogeological attributes of the area. The study recommends that the miners be grouped into association and trained on modern mining techniques that are environmental friendly. The polluted soils in the area should be remediated and proper sensitization on the dangers associated with artisanal mining should be carried out in the area. Periodic monitoring of the soil quality in the area is advocated

3. MATERIAL AND METHOD

A. Description of the studyb area

Ashaka Cement Company is located in Jalingo Village of Bajoga, Funakaye local government area of Gombe State, north eastern Nigeria. It was established in 1967, with an installed capacity of 500,000 MT [15] to meet the needs of construction works in the Northeastern part of Nigeria.

The factory lies in the Northern part of Gombe between longitude 100 45'N and 110 00'N and latitude 110 15'E and 110 30'E. The company produced huge amount of dust and gaseous pollutants to the unsuspecting communities scattered in the area in time past. Prior to now, large proportion of the dust was deposited on farmlands, homes and water bodies including the River Gongola.

B. Sample Collection

Samples were collected using a plastic hand trowel by sweeing the top most soil (5cm depth). Collection was done at sample sites; SS1 (the limestone) inside the quarry whereas SS2 Darumfa village and SS3 Lariski village. Two background top soil samples were collected from the village about 2km away from the study are, and one limestone rock sample was collected from the quarry section of the company. Four different samples were collected from eacgh sites at the interval of three (3m) meters apart and pulled together to representa sample. They were stored in a polythene bags and transportedto the laboratory immediately and spread on a precleaned surface. Soil samples were air-dried and granded using pressed machine for pretreatment and analysis. Collection was made monthly for a period of four month, from the month of October, 2013 to January 2014.

C. Reagents and Chemicals

All analysis were performed with Analitical grade chemicals and distilled water through out, unless otherwise stated.

D. Soil pH Determination

The pH of the soil samples before planting and after harvest was measured using a calibrated PHS-25 meter and three replicated determinations were carried out on each sample based on the manufacturer's instruction for the pH meter

E. Sample Pretreatment and Analysis

The collected samples were air dried and pulverized into fine pwder before being sieved to obtain a powdered matrix of particle size <75µm. Three pellets ofmass between 0.3-0.5g and diameter of 25mm were prepared from each sample for analysis. The heavy metals were then analysed using Wavelengh Dispersive X-ray Fluorescene (WDXRF) [8].

F. Determination of Moisture

5.0g of soil sample was weighed into a watch glass and placed inside an oven regulated at 110oC. It was heated, cooled in a desiccator and weighed, repeating these steps until constant weight was obtained. The difference in the weight was read as the weight of the moisture.

G. Reagents and Chemicals

All analysis were performed with Annular grade chemicals and distilled water through out, unless otherwise stated.

4. Results and Discussion

A. Results

Table: 1 Mean Concentration (µg/g) of the metals: Cu, Mn and Zn determined in the Soil and Limestone.

Element/Sample	Cu(µg/g)	Mn(µg/g)	Zn(µg/g)
SSI	0.518 ± 0.029	0.700 ± 0.033	0.093 ± 0.029
SS2	0.730gkpt ± 0.029	0.350efty ± 0.203	0.156pn ± 0.029
SS3	0.082 ± 0.070	0.618 ±0.029	1.480 ± 0.024

Mean with the same letter within a column are not significantly different at ($P \leq 0.05$) according to the Turkey test. Data are presented in mean ± SD (n=4). SS1 = Limestone sample from the (quarry), SS2 and SS3 Soil Sample from thr village (Darumfa and Lariski).

Table 1 above show the level of the elements determined in soil sample from Darumfa, Lariski village and the quarry section of the company. In all the elements determine in this study, Zinc has the highest concentration of (1.480± 0.024µg/g) in soil from Darumfa village whereas the least value (0.156±0.0260µg/g) was found in soil from Lariski village. The highest level of Mn (0.618± 0.029 µg/g) was found in the soil from Darumfa village and the least concentration (0.350± 0.203µg/g) comes from the soil village Lariski. Copper was found at detectable levels in soil from all the two samples with average concentrations (0.730± 0.029 µg/g), and (0.082± 0.070 µg/g) for the side soil from the village of Darumfa and soil from the village Lariski respectively.

