Determination Of Heavy Metals In Soils In Nigerian Agip Oil Company Obiafor/Obrikom Environs

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***Abstract*—The project work considered the Determination of Heavy Metals in Soil in Nigerian Agip Oil Company Obiafor/Obrikom Environs. It aimed at investigating the presence of heavy metal contamination in Obrikom community soil following oil and gas exploration activities by Nigerian Agip Oil Company. Soil samples were randomly collected from 7 selected locations. Three samples were taken from each location at depths of 0-15cm, 15-30cm and 30-45cm with the aid of the Auger, and a GPS for geographic location. The concentrations of 4 selected test parameters of Pb, Cr, Cu, and Fe were determined by Aqua regia digestion and AAS method. The mean values and standard deviations of the various test parameters per location were obtained as follows; Soil samples from pipeline (Cu=21.21±0.26, Pb=26.99±0.42, Cr=15.03±0.22, Fe=20623.67±6.60), Soil samples from Ag ip roadside (Cu=24.02±0.07, Pb=99.37±0.81, Cr=17.38±1.18, Fe=67510.67±15.54), Soil samples from welding workshop-(Cu=24.08±0.35, Pb=45.20±0.27, Cr=21.12±0.12, Fe=56269±13.49), Soil samples from dumpsite (Cu=72.82±0.76, Pb=90.28±0.28, Cr=21.47±0.47, Fe=31129.67±4.10), Soil sample from Onosi Ogu (Cu=16.90±0.81, Pb=38.99±0.05, Cr=12.01±0.01, Fe=30376.67±1.24), Soil s ample from Farmland(Cu=24.19±0.1;Pb=60.21±0.14; Cr=15.07±0.06; Fe=44628.67±2.87), Soil sample from household garden-(Cu=9.05±0.16, Pb=24.02±0.03; Cr=18.14±0.05, and Fe=46874.67±6.13). The results were compared with DPR standards, with all values below the target and intervention limits, except for values of copper at the dumpsite and lead at both the dumpsite and Agip-roadside respectively which were above just the DPR's target value of 36mg/kg for copper and 80mg/kg for lead. These values did not indicate serious contamination treats since they were still below the DPR's Intervention values of 160mg/kg for copper and 530mg/kg for lead. Analysis of variance (ANOVA) showed that there was no significant difference in concentrations of Cu, Pb, Cr and Fe across the various sample location at 5% level of significance. Inferentially, the soil in NAOC OB/OB environs was comparatively said to be within acceptable limits with little variation in just the target values of lead and copper at Agip-roadside and the dumpsite and therefore required only mitigation measures preferably phytoremediation {crops like alpine pennycress (*Thlaspi caerulescens*), *for Cu and* corn (*Zea mays* L.), for Lead} in other to alleviate the present contamination level of those sites.**

INTRODUCTION

Soil as a basic human environment, upon which they live, and from which they make their livelihood, has over time been exposed to various forms of contaminations arising more from anthropogenic factors than it is from natural factors. Anthropogenic activities arising from urbanization (combustion from transportation, municipal wastes, sewage sludge, medical/pharmaceutical wastes etc.) Agricultural practices (including application of fertilizers, pesticides and herbicides), industrialization (Mining, manufacturing and construction), the use of synthetic products (including plastics, polythene, batteries, paints, tins/cans, and other range of chemical products), crude/petrochemical spillage, metal scraps, leaded gasoline are common sources that could contaminate or further increase the heavy metal load of the soil. Heavy metals also occur naturally, but rarely at toxic levels.

Soils are the major sinks for heavy metals released into the environment by aforementioned 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 their total concentration in soils persists for a long time after their introduction.

Due to the disturbance and acceleration of nature's slowly occurring geochemical cycle of metals by man, most soils of rural and urban environments may accumulate one or more of the heavy metals above defined background values high enough to cause risks to human health, plants, animals, ecosystems, or other media (*D'Amore, et al 2005).* Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil- plant-animal-human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems *(McLaughlin et al, 2000 & Ling et al 2007).*

Chemicals like heavy metals once introduced to the environment by one particular method may spread to various environmental components, which may be caused by the nature of interactions occurring in this natural system. Heavy metals may chemically or physically interact with the natural compounds, which change their forms of existence in the environment. In general they may react with particular species, change oxidation states and precipitate (*Dube et al, 2000*).

Excess heavy metal accumulation in soils is toxic to humans and other animals. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long- term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer.

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 is possible. Chronic problems associated with long-term heavy metal exposures are: Lead – mental lapse, Cadmium – affects kidney, liver, and GI tract. Arsenic – skin poisoning, affects kidneys and central nervous system.

The most common problem causing *cationic* metals (metallic elements whose forms in soil are positively charged cations e.g., Pb^{2+}) are mercury, cadmium, lead, nickel, copper, zinc, chromium, and manganese. The most common anionic compounds (elements whose forms in soil are combined with oxygen and are negatively charged e.g., $MoO4^{2-}$) are arsenic, molybdenum, selenium, and boron *(USDA, 2000).*

Excess concentrations of some heavy metals in soils such as Cd^{2+}, Cr^{6+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} have caused the disruption of natural aquatic and terrestrial ecosystems *(Gardea-Torresdey et al, 1996 & Meagher, 2000)*. Although some metals are immobile and persistent, other metals are mobile, and, therefore, the potential of transfer either through the soil profile down to the groundwater aquifer or via plant-root uptake (bioavailability) is likely. Cadmium and lead, which have no known beneficial effects, may become toxic to plants and animals if their concentrations exceed certain values (*Gough et al, 1979*).

