SPECIATION OF HEAVY METALS IN SUSPENDED DUST IN TWO NIGERIAN COMMUNITIES AROUND STONE CRUSHING SITES

BY

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CERTIFICATION

This research work was carried out by Olakunle Alexander Ugweh. It was supervised and approved in accordance with the partial fulfillment of the award of Bachelor of Science (B.Sc.) degree in Biochemistry, Federal University Oye-Ekiti, Ekiti, Nigeria.

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DEDICATION

This research project is dedicated to God Almighty, for endowing me with my parents and every other person who were pivotal to the successful completion of my course of study and this project.

ACKNOWLEDGEMENT

Looking back from where it all started, I cannot but express my profound gratitude to God, the creator of the universe, the alpha and the omega for the privilege and divine wisdom given me to commence and finish this project.

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I appreciate the prayers and support of my aunties (Musiliat Kuti and Esther Omedo), my great uncle (Suleiman Kuti), and my helper (Mr. Aregbesola Kunle), MORE BLESSING.

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To my indefatigable supervisor, Dr. Olumayede, I want to sincerely register my thanks for giving me the opportunity to work under your supervision, the erudite tutelage, discipline, and fatherly concern and encouragements shown towards the success of this project work, I pray God the accorder of rewards to bless you abundantly and sustain you with all the good things of life.

I also appreciate the efforts of all my lecturers who gave me the opportunity to drink from their spring of knowledge at one point or the other. May this spring never lose its essence, once again thank you.

To the "woman behind my smiles" ~~my~~ Head of Department (Dr. C.O. Akintayo), I say God bless you ma and continue to uphold you in all ramification. To the Industrial Chemistry graduating class of 2015, for the opportunity given me to serve as your leader, you are the best colleagues anywhere and I pray that we all meet at the top where we all belong. To all the technologist and staffs of Industrial Chemistry, I pray that the tie that binds us together will not be severed. God bless us all.

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Upon generation, dust particles are transported to distance from the factory sites, making residents in such neighborhood directly vulnerable to particulate matters contaminations (Liu *et al.*, 2006). In the course of transportation, metals are bind to the particulate dusts by physical and chemical processes thereby making them toxic to inhaler of such dust. Heavy metals such as Cr (chromium), Cu (copper), Ni (nickel), Pb (lead), Sb (antimony) and Zn (zinc) occur naturally in earth's crust in varying concentrations and are mostly discharged during stone quarrying/crushing. Previous researchers have reported heavy metal pollution in soils from the vicinity of quarrying sites with peculiar feature of decrease in concentration with increase in distance from quarrying sites (Sharma *et al.*, 2005).

Quarrying sites are full of activities that generate particulate of varying sizes fractions. In Nigeria, there has been little attention given to neighborhood of stone crushing sites which are liable to pollution arising from the dusts generated. It is pertinent to state that most of these stone crushing sites have been indiscriminately set up. Unfortunately, there have been growing increase in urbanization around most of the quarry site and data on atmospheric levels of heavy metals in vicinity of these sites are scare.

1.2 Justification for the study

Nigeria has different sites of ornamental stone quarries for extraction. Ondo and Ekiti states are examples of states where stone mining activities are carried out. Assessment of the air quality around quarrying sites has not been carried out hence the extents of exposure to these heavy metals and the risks posed are unknown. This becomes necessary following urbanization of towns around the sites with attendance increase in residential and public buildings.

1.3 AIMS AND OBJECTIVES

The aim of this study is to assess the heavy metal concentration in suspended dust around stone crushing site in the environment. In order to achieve the above stated aim, the following are the specific objectives of the study;

1. To identify heavy metals content of dust particles in communities around quarrying sites.
2. To determine the concentrations of Co, Ni, Cu, Zn, Mn and Pb for suspended dust in neighborhood of quarrying sites in the study area.
3. To fractionate the metals into various geochemical phases
4. To compare concentration of heavy metals in the neighborhood of quarrying sites with international acceptable limits.

1.4 Expected contribution

This study is expected to serve as

i. Baseline information on variability in the concentration of heavy metals in suspended dust.

ii. Created awareness on the impacts of stone quarrying on atmospheric pollution.

CHAPTER TWO

2.0.0. LITERATURE REVIEW.

2.1.0. HEAVY METAL: A BRIEF DESCRIPTION

A heavy metal is a member of a loosely defined subset of elements that exhibit metallic properties (Michael, 2010). It mainly includes the transition metals, some metalloids, lanthanides, and actinides. Many different definitions have been proposed, some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity(Michael, 2010). The term *heavy metal* has been called a "misinterpretation" in an IUPAC (International Union of Pure and Applied Chemistry) technical report due to the contradictory definitions and its lack of a "coherent scientific basis". There is an alternative term *toxic metal*, for which no consensus of exact definition exists either. Heavy metals occur naturally in the ecosystem with large variations in concentration (Gowd *et al.*, 2010). In modern times, anthropogenic sources of heavy metals, i.e. pollution, have been introduced to the ecosystem. Suspended dusts derived from quarrying sites are especially prone to contain heavy metals (Atiemo *et al.*, 2012), so heavy metals are a concern in consideration of suspended dust around quarrying sites.

Heavy metals can also be defined as trace metals with densities greater than $5gcm^{-3}$ (Duffus, 1980). Adverse effects of elevated concentrations of heavy metals to soil functions, soil microbial community composition and microbial growth have long been recognized under both field and laboratory conditions (D' Ascoli *et al.*, 2005).

2.2.0. DESCRIPTION OF SELECTED HEAVY METALS

There is a lot of heavy metal that poses a threat to human health, but for the sake of these study heavy metals that are most likely present in neighborhood of quarrying sites was briefly looked into. According to Atiemo *et al.*, (2010), heavy metals such as Iron (Fe), Manganese (Mn), Copper (Cu), Zinc (Zn), Cadmium (Cd), Chromium (Cr), Nickel (Ni), and Lead (Pb) were discovered in an area of stone crushing site in Accra, Ghana. However, this research looked into five (5) of these heavy metals which includes: Cobalt (Co), Nickel (Ni), Cadmium (Cd), Copper (Cu), and Lead (Pb).