Limestone has the highest level of Mn (0.700± 0.033 µg/g) and Cu with concentration of (0.518± 0.029 µg/g) whereas Zn has the least concentration (0.093± 0.029 µg/g). This was observed in the limestone sample from the deposit of quarried material. In all the elements determine in limestone in this study, cadmium has the least concentration of 0.079± 0.068 µg/g and Pb with highest concentration, whereas Cu 0.518± 0.029 µg/g)

B. DISCUSSION

The table table above shows the level and distribution of the metals in the sampling site. High level of Zn (1.480± 0.024 µg/g) was found in the soil from Lariski whereas the element Zn was found with higher concentration (3420 mg/ kg^{-1}) in soil from North-Esthern Nigeria [2]. It was however found a higher concentration (190mg/kg^{-1}) in south westhern Nigeria [11]. The level of Cu (0.730± 0.029 µg/g) observed in the soil from Darumfa village ,whereas the element was found below the detection limits in the soil from from Kituwi and Mwanyani [24], whereas in soil from south westhern Nigeria Cu has a higher concentration of 14.20 mg/kg^{-1} [11]. The level of Copper observed in the limestone from all the regions sampled inferred that the origin of copper in soils was not only weathering and other geochemical processes of rocks, minerazation but also the quarry activities taking place in the region. The level of Mn observed (0.618±0.029 µg/g) in soil from Lariski village, the element was found with high concentration (44.0ppm) in soil from Mecse [8] The results show that Mn was generally more abundant in soil from the villages than in limestone for each particular region showing that the soil Mn could have originated from other rocks within the region and not the limestone ore. These results are similar to the results reported in Hungary [8]. This element has a higher concentration 710 mg/kg^{-1} in soil from south western Nigeria [11]. Heavy metals in soils originated from mineralization of the region as well as weathering of rocks found within the area. The elements Cu and Zn (0.518± 0.029 µg/g) and (0.093± 0.029 µg/g) have the average concentration in limestone while in [8] was found Cu below detection limit in kituwi while in Mwanyawi with higher concentration [24]. The spread of heavy metals is a common phenomenon near factories due to damping of mine tailings. Zn, Cu and Mn concentrations have been shown to be enhanced and to have increased as well as spread to nearby areas [6]. The level of Cu observed (8.87 mg/kg^{-1}) in limestone from South-Western Nigeria [11], while from table 1 in limestone of this study was found with low concentration (0.518± 0.029 µg/g). Manganese was found with lower concentration (0.700±0.033 µg/g) in limestone from table 1 in this study, whereas the element observed with higher concentration (303 mg/ kg^{-1}) in limestone from South-Western Nigeria [11]. The level of Zn was found with low concentration (1.480±0.024 µg/g). in soil from the village of Lariski whereas the element Zn was found with higher concentration (3420 mg/ kg^{-1}) in soil from North-Esthern Nigeria [2]. The element Cu has low concentration (0.730±0.029µg/g) in soil from Darumfa whereas the element was found with highest concentration (121.65 mg/ kg^{-1}) in soil from Aflao Japan [4]. Mn has the low concentration (0.350±0.203 µg/g) in soil from Darumfa village while found with highest concentration (2223.93 mg/ kg^{-1}) in soil from Aflao Japan [4].

Limestone quarrying and processing (cement production) in this company are in the continuous process in the area. These simples that the soil heavy metal content is mainly du to both natural process such as weathering and other geochemical process of the rocks found within the area as well as the anthropogenic activities of the industry. The relatively high concentration of all the heavy metals Zn, Pb, Cu, Cr, Cd, Ni, and Mn, in soils especially the soil from Darumfa Village as compared to the limestone, which are from the same sampling points indicate that the soil metal content was higher than it could have been if it originated from the limestone ores. The are is hilly but surrounded by arable land with a domestic demand. This poses a great danger to the people living within the area as well as animals as some of these heavy metals may be washed into the rivers making them available to humans and biota.

5. CONCLUTION AND RECOMMENDATION

A. Conclusion

The soil in the two villages Darumfa and Lariski is relatively contaminated with the observed heavy metals but as time on with continuous emission from he industry, pollution may arise as a result of accumulation. The level of the heavy metals observed may be attributed to industrial emission since less or no agricultural activity that is taking place near the villages. The level of contamination by the heavy metals increase in the industrial activities and decreases with increasing distance from the industry.

B. RECOMMENDATION

1. Industry should be located far away from residential areas in order to reduce the effect of environmental pollution in the study area;

2. We recommended controlled damping of mine tailing, mine water and any other effluence from the factories so as to ensure that the heavy metals do not spread to the neighbouring arable land and water bodies.

3. Frequent monintoring is also essential for environmental impact assessment once the mining and processing starts.

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