The adequate protection and restoration of soil ecosystems contaminated by heavy metals require their characterization and remediation. Contemporary legislation respecting environmental protection and public health, at both national and international levels, are based on data that characterize chemical properties of environmental phenomena, especially those that reside in our food chain *(Kabata-Pendias and Pendias, 2001).*

AIM

This research work aimed at investigating the presence of heavy metal contamination in Obrikom community soil following oil and gas exploration activities by Nigerian Agip Oil Company.

OBJECTIVE

To Determine the concentration of lead, chromium, iron, and copper in the soil of Obrikom community, in ONELGA Rivers State within NAOC's operational environment and

To evaluate the extent of soil contamination by these heavy metals, comparing their levels with prescribed benchmark values (acceptable limits) for soil heavy metals.

To determine if there was any significant difference in concentrations of heavy metals across various locations by means of statistical analysis.

There are 35 metals that concern us because of occupational or residential exposure; 23 of these are the heavy elements or "heavy metals": antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc *(Glanze, 1996).* "Heavy metals" are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 4°C (39°F). Simply stated, specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well-known toxic metallic elements with a specific gravity that is 5 or more times that of water are arsenic, 5.7; cadmium, 8.65; iron, 7.9; lead, 11.34; and mercury, 13.546 *(Lide, 1992).* heavy metals is a collective term for metals of high atomic mass, particularly those transition metals that are toxic and cannot be processed by living organisms, such as lead, mercury, and cadmium (Silveira et al, 2003). Tobias et al (2012) carried out analysis on soil in a densely populated and heavily industrialized city of Aba, in Nigeria to ascertain the environmental metals pollutants load. In his work randomly collected samples from different parts of Aba metropolis and a sub- urban community considered less polluted (to serve as control) were analyzed for heavy and non-heavy metals with results indicating that the mean concentrations for most of the metals analyzed were high with respect to FEPA and WHO standards.

Opaluwa, et al (2012), also carried out heavy metal investigation on concentrations in soils, plant leaves and crops grown around dump sites in Lafia metropolis, Nasarawa State Nigeria. In their work heavy metal levels of selected heavy metals including As, Cd, Co, Cu, Fe, Ni, Pb and Zn in soils, plant leaves and crops from farmlands around dump sites were determined using digestion and Atomic Adsorption Spectrophotometric methods; the results of which were all higher than those from a control site suggesting possible mobility of metals from dumpsites to farmlands through leaching and runoff. However these values were below WHO permissible limits. A geo-environmental evaluation of heavy metals in and around hazardous waste disposal sites located in the north-western part of Hyderabad (India) was undertaken to determine the degree of contamination of soil environment. Findings from their work showed that, an average concentration of As, Cr, Pb exceeded the threshold and natural background values, while the uppermost concentrations of Cu, Ni and Zn exceeded the prescribed threshold limit *(Vandana et al, 2011).*

In central Transylvania, Romania, a research was also carried out to assess the concentration of five soil heavy metals (Pb, Co, Cr, Cu, Hg) in forty sampling sites. From their findings using Inductively Coupled Plasma Spectrometry method, some locations had concentrations exceeding acceptable limits by Romanian guideline. The concentration of lead was 1521.8ppm and copper 1197.6ppm in Zlatna, whiles that of Chromium was found in Tarnaveni to be 1080ppm *(Sorana et al 2008).*

Zeng-Yei Hseu et al (2002) carried out a study to access the total contents of Cd, Cr, Cu, Ni, Pb, and Zn in the freshwater sediments and the arable and non-arable soils of Taiwan, and to compare the different digestion methods for their determination. Several digestion methods including the *aqua regia* and different combinations of concentrated acids ($HClO_4$, HNO_3, H_2SO_4, or HF) were compared. They concluded that the Baker and Amacher method were best for Cd, Cr, Cu, Ni, and Zn; the Reisenauer method for Cr, the *aqua regia* method for Cu, Ni, and Zn; and the Burau method for Pb. Iwegbue et al (2013) examined the concentrations, contamination/pollution index, anthropogenic input and enrichment factors for metals in soil in the vicinity of cassava processing mills in sub-urban areas of Delta State of Nigeria. The concentrations of metals in all sites and depths ranged from 0.1 to 383.2 mg kg-1 for Mn, 4.0 to 11.3 mg kg-1 for Ni, 1746.4 to 2839.6 mg kg-1 for Fe, 0.01 to 3.70 mg kg-1 for Cr, 3.7 to 29.5 mg kg-1 for Cu, 21.9 to 97.3 mg kg-1 for Zn, 0.01 to 1.60 mg kg-1 for Cd and <0.01 to <0.01 mg kg-1 for Pb. The concentrations of metals at these sites were below the Department of Petroleum Resources target values for metals in soils except for Cd in some sites. A significant fraction of these metals arose from anthropogenic sources. The total content of heavy metals in a soil are the sum of the concentrations of elements derived from minerals in the geological parent material on which the soil has developed (lithogenic source) and inputs from a wide range of possible anthropogenic (contamination) sources. *(Alloway, 2013).* Heavy metals occur naturally in the soil environment from the pedogenetic processes of weathering of parent materials at levels that are regarded as *trace* (<1000mg kg^{-1}) and rarely toxic *(Kabata-Pendias and Pendias 2001; Pierzynski et al 2001).*