2.2.1. Co - Cobalt

Cobalt is a compound that occurs in nature. It occurs in many different chemical forms. Pure cobalt is a steel-gray, shiny, hard metal. Cobalt used in industry is imported or obtained by recycling scrap metal that contains cobalt. It is used to make alloys (mixtures of metals), colored pigments, and as a drier for paint and porcelain enamel used on steel bathroom fixtures, large appliances, and kitchen wares. Small amounts naturally occur in food. Vitamin B_{12} is a cobalt-containing compound that is essential for good health. Cobalt has also been used as a treatment for anemia, as it causes red blood cell production. Some natural sources of cobalt in the environment are soil, dust, and seawater. Cobalt is also released from burning coal and oil, and from car and truck exhaust. Cobalt enters the environment from natural sources and from the burning of coal and oil. Cobalt stays in the air for a few days. Pure cobalt does not dissolve in water, but some of its compounds do. Cobalt can stay for years in water and soil. It can move from the soil to underground water. Plants take up cobalt from the soil (Rastmanesh *et al.* 2010).

2.2.2. Ni - Nickel

Nickel is a very abundant element. In the environment, it is found primarily combined with oxygen (oxides) or sulphur (sulphides). It is found in all soils and is emitted from volcanoes. Pure nickel is a hard, silvery-white metal that is combined with other metals to form alloys. Some of the metals that nickel can be alloyed with are iron, copper, chromium, and zinc. These alloys are used in the making of metal coins and jewelry and in industry for making metal items. Nickel compounds are also used for nickel plating, to color ceramics, to make some batteries, and as catalysts that increase the rate of chemical reactions. Nickel and its compounds have no characteristic odor or taste. Nickel is required to maintain health in animals. A small amount of nickel is probably essential for humans, although a lack of nickel has not been found to affect the health of humans. Small nickel particles in the air settle to the ground or are taken out of the air in rain. Much of the nickel in the environment is found with soil and sediments because nickel attaches to particles that contain iron or manganese, which are often present in soil and sediments (Atiemo *et al.* 2012).

2.2.3. Cd - Cadmium

Cadmium is a natural element in the earth's crust. It is usually found as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulphur (cadmium sulphate, cadmium sulphide). It does not have a definite taste or odour. All soils and rocks, including coal and mineral fertilizers, have some cadmium in them (Lacatusu *et al.*, 2009). The cadmium that industry uses is extracted during the production of other metals like zinc, lead, and copper. Cadmium does not corrode easily and has many uses. In industry and consumer products, it is used for batteries (Ni-Cd batteries of mobile phones), pigments, metal coatings, and plastics. A constituent of easily fusible alloys, soft solder and solder for aluminum; used in electroplating and as deoxidizer in nickel plating; used in process engraving, in electrodes for cadmium vapor lamps, photoelectric cells, photometry of ultraviolet sun-rays; filaments for incandescent lights. The powder is also used in dentistry, as an amalgam (1 Cd: 4 Hg).

Cadmium enters air from mining, industry, and burning coal and household wastes. Cadmium particles in air can travel long distances before falling to the ground or water. It enters water and soil from waste disposal and spills or leaks at hazardous waste sites. It binds strongly to soil particles. Some cadmium dissolves in water. It does not break down in the environment, but can change forms (Leung *et al.*, 2010). Fish, plants, and animals take up cadmium from the environment (Lu *et al.*, 2010). Cadmium stays in the body a very long time and can build up from many years of exposure to low levels.

2.2.4. Cu – Copper

Copper is a heavy, reddish-brown metal that has a density of $8.95 gcm^{-3}$. It is very malleable and ductile. Copper is a good conductor of heat and electricity. Copper was one of the first metals to be discovered and used by man. It is a stable metal readily obtained from its compounds. Copper ores are widely found around the world. The main ores are copper pyrites, malachite, chalcocite and cuprite (Jumoke, 2004).Copper is used in wires and cables for conducting electricity because of its high electrical conductivity. It is second to silver and it is much cheaper. It is also used to make water pipes and boilers because of its resistance to chemical attacks. Finely divided copper is used industrially as a catalyst in the oxidation of methanal (Jumoke, 2004).

2.2.5. Pb - Lead

Lead is a naturally occurring bluish-grey metal found in small amounts in the earth's crust. It has no special taste or smell. It can be found in all parts of our environment. Most of it came from human activities like mining, manufacturing, and the burning of fossil fuels (Atiemo *et* *al.*, 2012). Lead is used as a construction material for equipment used in sulphuric acid manufacture, petrol refining, halogenation, sulfonation, extraction and condensation (Lu *et al.*, 2009). It is used in storage batteries, alloys, solder, ceramics and plastics. It is also used in the manufacture of pigments, tetraethyl lead and other lead compounds, in ammunition, and for atomic radiation and x-ray protection. Lead is used in aircraft manufacture, building construction materials (alloyed with copper, zinc, magnesium, manganese and silicon), insulated cables and wiring, household utensils, laboratory equipment, packaging materials, reflectors, paper industry, printing inks, glass industry, water purification and waterproofing in the textile industry. Lead itself does not break down, but lead compounds are changed by sunlight, air, and water (Rastmanesh *et al.*, 2010). When released to the air from industry or burning of fossil fuels or waste, it stays in air about 10 days. Most of the lead in soil comes from particles falling out of the air. City soils also contain lead from landfills and leaded paint. Lead sticks to soil particles. It does not move from soil to underground water or drinking water unless the water is acidic or "soft". It stays a long time in both soil and water (Atiemo *et al.*, 2012).

