Levels of Heavy Metals from selected Soils in Crude Oil Mining Residences of Niger Delta

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Abstract

The current level of heavy metals (Cd, Hg, As, Pb and Zn) in the crude oil polluted soils of Egwa 1, Kurutie, Okerenkoko and Kurukunama has been studied using Atomic Absorption Spectrophotometer (Varian AA240). Samples were digested with aqua regia before metal analysis. Result of analysis revealed that Mercury and Arsenic concentrations were above the acceptable values of these metals in soil, and the concentrations of Cadmium, Lead and Zinc were within the acceptable limits allowed in soil. Top soils from each study location proved to have higher accumulation of these metals in study. In some locations, the least amount of heavy metals was accumulated at the mid soils. The Cadmium concentration from the four locations ranges from 0.15±0.01 to 1.11±0.01 mg/Kg. The concentration of Mercury from the four study locations ranged from 3.40±0.04 to 6.31±0.08 mg/Kg. The Arsenic concentration from both study locations ranged from 2.00±0.02 to 5.40±0.05 mg/Kg. Concentrations of Pb from both study locations ranged from 0.20±0.01 to 0.54±0.01 mg/Kg. The concentration of Zinc in both locations ranged from 2.48±0.03 to 6.34±0.02 mg/Kg.

Keywords: Heavy metal, Soil, Niger Delta, Pollution

1.0 Introduction

One of the major environmental threat to the Niger Delta residences is the heavy metal pollutions, contaminating food sources. Sources of these heavy metals includes crude oil exploration, fertilizer application, pesticide effluents, sewage sludge, waste disposal, smelting and vehicle exhausts. It has been established that in every 1000kg of a normal soil in an environment contains about 0.2g of Cadmium, 0.5g of Mercury, 16g of Lead, 80g of Nickel and 200g of Chromium [1]. However, these concentrations always vary depending on the predominant sources of these heavy metal contamination in the environment. There are lots of adverse effects associated with the heavy metal pollution in soil and water and thus of great concern to environmental health, public health and agricultural production [2-5]. In the study of Nworu *et al.*, (2018); they analysed the presence of Zn, Pb, Fe, Mn, Cu, As, Cd, Cr and Ni on cassava and yam tubers from contaminated soil caused by Lead-Zinc mining. The metal concentrations in both yam and cassava samples were all above the WHO permissible limits from both affected locations except Chromium metal which falls within the WHO permissible/consumable limit. The ailment and incessant death of the underage children observed in the community could be traced to the health implications associated with these heavy metals as they are mostly chronic, harmful and could be lethal at elevated concentrations.

It is observed that the industrial mining activities in the studied area have caused the mobility and transportation of these metals across the farm lands. It was observed that the wastes from the mining sites are not properly managed and are indiscriminately disposed in any available lands [6]. Pollution of soil is as a result of industrial and urban waste disposal and agrochemical usage [7-9].

In soil chemistry, heavy metals are classified as special groups of elements. This is because of their toxicity seen on plants at high concentrations. In previous studies on heavy metals in soils, there is no record on the degree of hazard of any given heavy metal in soils. It was just three heavy metals; Hg, Cd, and Pb that was established during the Global Monitoring Program which was adopted by the United Nation in 1973 [10]. Later, in the report delivered by the Executive Director of the United Nation Environmental Program (UNEP), seven other heavy metals (Cu, Sn, V, Cr, Mo, Co, and Ni) and three metalloids (Sb, As, and Se) were added to the list of the most hazardous elements [11]. These recommendations given has served as the parameter for monitoring heavy metals in soils. Other sources of heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric sources [12]. Environmental pollution is very prominent in industrial source areas such as mining, foundries and smelters, and other metal-based industrial operations [3, 12, 13].