Limestones comprise mainly grains of calcite ($CaCo_3$) mostly derived from microscopic marine organisms. Sulphides can occur in some limestones and clay-rich calcareous marls are often found to be rich of heavy metals. *(Alloway, 2013).* All Fe oxide-rich sediments, including ‘ironstones’ which are defined as containing >30% Fe oxides, are generally found to have accumulated relatively high concentrations of As, Ba, Cu, Mo, Ni, Pb, V and Zn. *(Robinson, et al 2007).* Metallogenic ores can give rise to anomalously high concentrations of heavy metal in soils when outcrops of rocks containing these ores undergo natural (geochemical) weathering *in situ*, or the products of weathering are dispersed locally by geomorphological process and undergo subsequent weathering. However, much larger areas can be affected by anthropogenic pollution when these ores are mined and smelted *(Rashidinejad, et al 2008).* Huge amounts of fertilizers are frequently applied to soils in concentrated farming systems to deliver suitable N, K and P for crop growth. The complexes used to offer these elements comprise rare quantity of heavy metals (for example Cadmium and Lead) as contaminations, that, after continual fertilizer application may meaningfully proliferate their quantity in the soil *(Jones and Jarvis, 1981).* Mineral materials such as query waste, construction residues, demolition wastes, furnace slags, ashes and harbor dredging are often referred to as ‘technogenic’ materials. These are important sources of heavy metal contamination in urban and industrial areas. Deposits of these materials, including spillages *en route* and dusts dispersed into the atmosphere from them can greatly influence the heavy metal content of soils *(Meuser, 2010).* Several common pesticides used fairly extensively in agriculture and horticulture in the past contained substantial concentrations of metals. For instance in the recent past, about 10% of the chemicals have approved for use as insecticides and fungicides in UK were based on compounds which contain Cu, Hg,Mn, Pb, or Zn. Examples of such pesticides are copper-containing fungicidal sprays such as Bordeaux mixture (copper sulphate) and copper oxychloride *(Jones and Jarvis, 1981).* Lead arsenate was used in fruit orchards for many years to control some parasitic insects *(McLaughlin et al., 2000).* Worldwide, it is estimated that 20 million hectares of arable land are irrigated with waste water. In several Asian and African cities, studies suggest that agriculture based on wastewater irrigation accounts for 50 percent of the vegetable supply to urban areas *(Bjuhr, 2007).* The application of numerous biosolids (e.g., livestock manures, composts, and municipal sewage sludge) to land inadvertently leads to the accumulation of heavy metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn, Tl, Sb, and so forth, in the soil *(Basta, 2005).* Heavy metals most commonly found in biosolids are Pb, Ni, Cd, Cr, Cu, and Zn, and the metal concentrations are governed by the nature and the intensity of the industrial activity, as well as the type of process employed during the biosolids treatment *(Mattigod, and Page, 1983)*. Mining and milling of metal ores coupled with industries have bequeathed many countries, the legacy of wide distribution of metal contaminants in soil. During mining, tailings (heavier and larger particles settled at the bottom of the flotation cell during mining) are directly discharged into natural depressions, including onsite wetlands resulting in elevated concentrations *(DeVolder, 2003).* Other materials are generated by a variety of industries such as textile, tanning, petrochemicals from accidental oil spills or utilization of petroleum-based products, pesticides, and pharmaceutical facilities and are highly variable in composition. In addition, many are potentially hazardous because of their contents of heavy metals (Cr, Pb, and Zn) *(Sumner, 2000).*

HEAVY METALS, THEIR CHARACTERISTICS AND TOXICITY

Lead is a metal belonging to group IV and period 6 of the periodic table with atomic number 82, atomic mass 207.2, density 11.4 g cm.3, melting point 327.4.C, and boiling point 1725.C. It is a naturally occurring, bluish gray metal usually found as a mineral combined with other elements, such as sulphur (i.e., PbS, PbSO4), or oxygen ($PbCO_3$), and ranges from 10 to 30mg kg^{-1} in the earth's crust *(USDHHS, 1999).* Typical mean Pb concentration for surface soils worldwide averages 32mg kg^{-1} and ranges from 10 to 67mg kg^{-1} *(Kabata-Pendias, 2001).* Lead ranks fifth behind Fe, Cu, Al, and Zn in industrial production of metals (*Manahan, 2003*). Ionic lead, Pb(II), lead oxides and hydroxides, and lead-metal oxyanion complexes are the general forms of lead that are released into the soil, groundwater, and surface waters. Lead (II) is the most common and reactive form of Pb, forming mononuclear and polynuclear oxides and hydroxides *(GWRTAC, 1997).* Inhalation and ingestion are the two routes of exposure, and the effects from both are the same. Lead accumulates in the body organs (i.e., brain), which may lead to poisoning (plumbism) or even death. Children exposed to lead are at risk for impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration, with children under the age of six being at a more substantial risk. Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints when exposed to lead *(NSC, 2009).* Lead is not an essential element. Lead can cause serious injury to the brain, nervous system, red blood cells, and kidneys *(Baldwin, and Marshall, 1999).* In general, plants do not absorb or accumulate lead. It has been considered safe to use garden produce grown in soils with total lead levels less than 300 ppm. The risk of lead poisoning through the food chain increases as the soil lead level rises above this concentration. Most of the risk is from lead contaminated soil or dust deposits on the plants rather than from uptake of lead by the plant *(Rosen, 2002).* Copper is a transition metal which belongs to period 4 and group IB of the periodic table with atomic number 29, atomic weight 63.5, density 8.96 g cm.3, melting point 1083.C and boiling point 2595.C. The metal's average density and concentrations in crustal rocks are 8.1 ~ 103kgm^{-3} and 55mg kg^{-1}, respectively *(Davies and Jones, 1988).* Copper is the third most used metal in the world (VCI, 2011). Copper is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. In plants, Cu is especially important in seed production, disease resistance, and regulation of water. Copper is indeed essential, but in high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. In fact, unlike some man-made materials, Cu is not magnified in the body or bioaccumulated in the food chain. In the soil, Cu strongly complexes to the organic implying that only a small fraction of copper will be found in solution as ionic copper, Cu(II). The solubility of Cu is drastically increased at pH 5.5 *(Martinez and Motto, 2000),* which is rather close to the ideal farmland pH of 6.0–6.5 *(Eriksson, 1997).*