2.3.0. ENVIRONMENTAL IMPACTS OF HEAVY METALS

Heavy metals are deemed serious pollutants because of toxicity, persistence and non-degradability in the environment (Hakan, 2006). In recent years, it has been investigated that heavy metals from point and non – point sources impair water system including drinking wells, causing lesions (Henry *et al.*, 2004). Environmental contamination and exposure to heavy metals such as mercury, cadmium and lead is a serious growing problem throughout the world. Human exposure to heavy metals has risen dramatically in the last 50 years as a result of an exponential increase in the use of heavy metals in industrial processes and products (Atiemo *et al.*, 2012). According to Rattan *et al.* (2005), accumulation of heavy metals in the soil has potential to restrict the soil's function, causing toxicity to plants and contaminate the food chain and this makes residents directly vulnerable to soil contaminants. Other environmental impacts of heavy metals include the following: Global warming, Photochemical Oxidant Creation, Acidification, Ecotoxicity of water, Eutrophication, Abiotic resource depletion.

2.4.0. HEALTH EFFECTS OF HEAVY METALS

Exposure to heavy metals is normally chronic (exposure over a longer period of time), due to food chain transfer. Acute (immediate) poisoning from heavy metals is rare through ingestion or dermal contact, but it is possible. Exposure of residents to high concentrations of heavy metals such as lead, can lead to numerous health problem, especially in neurological, respiratory and excretory systems (Partiarca *et al.*, 2000). According to Atiemo *et al.* (2012), lead, Pb, is known to cross the brain barrier and exert toxic effect on children which could also lead to cancer later in life. Acute effects of cadmium occur by breathing high levels dust or fumes and may cause throat dryness, cough, headache, vomiting, chest pain, extreme restlessness and irritability, pneumonitis, possibly bronchopneumonia and can cause death due to severe lung damage (Gowd *et al.*, 2010).Eating food or drinking water with very high levels (metal and compounds) increases salivation, severely irritates the stomach, leading to vomiting and diarrhea. Skin contact with cadmium is not known to cause health effects in humans or animals. Long term exposure to lower levels of cadmium in air, food, or water leads to a buildup of cadmium in the kidneys and possible kidney disease. Other potential long term effects are lung damage and fragile bones, abdominal pain and choking.

Animals given cadmium in food or water show high blood pressure, iron-poor blood, liver disease, and nerve or brain damage (Bridgen *et al.*, 2008).

2.5.0. EFFECTS OF SUSPENDED DUST ON WORKERS

Some people involved in the business of stone crushing usually serve as an agent of transport of these heavy metals. According to Atiemo *et al.* (2010), the high degree of heavy metal contamination in a school around the study area used for the research was due to the quarry site workers using the place as a resting place after work and as such lead to the contamination of the school compound. Most of the effects of exposure to heavy metals in quarry sites can affect their respiratory, nervous, endocrine and immune systems and could increase the risk of cancer later in life (Huu *et al.*, 2010).

2.7.0. HEAVY METAL CONTAMINATION IN NEIGHBORHOOD OF STONE CRUSHING SITE

In Nigeria, pollution problems associated with incidents of heavy metal contamination around neighborhood of quarry site have been the subject of many reports (Onianwa *et al.*, 2001). Quarry site house all sorts of materials such as industrial and commercial scrap, scrap metals, junk cars. Many of these materials do not degrade and only benefit the environment if they are recycled properly. Quarry site are full of contaminants that are toxic and have negative environmental effects. They can also leach into surface or ground water sources or into the air during incineration.

In 1990, Canada banned lead and added Methylcyclopentadienyl Manganese Tricarbonyl (MMT) to gasoline. MMT is an organic derivative of manganese, which is added to gasoline as an antiknock agent and to improve octane rating. Adverse effects of elevated concentrations of heavy metals to soil functions, soil microbial community composition and microbial growth have long been recognized under both field and laboratory conditions. (D'Ascol *et al.*, 2005). Many metals are biologically essential, but all have the potential to be toxic to biota above certain threshold concentrations (David and Johanna, 2000). Crops raised on metal contaminated soils accumulate metals in quantities excessive enough to cause clinical problems both to animals and human beings consuming those metal rich plants (Rattan *et al.*, 2005). Thus, accumulation of heavy metals in the soil has potential to restrict the soil's function, causing toxicity to plants and contaminate the food chain. Possibility may arise to dig a well in neighborhood of quarry sites. Soil, being a complex porous material, retains and transports hazardous pollutants to ground water (Liu *et al.*, 2006).

Heavy metal contamination of urban top soil usually derives from anthropogenic sources such as emissions from automobile exhaust, waste incinerations, land disposal of wastes, uses of agriculture inputs, emissions from industrial processes and wet and/or dry atmospheric deposits (Onianwa *et al.*, 2001; Zhenli *et al.*, 2005).

CHAPTER THREE

3.0.0. MATERIALS AND METHODS

3.1.0 METHODOLOGY

3.1.1 STUDYAREA

This study was conducted in parts of Ondo and Ekiti states. The selected sites for the study are; Itaogbolu in Akure North and Olaebimi quarry site in Oye – Ekiti. The sites are located on 7 19 00N and 7 14 00E respectively. They all fall within the basement complex of geological settling characterized mainly by metamorphic rocks with a few intrusions of granites and porphyrites. The quarry sites are surrounded with rural settlement, but there is evidence of urbanization as few modern residential buildings are springing up here and there within the vicinity of the quarry. Blasting operations are carried out once or twice a week depending on demand. The quarry sites are characterized with blasting and crushing equipment, weighs bridge/loading station, limestone deposit, and heap of quarried limestone chippings. The local rock unit in the area is porphyritic Granite, characterized by large crystal of rock forming minerals, such as quartz, feldspar and biotite. (Adeyemo *et al*, 2012).