Essential heavy metals cause physiological and biochemical effects in animals and plants. They are very vital in different oxidation-reduction processes because they are core constituents of several key enzymes. For example, copper is an essential co-factor for different oxidative stress-related enzymes such as catalase, superoxide dismutase, peroxidase, cytochrome c oxidases, ferroxidases, monoamine oxidase, and dopamine β-monooxygenase [14-17]. This implies that copper is an essential element that is incorporated into a number of metalo-enzymes involved in haemoglobin formation, carbohydrate metabolism, catecholamine bio-synthesis, and cross-linking of collagen, elastin, and hair keratin. The ability of copper to cycle between an oxidized state, Cu(II), and reduced state, Cu(I), is applied in cupro-enzymes involved in redox reactions. Also, long term exposure to copper is linked to cellular damage leading to Wilson disease in humans [18, 19]. Similar to copper, several other essential elements are required for biological functioning, but, an excess amount of such metals produces cellular and tissue damage leading to a variety of adverse effects and human diseases. Other metals such as aluminium (Al), antinomy (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), cadmium (Cd), gallium (Ga), germanium (Ge), gold (Au), indium (In), lead (Pb), lithium (Li), mercury (Hg), nickel (Ni), platinum (Pt), silver (Ag), strontium (Sr), tellurium (Te), thallium (Tl), tin (Sn), titanium (Ti), vanadium (V) and uranium (U) have no established biological functions and are considered as non-essential metals. In biological systems, heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondrial, lysosome, endoplasmic reticulum, nuclei, and some enzymes involved in metabolism, detoxification, and damage repair [20-25]. Metal ions have been found to interact with cell components such as DNA and nuclear proteins, causing DNA damage and conformational changes that may lead to cell cycle modulation, carcinogenesis or apoptosis [26, 27].

Interest into this research came because of the emergency demand of the habitats of these creeks affected by crude oil exploration and gas flaring, as they requested that Federal Government have to conduct a proper Environmental Impact Assessment, EIA, and give appropriate compensation to the affected communities. The alarming request for environmental impact assessment in the environment was because of the pronounced environmental degradation of all the natural resources in the environment, the air, soil and water have been placed in a bad state as their major purpose has been jeopardized. Analysis of the soil from these four affected communities will portray the extent at which the environment has been degraded. Agricultural processes in most of these communities has been barred by these environmental pollutions. However, agricultural practices are still taking place in mini scale within some of the communities. Also, most habitats of these environments are not properly educated, hence do not know much about the pollution effects to their agricultural practices as plants grown on these soils have the abilities to bioaccumulate large amount of heavy metals, translocating them throughout their shoots which can easily find their way into food chains and greatly causes so much ailments when consumed.

2.0 Study Location

This research was carried out in four communities (Egwa 1, Kurutie, Okerenkoko and Kurukunama) within Escravos river in Warri Delta state, Nigeria.