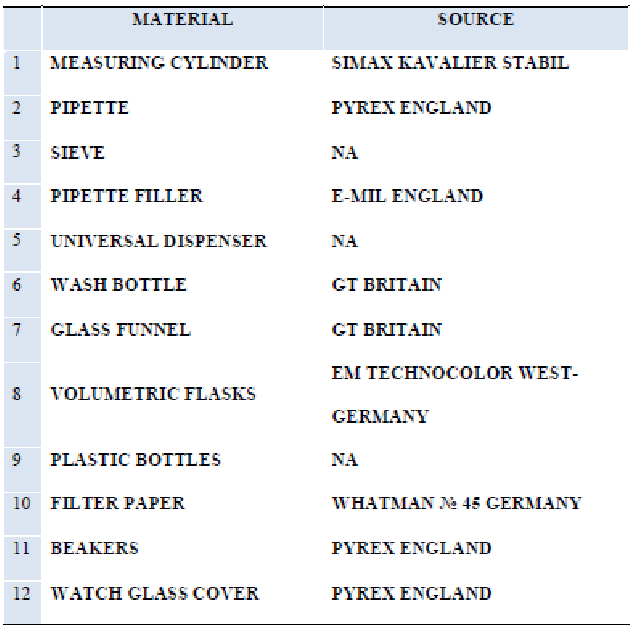
Chromium is a first-row *d*-block transition metal of group VIB in the periodic table with the following properties: atomic number 24, atomic mass 52, density 7.19 g cm−3, melting point 1875◦C, and boiling point 2665◦C. It is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Chromium is mined as a primary ore product in the form of the mineral chromite, FeCr2O4. Major sources of Cr contamination include releases from electroplating processes and the disposal of Cr containing wastes *(Smith, et al 1995).* Chromium (VI) is the form of Cr commonly found at contaminated sites. Chromium can also occur in the +III oxidation state, depending on pH and redox conditions. Chromium (VI) can be reduced to Cr (III) by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions often encountered in deeper groundwater *(Chrostowski, 1991).* Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content, and the amount of organic matter present. Soluble and un- adsorbed chromium complexes can leach from soil into groundwater. The leachability of Cr (VI) increases as soil pH increases *(Smith, et al 1995).* Chromium is associated with allergic dermatitis in humans *(Scragg, 2006).* Iron is a metal in the first transition series, of group 8 in the periodic table with the following properties: atomic number 24, atomic mass 52, solid density 7.874 g cm−3 (at 0, 101.325kPa), and liquid density of 6.98gcm^{-3}, melting point 1538◦C, and boiling point 2862◦C *(Wikipedia, 2014).* Iron is the sixth most abundant element in the Universe, and the most common refractory element *(McDonald et al 2010).* It is by mass the most common element on Earth, forming much of Earth's outer and inner core. Iron exists in a wide range of oxidation states, −2 to +6, although +2 and +3 are the most common *(Wikipedia, 2014).*

Most of the iron in soil is found in silicate minerals or iron oxides and hydroxides forms. The iron oxides and hydroxides in the soil are responsible for its reddish and yellowish colours. Iron is also indirectly responsible for much of the green colour of growing plants, because of its role in the production of chlorophyll *(Schulte, 2004).* The typical iron concentrations in soils range from 0.2% to 55% (20,000 to 550,000 mg/kg) and concentrations can vary significantly, even within localized areas, due to soil types and the presence of other sources. Iron can occur in either the divalent (ferrous or Fe+2) or trivalent (ferric or Fe+3) states under typical environmental conditions. Iron occurs predominantly as Fe+3 oxides in soils *(Bodek et al., 1988).* The divalent state (or ferrous state) can be oxidized to the trivalent state (or ferric state), where it may form oxide or hydroxide precipitates, and become unavailable to plants as a micronutrient *(Thompson and Troeh, 1973).* Roots of some plants are able to reduce iron from the ferric to the ferrous state, and allow iron uptake into the plant.