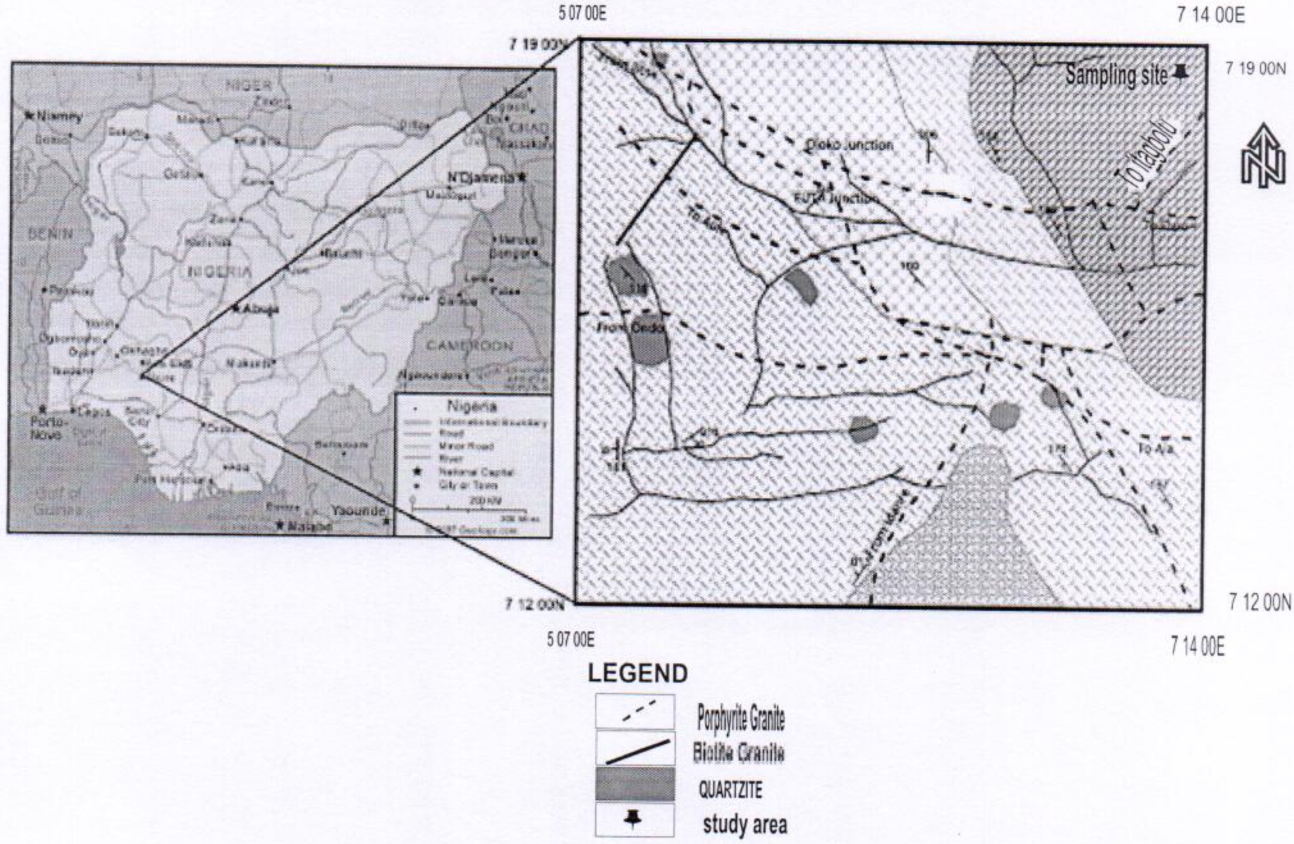

Fig. 1: Simplified geological map of Akure, showing the study area (Modified after Owoyemi, 1996), Left: Administrative map of Nigeria.

