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RADIOACTIVITY LEVEL AND HEAVY METAL SPECIATION OF OIL-IMPACTED SOILS AROUND MECHANIC WORKSHOPS IN AKURE, NIGERIA

BY

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CERTIFICATION

This is to certify that this research study was carried out by ORE Odunayo Timothy as part of the requirements for the award of Master of Science (M.Sc.) Degree in Chemistry under our supervision in the Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria. To the best of our knowledge, similar work has not been submitted elsewhere for an award of a degree.

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Dr. F.M. Adebiyi Date

Supervisor

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Prof. E. A. Oluyemi Date

Head of Department

DEDICATION

This research work is dedicated to the Father of lights, in whom is no darkness neither shadow of turning who blessed me with every good and perfect gifts from above.

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ABSTRACT

This study determined the elemental composition and heavy metal speciation of the soils around mechanic workshops in Akure, Nigeria, identified the naturally occurring radionuclides in the soils, evaluated the levels of radiological hazard indices from the radionuclide activity concentration and assessed the pollution status of the study area. These were with a view to evaluating the pollution status of the mechanic workshops with respect to heavy metals and radionuclide levels.

A total of fifteen (15) soil samples comprising of ten (10) oil-impacted soil samples collected from the mechanic workshops and five (5) control soil samples collected from areas with little or no anthropogenic inputs within Akure, Ondo State, Nigeria. The concentrations of metals in the soil samples were determined using Atomic Absorption Spectrometry while the activity levels of the radionuclides were determined using Gamma ray spectrometry.

The results showed that the total mean concentrations of Pb, Cu, Zn, Cd, Cr, Mn, As and Fe in the oil-impacted soils were 3.93 ± 0.09, 85.20 ± 0.95, 13.93 ± 0.09, 6.15 ± 0.07, 6.91 ± 0.08, 14.80 ± 0.10, 1.73 ± 0.03 and 162.90 ± 1.35 µg/g respectively. The heavy metals in the oil-impacted soils were considerably higher than those of the control soils. The data collected was subjected to descriptive statistical analysis to determine the geo-accumulation index (I_{geo}), pollution index (PI) and enrichment factor (EF) indicated that the mechanic workshops have uncontaminated to moderate contamination for Cu (0.51), Zn (0.49), Cd (0.86), Mn (0.67) and Fe (0.63), while there was moderate contamination for Pb (1.25), Cr (1.58) and As (1.45). The PI results suggested that the mechanic workshops are contaminated with all the heavy metals as the PIs are greater than 1. The EF results indicated minor enrichment for Pb (1.53), Cd (1.17), Cr (1.92), Mn (1.02) and As (1.76), while it indicated no enrichment for Cu (0.92) and Zn (0.90).

The results of the extraction showed relatively low bioavailability and mobility potential with more proportion retained in the residual fraction for all the metals. The mean activity concentrations of the radionuclides ^{232}Th, ^{238}U and ^{40}K in the oil-impacted soils were 0.89 ± 0.08, 132.13 ± 0.16 and 51.52 ± 0.06 Bq/Kg respectively. The radiological assessments in terms of the mean values of absorbed dose rate were (63.93 nGy/hr), annual equivalent dose rate (0.55 mSv/yr), internal hazard index (0.72 Bq/Kg), external hazard index (0.37 Bq/Kg), annual gonadal dose equivalent (428.22 μsvy^{-1}), representative gamma index (0.92) and radium equivalent (137.38 Bq/Kg).

The study concluded that the mechanic workshops studied were impacted with the analyzed heavy metals whose concentrations exceeded those of the control samples and standard permissible limits. The radiological assessment also indicated that long-term exposure of the radionuclides might pose intrinsic hazards to human health.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

In Nigeria and most developing nations, increased automobile repairs/workshops activities are due to ever-increasing demand for personal vehicles, most of which are used (Tokunbo) vehicles (Ololade, 2014). A common practice in Nigerian cities and towns is to allocate large tracts of land, sometimes reaching 5 ha or more, to groups of small scale auto-mechanic businesses and designate these as villages where they locate their workshops and repair yards to offer their services to the public. It is presumed that there are environmental threats associated with this practice (Adelekanand Abegunde, 2011).