The general rule governing the mobilization and fixation of iron are that oxidizing and alkaline conditions promote the precipitation of insoluble iron Fe^{+3} oxides, whereas acidic and reducing conditions promote the solution of ferrous (Fe^{+2}) compounds. The availability of ferrous vs. ferric iron is also dependent on the soil-water status of a particular environment. For example, reduced environments (which include lowland or waterlogged soils) promote the availability of ferrous iron to plants, while oxidized environments (upland or well-aerated soils) promote the precipitation of ferric-oxide compounds, which are not available to plants for uptake. If excess ferrous iron occurs, iron toxicity may occur in plants, but this is highly dependent upon plant species. Likewise, if ferrous iron is not available in soils due to precipitation of ferric iron compounds, iron deficiency or chlorosis may occur. Proper soil management can help control the pH and soil-water status and allow optimal concentrations of bioavailable ferrous iron to plants *(USEPA, 2003).*

MATERIALS AND METHODOLOGY

TABLE 3.1: LIST OF APPARATUS USED FOR THE SEARCH



	MATERIAL	SOURCE
1	MEASURING CYLINDER	SIMAX KAVALIER STABIL
2	PIPETTE	PYREX ENGLAND
3	SIEVE	NA
4	PIPETTE FILLER	E-MIL ENGLAND
5	UNIVERSAL DISPENSER	NA
6	WASH BOTTLE	GT BRITAIN
7	GLASS FUNNEL	GT BRITAIN
8	VOLUMETRIC FLASKS	EM TECHNOCOLOR WEST-GERMANY
9	PLASTIC BOTTLES	NA
10	FILTER PAPER	WHATMAN № 45 GERMANY
11	BEAKERS	PYREX ENGLAND
12	WATCH GLASS COVER	PYREX ENGLAND

TABLE 3.2LISTS OF REAGENTS USED IN THE RESEARCH

S/N	REAGENT	SOURCE
1	HYDROCHLORIC ACID	RIEDE-DE HAEN, FRANCE
2	NITRIC ACID	FLUKA FEINCHEMIKALEIN, GERMANY
3	LEAD SOLUTION	FIN CHEMICALS, MILAN ITALY
4	CHROMIUM SOLUTION	FIN CHEMICALS, MILAN ITALY
5	CUPPER SOLUTION	FIN CHEMICALS, MILAN ITALY
6	IRON SOLUTION	FIN CHEMICALS, MILAN ITALY
7	DEMINERALISED WATER	NA
8	ACETYLENE	NA
9	AIR	NA

TABLE 3.3: LIST OF EQUIPMENT/MACHINES USED FOR RESEARCH

S/N	NAME	SOURCE/MODEL
1	ATOMIC ADSORPTION SPECTROPHOTOMETER (AAS)	PERKIN-ELMER, AANALYST 100 ATOMIC ADSORPTION SPECTROPHOTOMETER
2	ELECTRONIC WEIGHING BALANCE	METTLER TOLEDO AB204-8
3	HOT PLATE	BOBBY STUART HOTPLATE

STUDY AREA

Obrikom is a place located in Ogba/Ndoni/Egbema Local Government Area (ONELGA) of rivers state and geographically at latitude: 5°23'41.4" (5.3948°) north of the equator and 6°40'6.7" (6.66685°) east of the prime meridiem; with an average elevation of about 22meters (72feet) *(Mapcarta, 2014).* It hosts the presence of the Nigerian Agip Oil Company (NAOC) OB/OB Gas Plant and other allied industries. Obrikom is densely populated with good network of roads and drainage system.

FIGURE 3.1 Map of OBRIKOM showing NAOC OB/OB Gas Plant

[Map adapted from Google map]

METHODS:

Parameters were analysed in the laboratory using atomic adsorption spectrophotometer:

SAMPLING EQUIPMENTS/LOCATION

The tools employed in the sampling of the soil includes: Shovel, Soil Auger, Machete, Polythene bags, Sample information tag sheet, and GPS device, Android phone. Samples were collected at selected locations; georeferencing data with projection system

(geographical lat/long coordinates in degrees, minutes, and seconds) were obtained by aid of GPS, and Aerial photographs of georeferenced locations were obtained by means of Android (Techno M3) device via Google Map as outlined below:

Fig.1 Map of Agip pipeline

Fig.2 Map of Agip roadside

Fig. 3 Map of Welding Workshop

Fig. 4 Map of Household Garden

Fig. 5 Map of Onosi Ogu

Fig. 6 Map of Farmland

Fig. 7 Map of Dumpsite Sampling Procedures

Soil samples were collected from each location by the aid of a soil Auger at selected depth of 0-15cm, 15-30cm, and 30-45cm. Sampled soils were placed in white polythene bags properly tagged with yellow cards containing sample information so as not to mix up the samples. A total of twenty one samples were collected from the seven locations, three per sampling site, and was sent to the laboratory for storage, processing and analysis. Soil samples were air dried, after which dried samples were then ground by means of a mortar and pistol and then sieved. The sieved soils were placed in tagged polythene bags before the weighing commenced. Weighing of the soil samples was then accomplished by means of a high precision electronic Balance. Exactly 5g of homogenised soil samples obtained from the sample preparation procedure above was carefully weighed into a beaker by means of an electronic balance (of 0.0001g precision). 50ml of freshly prepared Aqua regia (12.5ml HNO_3 + 37.5ml HCL i.e ratio 1: 3) was added. The beaker was covered and the contents heated for 2hours by means of hot plate. The mixture was allowed to cool and then filtered through a whatman No. 42 filter paper into a 100ml standard volumetric flask. The volume of the filtrate was then made up to the 100ml mark with de-ionized water. Exactly 10ml of 1000ppm Fe, Pb, Cr and Cu solutions were respectively placed in 100ml volumetric flasks and the volumes made up to the mark with demineralised water; the resulting stock standard solution consisting of 100ppm each of Fe, Pb, Cu, and Cr. About 1.0, 2.0, 4.0, 6.0, 8.0ml of the mixed stock standard solution were respectively placed in a 100ml volumetric flask using the graduated pipette. To each was added 10ml of hydrochloric acid and its volumes made up to the mark with demineralised water, the working solutions contained 1, 2, 4, 6, 8ppm each of Fe, Pb, Cr and Cu respectively *(GRP, 2000).* Specific hallowed cathode lamps of Cu, Fe, Pb and Cr; air, acetylene, blanks, standard solutions and digested samples were employed in the AAS analysis. A specific hallowed cathode lamp was installed and properly aligned by setting the slit width, slit height, working position, lamp current, wavelength, and the parameters properly entered; then the lamp was turned on. The pressure and flow rate of both gasses were set using the oxidant and fuel control knobs and also the burner height was adjusted. The flame was then ignited and optimized for the installed lamp. The blanks were aspirated (zeroed), followed by the standards whose concentrations were calibrated. Then the samples were finally aspirated and the concentrations read. This simple procedure was repeated for each batch (set of parameters) with the specific hallowed cathode lamps replaced in turn and standard conditions for each parameter appropriately set *(PERKIN-ELMER, 1997).*

RESULTS AND DISCUSSIONS

The individual data acquired for each heavy metal are as shown in Table 4.1 below, with just mean values and standard deviation of Cu, Pb, Cr and Fe for each location.

TABLE 2 MEAN VALUES OF ANALYTICAL RESULTS

S/N	DESCRIPTION	Cu mg/kg (ppm) x ± σ	Pb mg/kg (ppm) x ± σ	Cr mg/kg (ppm) x ± σ	Fe mg/kg (ppm) x ± σ	LOCATION COORDINATES
1	SS_1	21.21±0.26	26.99±0.42	15.03±0.22	20623.67±6.60	N5°23'18.7332" E6°40'45.7716"
2	SS_2	24.02±0.07	99.37±0.81	17.38±1.18	67510.67±15.54	N5°23'33.6156" E6°39'45.3672"
3	SS_3	24.08±0.35	45.20±0.27	21.12±0.12	56269±13.49	N5°23'45.4128" E6°40'18.0048"
4	SS_4	72.82±0.76	90.28±0.28	21.47±0.47	31129.67±4.10	N5°23'42.2484" E6°40'41.8188"
5	SS_5	16.90±0.81	38.99±0.05	12.01±0.01	30376.67±1.24	N5°23'30.9012" E6°39'2.0016"
6	SS_6	24.19±0.1	60.21±0.14	15.07±0.06	44628.67±2.87	N5°23'38.2668" E6°40'40.4148"
7	SS_7	9.05±0.16	24.02±0.03	18.14±0.05	46874.67±6.13	N5°23'52.7856" E6°40'25.5648"

KEY

SS= Soil Sampe

SS1 = Soil sample from Agip pipeline

SS2=Soil Sample from Agip road side

SS3 =Soil Sample from Welding workshop

SS4 =Soil Sample from Dump site

SS5 =Soil Sample from Onosi ogu

SS6 =Soil Sample from farmland

SS7 =Soil sample from Household Garden

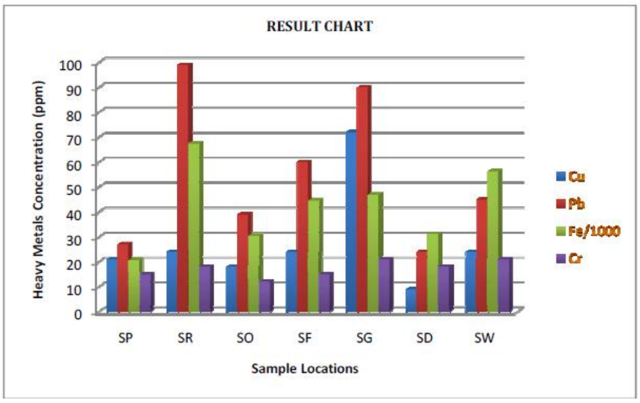


FIGURE 9 MEAN CONCENTRATIONS OF HEAVY METALS IN SAMPLED SITES

DISCURSIONS

The table of results above presents the average value of each parameter in each study location. Comparisons were drawn from DPR's Target and Intervention values for a standard soil. Further comparisons were on the basis of statistical calculation made to ascertain the level of difference in concentration of each heavy metal; first at various depths in each location by means of standard deviation and secondly, the differences in distribution of heavy metal concentration across the various locations by means of ANOVA.

Copper

As stated in the table of results above, and as clearly illustrated in the figure below; the mean concentration of copper in all the study locations where below both the target value and intervention limits of DPR, except for soil samples from the dump site which exceeded the target value an indication of a growing risk of copper pollution in the soils around that area if mitigation measures are not put in place quickly to check its increase and a possible spread through runoffs and infiltration. Its level is however yet below the DPR's Intervention Value thus the dumpsite is not presently at an alarming contamination stage which should necessitate an environmental pollution emergency.