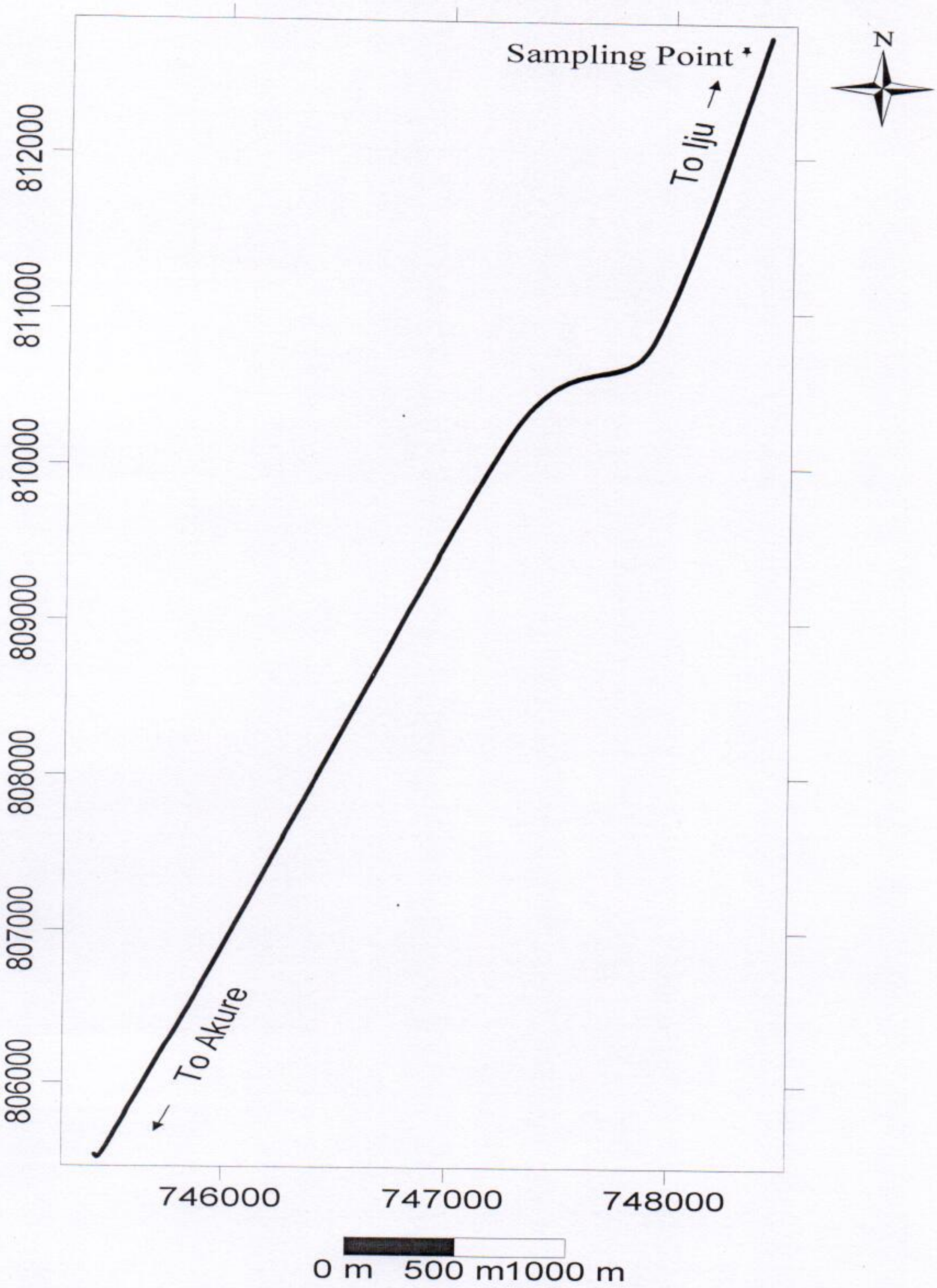

Fig. 2: Location map of the study area, showing the sampling point.

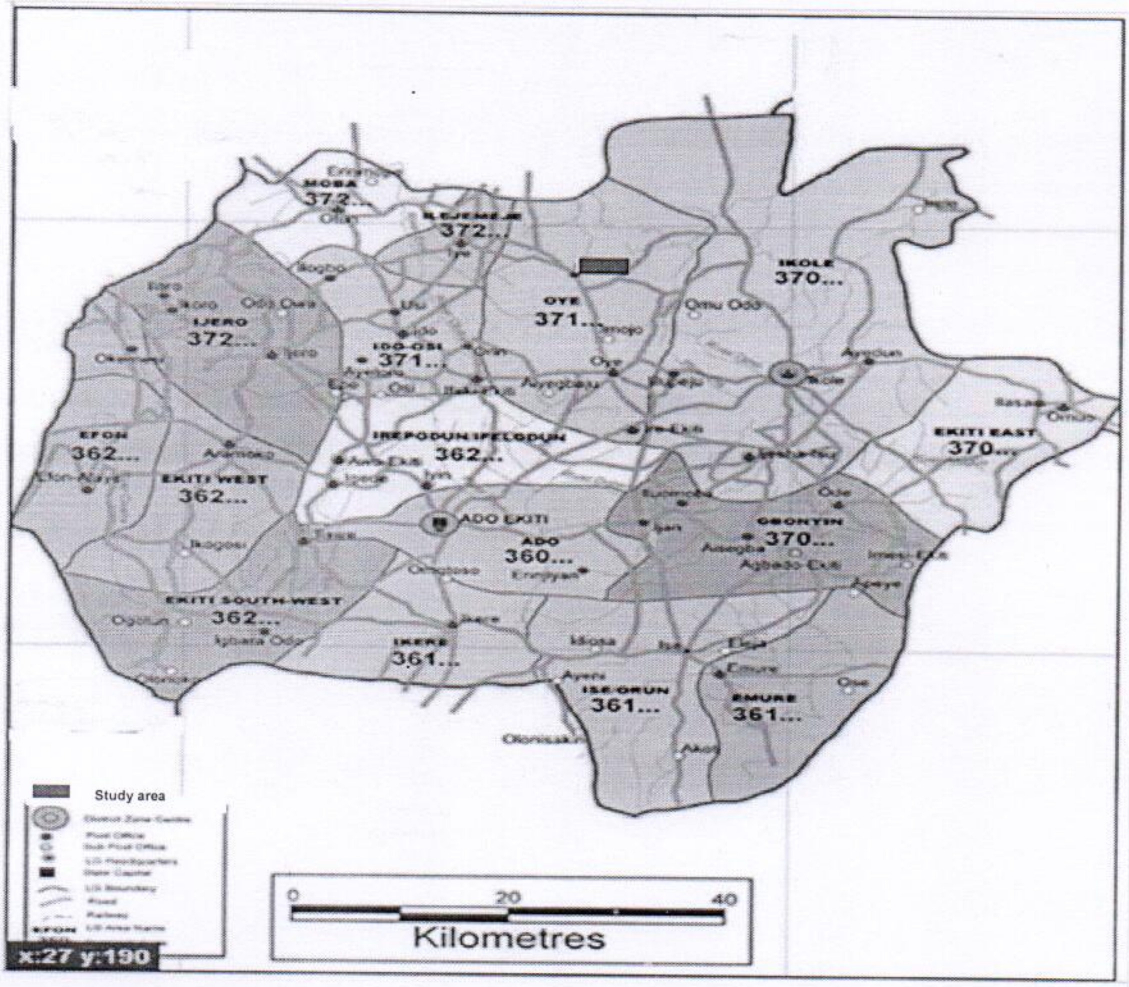

Fig. 3: Simplified geological map of Ekiti, showing the study area

3.1.2 Sampling design, collection, and preparation

A total of 30 suspended dust samples were collected systematically between 2 and 3 km from the crushing/blasting sites. Four suspended dust samples were obtained within the crushing/blasting arena and represented as samples at zero meters. Subsequent four suspended dust samples were collected within radii of 100, 200, 300, 400 and 500 m away from the crushing and blasting zone. All these samples added up to the 30 samples mentioned earlier. Samples at each point were collected randomly and combined to form composite samples. A plastic hand trowel was used to scoop the samples and they were stored in polythene bags and transported to the laboratory immediately for pretreatment and analyses. Sampling implements and other work surfaces were always thoroughly cleaned between samples during sample preparation and analyses. All samples were safely transported to the laboratory and spread on a pre- cleaned surface.

3.1.3 SAMPLING PROCEDURE

The samples after storage were digested for the extraction of heavy metals (Mn, Ni, Cd, Cr, Zn, Cu, and Pb) in the laboratory.