It is a known fact that automobiles introduce a number of toxic metals into the environment (Lonati*et al.*, 2006). Auto tire wear, degradation of parts and greases, peeling paint and metals in auto-catalysts are sources of heavy metal pollution (Pecheyran*et al.*, 2000). Increased imports of reconditioned automobiles have led to increased wear and tear, mushrooming of open-air garageand elevatedconcentration levels of heavy metals in the soils (Onianwa*et al.*, 2001).

Heavy metal pollution refers to cases where the quantities of these elements in soils are higher than themaximum allowable concentrations, and this is potentially harmful to biological life at such locations. Metals are persistent pollutants that can be biomagnified in the food chains, becoming increasingly dangerous to human beings and wildlife. Therefore, assessing the concentrations of pollutants in different components of the ecosystem has become an important task in preventing risk to natural life and public health. Heavy metals enter into the environment mainly via three routes namely: (i) deposition of atmospheric particulate, (ii) disposal of metal

enriched sewage sludges and sewage effluents and (iii) by-products from metal mining process. Soil is one of the repositories for anthropogenic wastes.(Adelekan*et al.*,2014).Biochemical processes can mobilize them to pollute water supplies and impact food chains. Heavy metals such as Cu, Cr, Cd, Ni, and Pb are potential soil and water pollutants(Adelekan and Abegunde, 2011). Globally, the problem of environmental pollution due to heavy metals has begun to cause concern in most large cities since this may lead to geoaccumulation, bioaccumulation and biomagnifications in ecosystems (Adelekan and Abegunde, 2011).

Heavy metal contaminants in the environment are eventually deposited in soils in some form of a low solubility compound, such as pyrite or sorbed on surface-reactive phases, such as Fe and Mn oxides (Cooper *et al*., 2005; Hamilton- Taylor *et al*., 2005). Lead (Pb) is the most common environmental contaminant found in soils. Unlike other metals, lead has no biological role, and is potentially toxic to microorganisms (Sobolev and Begonia, 2008). Soils are the major sinks for heavy metals released into the environment by anthropogenic activities and unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation (Kirpichtchikova*et al*., 2006) and the total concentration of heavy metals in soil persist for a long time after their introduction (Adriano, 2003). Changes in their chemical forms (speciation) and bioavailability are, however, possible.

Mankind has always been exposed to radiation from naturally occurring radionuclides. The naturally occurring radionuclides include the primordial radionuclides such as uranium ^{238}U, thorium ^{232}Th and potassium (^{40}K) and nuclides of ^{14}C, ^{87}Rb(Carlson *et al*., 2003). The substances in which these naturally occurring radionuclides show up are described by the acronym Naturally Occurring Radioactive Materials (NORM) and these are known to have a wide occurrence. NORM is an inherent of many geologic materials and is consequently encountered during geologically related activities. Radiation can cause sterility, making

reproduction impossible. It can also cause mutations in developing embryos, which are usually detrimental or even fatal(World Nuclear Association (WNA), 2003).

Heavy metals and radionuclides are of considerable environmental concern due to their toxicity and cumulative behavior. Incidence of metallic poisoning arising from contamination of water, soil, food and feeding stuffs are well documented (Ezeonu, 2004). Toxicity from oil pollution can lead to respiratory illness, kidney disease, neurological diseases etc. in humans (Ndubuisi and Asia, 2007). Today, the monitoring of heavy metals and radionuclides in the environment is fast becoming an essential aspect of pollution study. There is a growing need to promote sustainable living, where it is acknowledged that any form of environmental risk could be detrimental to the ideology of sustainability. There is general support, therefore, to expose all possible threats to environmental safety especially from energy sources such as fossil fuels and biofuels. It is well known that the chemical species of interest are toxic at elevated levels prompting an increasing demand for accurate information linked to potential environmental hazards of this nature (Pillay*et al*., 2014).

Unchecked industrial and human activities have contributed significantly to elevated levels of heavy metals in surface and subsurface soils when compared to those contributed from geogenic or natural processes (Dasaram*et al*., 2010). Their pollution of the environment even at low levels and the resulting long-term cumulative health effects are among the leading health concerns all over the world. The concern is heightened by their persistence in the soil and their tendency to bioaccumulate, move along the food chain and also poison soil microorganisms (Udousoro*et al*., 2010).

One of the major sources of the increase in heavy metal concentration of the ecosystem is auto mechanic activities (Adewole and Uchegbu, 2010). These auto mechanic workshops are found in clusters of open plots of land in the vicinity of urban towns and cities (Nwachukwu*et al*., 2010; Nwachukwu*et al*., 2011). Within the clusters are people w