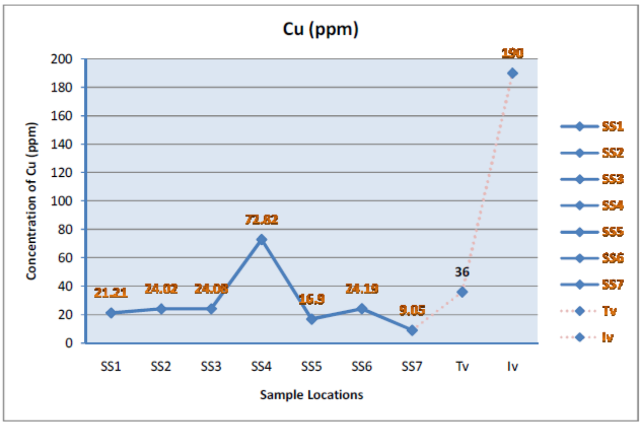


FIGURE 10 MEAN CONCENTRATIONS OF COPPER IN SAMPLED SITES

Statistical findings:

Differences in copper concentration at various depths of 0-15cm, 15-30cm and 30- 45cm in each location were determined by means of population standard deviation method. Statistical calculations revealed the following results for SS1-(21.21±0.26); SS2 (24.02±0.07); SS3 (24.08±0.35); SS4 (72.82±0.76); SS5 (16.90±0.81); SS6 (24.19±0.1); SS7 (9.05±0.16) indicating minimal differences in concentration of copper across the selected depths. The difference in copper concentration across all the locations was also determined by means of a Single Factor Analysis of Variance (ANOVA) at 5% level of significance. The results obtained as made available at Appendix IIIA gave an F-value of 0.00035, which was within the acceptable region with a P-value=0.99965. Since $\alpha \leq P=0.999965$ therefore it was concluded that there were no significant difference in the concentration of copper across the various location at 5% level of significance.

Lead:

From the analytical results obtained the mean concentration of Lead in all the study locations where found to be below both the target value and intervention limits of DPR, except for that of the Agip road side (99.37mg/kg) and that of the dump site (90.28) which exceeded just the target value as clearly illustrated in the graph below. This is indicative of lead contamination at these sites rendering the land unfit for human, plants and animals. Since these values are yet below the intervention values, the contamination level is not presently at a serious stage. However the need to check its increase is necessary to avert the risk of long term effects and a possible increase to alarming proportions in the nearest future.

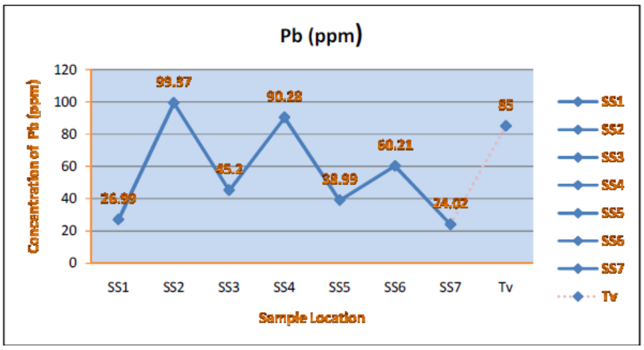


FIGURE 11 MEAN CONCENTRATIONS OF LEAD IN SAMPLED SITES

Statistical findings:

The differences in Lead concentration at various depths of 0-15cm, 15-30cm and 30- 45cm in each location were determined by means of population standard deviation method. Calculations revealed the following results for SS1-(26.99±0.42); SS2 (99.37±0.81); SS3 (45.20±0.27); SS4 (90.28±0.28); SS5 (38.99±0.05); SS6 (60.21±0.14); SS7 (24.02±0.03) indicating minimal differences in concentration of Lead across the selected depths.

The difference in Lead concentration across all the locations was also determined by means of a Single Factor Analysis of Variance (ANOVA) at 5% level of significance. The results obtained as made available at Appendix IIIB gave an F-value of 0.000652, which was within the acceptable region with a P-value=0.999348. Since α≤P=0.999348 therefore it was concluded that there were no significant difference in the concentration of Lead across the various location at 5% level of significance.

Chromium:

The concentration of Chromium for all samples analysed were found to be below the target value of DPR's regulatory limit. Hence the soil at various locations are said to be free from chromium contamination.

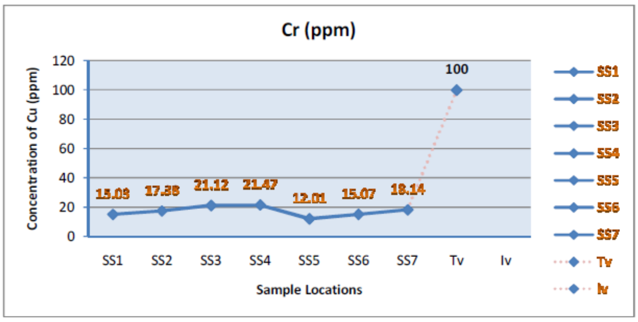


FIGURE 12 MEAN CONCENTRATIONS OF CHROMIUM IN SAMPLED SITES

Statistical findings:

The differences in Chromium concentration at various depths of 0-15cm, 15-30cm and 30-45cm in each location were determined by means of population standard deviation method. Calculations revealed the following results for SS1-(15.03±0.22); SS2 (17.38±1.18); SS3 (21.12±0.12); SS4 (21.47±0.47); SS5 (12.01±0.01); SS6 (15.07±0.06); SS7 (18.14±0.05) indicating marginal difference in concentration of Chromium across the selected depths.