3.1.4 DIGESTION PROCEDURE

MATERIALS USED

Heating source (e.g. block digester, hotplate, water bath) capable of maintaining a sample extract temperature of 95 ± 5°C, Fume cupboard, Gloves and nose mask, Conical flask, Measuring cylinder, Standard flask, Beakers, Electronic weighing balance, Filter paper

REAGENTS USED

1. Acetic acid
2. Distilled water

3. Hydrofluoric
4. Nitric acid
5. Hydrogen peroxide
6. Ammonium acetate

FRACTIONATION PROCEDURE

To determine the fractionation pattern and heavy metals in the suspended dust, the four step sequential extraction protocol was used (Golal et al, 2011).

- Step 1 (exchangeable and acid soluble fraction):

40ml of 0.11M acetic acid was added to 1g of the suspended dust sample in a 50ml polyethylene centrifuge tube. The tube was shaken for 16h at room temperature at a speed of 23± rpm, using an end-over-end shaker. The extract was separated from the solid residue by centrifugation (3000 rpm for 20min) with a centrifuge, and decanted into a polyethylene bottle stored at 4^0c. The residue was washed by shaking with 20ml distilled water for 15min, centrifuging and supernatant discarded.

- Step 2: (reducible fraction), 40ml of 0.5M hydrofluoric and nitric acid was added to the residue from step 1, and the extraction performed as in step 1 .
- Step 3: (oxidisable fraction), 10ml of 8.8M hydrogen peroxide was added in aliquots to the residue from step 2. The vessel was covered loosely and digested at room temperature for 1h with occasional agitation. It was then placed on a Clifton water bath and digested at 85^0c. Another 10ml of the hydrogen peroxide was again added, and was further heat to near dryness. Thereafter 50ml of 1.0M ammonium acetate was added, and the extraction performed as in previous steps.

- Step 4: (residual step), the residue from step 3 was transferred into a suitable vessel and was digested in aqua-regia.
- Finally the filtrates were taken out for analysis. The various heavy metals in the filtrates were analyzed using AAS (Buck Scientific model 200A/210).
- The quality control of the methods was determined by the analysis of some samples spiked with known standard and subjected to some process as the samples so as to determine the accuracy and precision of the method used.
- Sequential extraction is a powerful method for determining different binding forms and mobility of metals in soil matrix.

3.3.0 STATISTICAL ANALYSIS

Descriptive statistics (mean, minimum, maximum and standard deviations) were analyzed using Statistical Package for Social Sciences (SPSS 17.0). However, the advance statistical methods employed in this project research include matrix correlation analysis. The correlation analysis was conducted by a Pearson correlation, and the tables represented with the aid of a bar chart.

CHAPTER FOUR

4.0.0 RESULTS AND DISCUSSION

Heavy metals contamination exists in the environment through many anthropogenic processes such as metal plating facilities, mining operations, tanneries, as well as in other non-point sources. Ten trace metals (As, Cr, Cu, Fe, Mn, Pb, Co, Cd, Ni and Zn) were detected in dusts samples collected in the studied center. For site 1, Cd was found to be mostly present in the exchangeable and water soluble fraction (63% and 76% respectively) and significantly present in the reducible fraction (25% and 19% respectively). The acid soluble and reducible fraction together represent 88% and 95% respectively showing that Cd in these samples is potentially bioavailable and if the condition of the dust become more anoxic, the metal could be released into water.

To confirm the total concentration of a metal does not suffice in predicting bioavailability and environmental risk, we hypothesized that metals availability in dust particles followed a decreasing order from the first step toward the last step in a sequential extraction.

We attempted the fractionation and validation of the sequential extraction steps. The results of the certified and found values of the analytical method in the various steps are presented in Table 1.

Table 1: The results of analysis of Certified and found results for BCR 701 ((μgg-1)

Sites	AKURE	OYE-EKITI
Cd	0.057 ± 0.0003	0.041 ± 0.0002
Co	0.033 ± 0.0003	0.068 ± 0.0004
Fe	0.104 ± 0.0008	0.087 ± 0.0003
Mn	0.091 ± 0.0006	0.042 ± 0.0008
Pb	0.091 ± 0.0006	0.065 ± 0.0004
Zn	0.102 ± 0.0017	0.081 ± 0.0018
Ni	0.069 ± 0.0008	0.048 ± 0.0008
Cr	0.088 ± 0.0014	0.050 ± 0.0023
Cu	0.081 ± 0.0008	0.109 ± 0.0003
As	0.036 ± 0.0004	0.021 ± 0.0005

We measured the variation of total metals and the results were presented in Table 2.

It is interesting to note that ANOVA test of the results show that there exist significantly ($p<0.05$) spatial variation of metal levels in dusts among the sites. It can be observed that the concentration ranges of the metals ranked in the order Zn (11.82-70.49) > Cr (9.02-18.58) > Pb (9.02-11.12) > Cd (9.01-18.58) > Mn (9.00-5.81) > Cu (8.54-10.54) > Ni (0.87-5.55).

The high concentrations of Zn and Cr are an indication that the particulates originated from weathering of local geological materials due to erosion and construction works. Zn and Cr are commonest elements in earth crust and exist in ores such as chromites ($FeCr_2O_4$) and cryolite ($FeCrO_4$). Other sources of Zn and Pb include vehicular emissions; escape from gasoline dispensing, tire and brake wear, electronic waste.

Table 2: Descriptive statistics of total metal content (μgg-1) ± standard deviation of dust sampled

Sites	AKURE	OYE-EKITI
Zn	70.49± 16.27	11.82± 0.88
Cu	10.54 ± 1.05	8.54± 1.05
Pb	11.12 ± 3.17	9.02± 3.17
Cr	18.57± 2.75	9.02± 1.54
Ni	5.55± 9.12	0.87± 9.12
Mn	5.81± 0.10	9.00± 0.03
Cd	10.63± 1.03	9.01± 0.09
Fe	9.53± 1.12	6.06± 1.8
Cd	86.20 ±5.34	82± 2.88
As	1.72± 3.17	2.79± 1.05

The results also showed good agreement between the found and certified values in most steps. The percentage recovery levels were within 100±5% in all steps.