The difference in Chromium concentration across all the locations was also determined by means of a Single Factor Analysis of Variance (ANOVA) at 5% level of significance. The results obtained as made available at Appendix IIIC gave an F- value of 0.007154, which was within the acceptable region with a P-value=0.992874. And since α≤P=0.992874 therefore it was concluded that there was no significant difference in the concentration of Chromium across the various location at 5% level of significance.

Iron:

From the results of the spectrometric analysis of various samples it was found that samples from Agip roadside had a higher value of iron concentration than the others followed by that from the welding workshop which could be an indication of higher activity involving use of iron around these areas considering the proximity of the sample point along Agip roadside with NAOC Ob/OB operational land area and the site of the Gas turbine whose recent construction and on going expansion could have imparted the soil around that area with increase iron concentration. The target value and Intervention values for iron is not available on the DPR's regulatory limit.

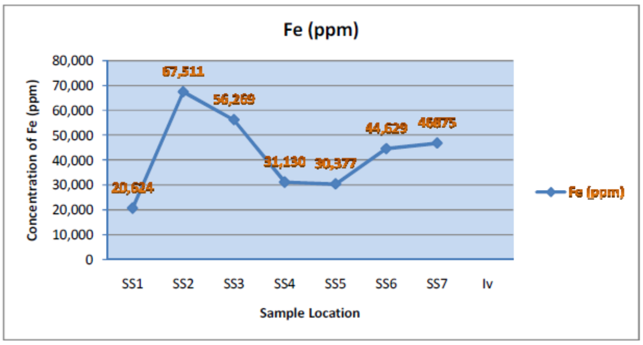


FIGURE 4.5 MEAN CONCENTRATIONS OF IRON IN SAMPLED SITES

Statistical findings:

The differences in Iron concentration at various depths of 0-15cm, 15-30cm and 30- 45cm in each location were determined by means population of standard deviation method. Calculations revealed the following results for SS1-(20623.67±6.60); SS2 (67510.67±15.54); SS3 (56269±13.49); SS4 (31129.67±4.10); SS5 (30376.67±1.24); SS6 (44628.67±2.87); SS7 (46874.67±6.13) indicating comparative difference in concentration of iron across the selected depths.

The difference in Iron concentration across all the locations was also determined by means of a Single Factor Analysis of Variance (ANOVA) at 5% level of significance. The results obtained as made available at Appendix IIID gave an F-value of 0.000000543, which was within the acceptable region with P-value=0.99999945. And since α≤P=0.99999945, it was therefore concluded that there were no significant difference in the concentration of Iron across the various location at 5% level of significance.

CONCLUSION

Summarily, given the available data on the concentrations of Cu, Pb, Cr and Fe, obtained from analysis of twenty one soil samples (from seven locations) by methods of wet digestion- Aqua regia and AAS, and by comparison with DPR's standards for soil, a clear inference was therefore drawn stating that a sizeable proportion of the sample data revealed soil conditions which fell below both the target limits and the intervention values stipulated by DPR. Deductively, the concentration of the soil heavy metals of Cu, Pb, Cr, and Fe of NAOCs operational environs-Obrikom as a case study, are said to be comparatively within the recommended limits with little variance in terms of Copper at the dump site and lead at both the dumpsite and Agip-roadside exceeding just the target value. Again from the statistical analysis of the given data by measure of dispersion- standard deviation and analysis of variance it was found that there was no significant difference in the concentrations of the concerned heavy metals across depths of 0- 15cm, 15- 30cm, 30- 40cm; and across various location at a 5% level of significance. The NAOC OB/OB operational environs –Obrikom, have minimal soil contamination from industrial and allied operations. This work does not in any way rule out the possibility of marked soil pollution in other areas and with regards to other heavy metals that were by academic constraint beyond the scope of this work nor does it in any way absolve NAOC from culpability as regards any past, present or near future environmental health violations.

RECOMENDATION

Following occurrence of certain heavy metals exceeding DPR's target values at two sample locations, the need to apply mitigation measures should be done without much ado in other to alleviate the present contamination status of the soil so as to forestall an unwarranted future pollution to an intervention degree. Further studies should be carried out extensively at a spatial and timescale level to ascertain the extent of soil contamination of NAOC OB/OB operational environs that were beyond the scope and delimitation of this research project.

- A holistic monitoring, mitigation and remedial framework be setup and thoroughly implemented to safeguard the soil environment and by extension the ecosystem from timescale deterioration arising from industrial and allied activities.

- As a quick response measure to contaminated sites, phytoremediation should be adopted at the copper and lead contaminated sites in other to reduce the pollution load of these sites:

Crops like alpine pennycress (*Thlaspi caerulescens*), *Ipomea alpine, Haumaniastrum robertii, Astragalus racemosus, Sebertia acuminate* have very high bioaccumulation potential for Cd/Zn, Cu, Co, Se, and Ni, respectively *(Lasat, 2000).* Willow (*Salix viminalis* L.), Indian mustard (*Brassica juncea* L.), corn (*Zea mays* L.), and sunflower (*Helianthus annuus* L.) have reportedly shown high uptake and tolerance to heavy metals such as Pb to a concentration level of 10,000–15,000mg/kg **(**Schmidt, 2003).

- Due to marked pollution at the dump site by both cupper and lead, it is recommended that an environmentally standard waste management system be set up, enforced and monitored effectively for both industrial and municipal wastes.

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