Figure 4 presents the concentrations of metals in different geochemical fractions of the particulates sampled. The results indicated that chemical association of metals varied significantly ($p>0.05$) among the sites and the association showed no clear order in the entire sampling site.

Pb, Cu and Cr were not detected in exchangeable fraction in most sites while low levels of metals (Ni, Zn, Mn and Cd) were observed in this fraction. The maximum of Ni and Cd were observed at sites Akure and Oye-Ekiti respectively.

The reducible fraction has the highest percentage of metals like Pb (40-60%), Mn (32.3-58%) at Akure and Oye-Ekiti respectively. According to Wu et al. (2004), metals fractionate in this fraction are mainly fixed in primary and secondary minerals and are chemically stable and biologically inactive.

Meanwhile, associations of Mn with reducible fraction have been reported earlier (Rico et al, 2009). In organic bound fraction, Cu predominated ranging from 54% to 74.8% in both sits. Metals associated with organic bound are not considered mobile or available and they are associated with high molecular weight stable humid substance.

The predominance of Cu in dust samples in organic fraction in this study indicates high organic or sulphide from wastes in the studied areas.

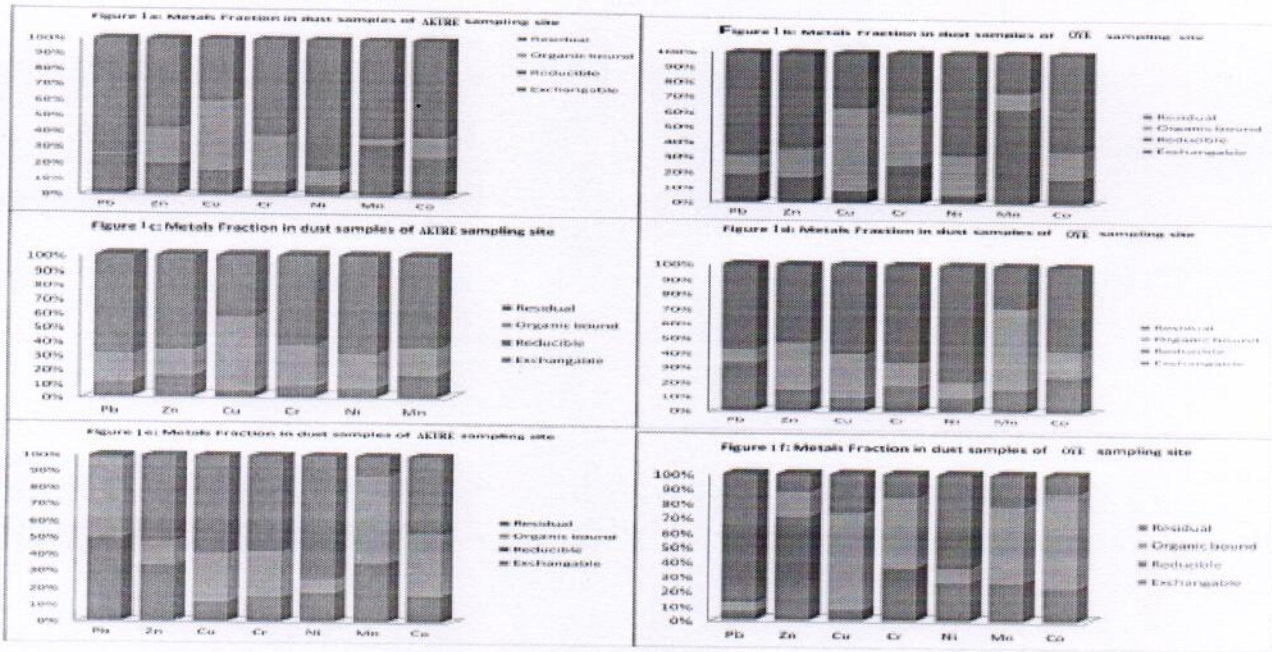

Figure 4: Metal distribution in dfferent fractions in dust samples at the sampling sites
The residual fraction has Ni, Cr and Zn in high percentage.

The significant of high amounts of

Zn in this fraction agrees with earlier observation of Okunola *et al,* (2015) that the metal is considered to be occluded inside crystalline structure and not readily available for absorption.

This observation is also consistent with earlier reports in urban street dust in Nigeria (Okunola *et al*, 2015; Gilbert and Osibanjo, 2009). The above observations clearly indicated that the bulk of the metals in the dust samples in this study were in non-mobile (non-exchangeable) fraction.

Generally, the range of 18.28 – 27.53 % total metals are bound to exchangeable, 32.58 – 47.39% for those bound to reducible fraction, and 6.43 – 16.2% for those bound to organic fraction, and 4.73 – 9.88% for those bound to residual fraction.

The final step of this report was to calculate the mobility factor for abundance metals at the various sampling sites as presented in Figure 5.

It could be observed that Pb, Zn and Mn had the high MF values in dust sampled in all sites. The high MF values of these metals are an indication of its high biological availability of the metal in dust.

Table 3: Heavy metals mobility factor (%) in the quarry dust

Sample	Pb	Zn	Cu	Cr	Ni	Mn	Co
AKURE	5.8	25.5	25.0	13.5	5.6	25.0	10.0
OYE-EKITI	5.5	17.5	16.0	13.2	5.6	17.4	9.2

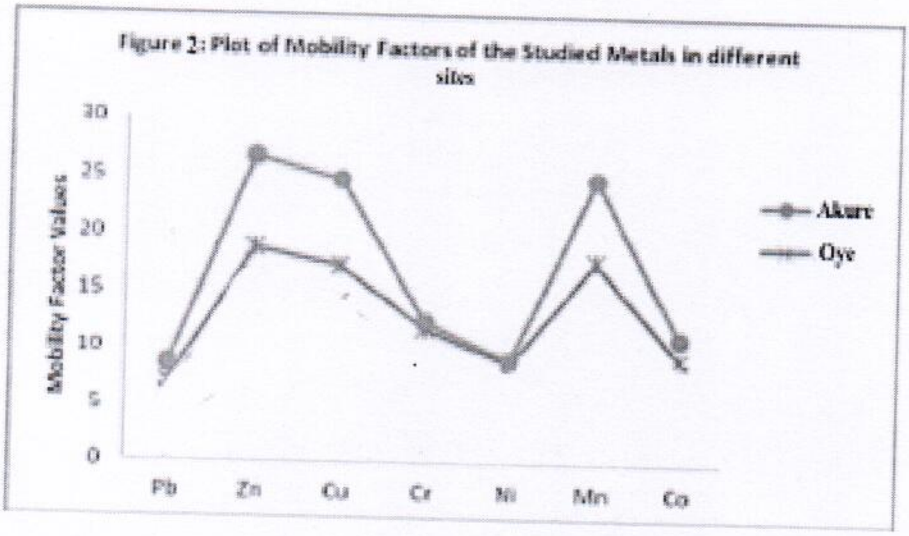

Figure 5: Plot of Mobility Factor of the studied metals at different sites.

The environmental risk factor was also calculated for abundance metals at the various sampling sites. The higest ERF values was obtained for Pb metal at the sampling sites and closely followed by Mn and Cu. The ERF values for these metals had positive values (greater than 0) in both sites. The major sources of these metals are from crushing of quarry rock. This is an indication that the presence of this metal in dust samples poses a great threat to health.

Lead toxicity causes reduction in haemoglobin, disturbance in the functioning of kidney, joint and reproductive system (Duruibe *et al,* 2007). Hence it suggest that monitoring of crushing of quarry rock dust in quarry centres around cities be looked into.

Table 4: Speciation of heavy metals in the quarry dust samples

Fractions	Concentration of heavy metals (mg kg^{-1})						
	Pb	Zn	Cu	Cr	Ni	Mn	Co
Water soluble	8.55	0.95	5.25	9.25	10.3	6.75	0.50
Exchangeable	52.5	24	8.62	38.5	28.5	38	2.92
Organically bound	196	175	560	260	280	113	22.0
Carbonate	533	282	330	161	268	296	133
Residual	4558	1810	1638	1828	2478	1126	620

The various metals content in the filtrates were analyzed by Bulk Scientific (model 200A) Atomic Absorption Spectrophotometer (AAS) using air-acetylene flame at optimum wavelenght of each metal. Standards used to caliberate the AAS were obtained as commercial BDH stock metal solutions from which working standard were prepared by appropriate dilution. The quality control of the methods includes the analysis of some samples spiked with known standard and subjected to some process so as to determine the accuracy and precision of the method used. The percentage recoveries were calculated after analysis of the BCR701, refernce material given as; % recovery = $C_{sp} - C/ C_a$ ……………..(1)

where C_{sp} is the spike sample concentration, C is sample concentration, and C_a is the added concentration.

The mobility factor (MF) and environmental risk factor (ERF) were calculated using equation 2 and 3 respectively.

$$MF = \frac{\text{Exchangeable} \times 100}{\text{Exchangeable + reducible + organic + residual}} \quad \text{……………… (2)}$$

Environmental risk factor (ERF) was determined as follow:

$$ERF = CSQV - C_i / CSQV \quad \text{…………………………………… (3)}$$

Where CSQV= metals concentration in residual fraction, C_i = metal concentration in the first three fraction.

Table 5: Comparisons of heavy metal content (μgg^{-1}) in this particulate dust in this study with other cities of the world.

Cities	Cd	Cr	Cu	Ni	Pb	Zn	Reference
Birmingham, UK	1.62	-	466.9	41	48	534	Charlesworth et al, (2003)
Hong Kong, China	21.8	-	24.8	-	93.4	1.68	Li et al, (2001)
Beijing, China	0.73	80.8	107.7	36.1	71.7	238.6	Han et al (2007)
Egypt, Egypt,	2.98	58.7	102	38.5	307	1839	Shinggu et al, (2007)
Oye-Ekiti, Nigeria	0.67	10.5	25.06	12.2	207	121	This Study
Akure	2.46	4.83	12.63	6.24	112.45	6.08	This Study

Comparing the levels of metals in this study with those of other cities of the word (Table 5), it can be found that the levels for the metals in dust of our studied centers are lower than other cities, even lower than cities like Hong Kong (Olumayede *et al*, 2013).

CHAPTER FIVE

5.0.0. CONCLUSION

The speciation pattern and toxicity of metals in airborne dust particulate samples in Akure and Oye-Ekiti were conducted. The presence of these metals in dust particles poses a significant environmental risk to both the workers in the quarry sites and the people around area.

The particulate dust samples collected from these cities show significant contamination by Pb, Cu, Cd and Zn. However, the contamination is relatively similar or lower than that of other cities in Jordan or worldwide. The kidney and the liver are the major target organs of Cd accumulation and exposure to Cd leads to renal tubular dysfunction, poor bone mineralization and testicular necrosis.

The sequential extraction method is used to assess the potential mobility and bioavailability of the metals in the particulate dusts. The mobility of these metals is related to their solubility and geochemical forms and it decreases in the order of extraction sequence.

Experimental results showed that

i. The sequential extraction revealed that bulk of the metals in the dust samples collected in this study exist in non-mobile fraction.

ii. The pollution indices employed revealed that Zn was the most abundant metal but Pb poses the greatest potential threat to the populae among the metals in the entire studied Centre, therefore there is the need to monitor quarry sites activities in Akure and Oye-Ekiti metropolis.

iii. This study indicated that air particle pollution due to metal such as Cd and Pb may Possess serious health risks to the residents in this rapidly developing cities.

However, the situation in future may become dangerous if the precautionary environmental requirements are not attended to.

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