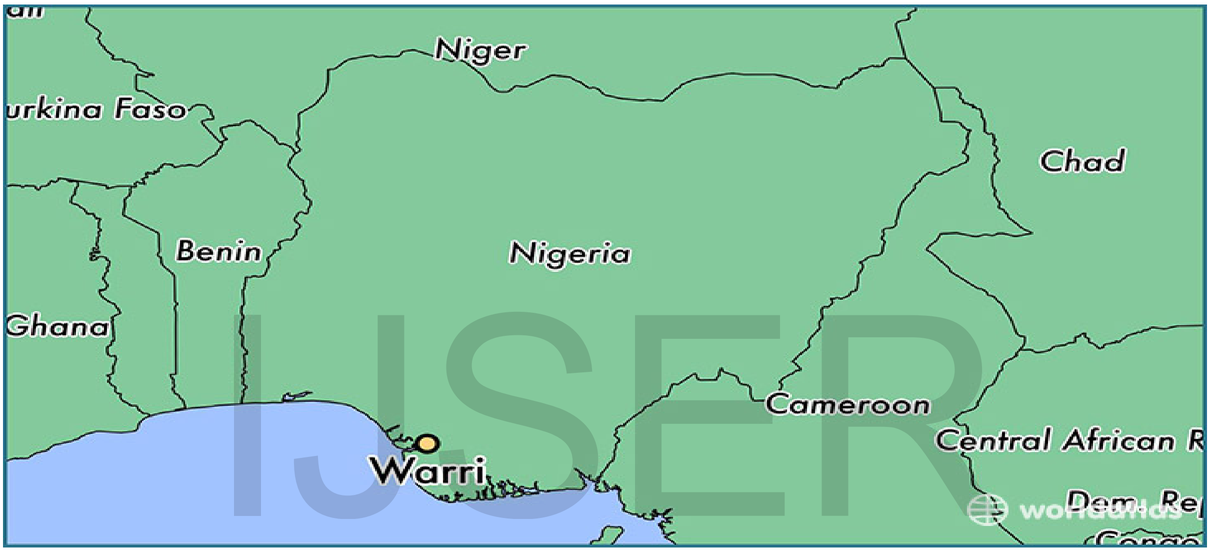

Figure 1: Map showing the study location

The Escravos River is a river in southern Nigeria. "Escravos" is a Portuguese word meaning "slaves" and the area was one of the main conduits for slave trade between Nigeria and the United States in the 18th century. The Escravos is a distributary of the Niger River, it flows for 57 kilometres, ending at the Bight of Benin of the Gulf of Guinea where it flows into the Atlantic Ocean. Chevron, a major US oil company, has its main Nigerian oil production facility at the mouth of the Escravos River. The city of Warri has a unique history that has not been documented well enough by historians. The name Warri pronvince was once applicable to the part of an area now called Delta State under the Colony and Protectorate of Southern Nigeria. Its boundary in the north east was Nsukwa/Isheagu creek near Kwale and Aboh,Forcados River in the south east and Jamieson Creek in the south west and later changed to Delta Pronvince. Warri city is one of the major hubs of petroleum activities and businesses in the southern Nigeria. It is a commercial capital city of Delta State, with a population of over 311,970 people according to the national population census figures for 2006. The city is one of cosmopolitan cities in southern Nigeria comprising originally of Itsekiri, Urhobo and Ijaw people. Warri is predominantly Christian with mixture of African traditional religions like most of the Southern Nigeria.

2.1 Sample Collection

With a pre-treated spoon, composite samples of the soil were collected within the soil depths of 0-30cm, 30-60cm and 60-90cm, each representing the top, mid and sub-soils respectively. Samples were properly labelled and stored in a treated polythene bag.

2.2 Sample Preparation
Samples were properly ground, sieved and sun dried for 8hours. This was done to remove any inherent moisture to avoid interference during sample analysis. The grounded soil samples were sieved with a 2.0 mesh size sieve to remove fragments of larger sizes and separate coarse grains from the metal rich fine grained soil samples.

2.3 Sample Digestion
The digestion process of AOAC [28] was modified and process applied. 5.00grams of each composite soil sample was weighed and digested with a 20mL of concentrated nitric acid and 10mL concentrated sulphuric acid until a clear and colourless solution was observed. The colourless solutions were filtered and diluted with a distilled water into a 100mL volumetric flask, made up to mark and stored in a clean container for metal analysis.

2.4 Spectrophotometric Analysis
For each of the metal Atomic absorption spectrophotometer calibration was carried out using a standard prepared from the metal salt. Metal concentrations of Cd, Hg, As, Pb and Zn were determined from each sample using Atomic Absorption Spectrophotometer (Varian AA240). This involves a direct aspiration of the aqueous clear solutions into an air-acetylene flame

3.0 Results
Table 1: Mean Concentration (mg/Kg) of Heavy Metal Distribution in the Soil from the Study Locations

		Metal Concentration (mg/Kg) [n=3]				
Sampling locations		Cd	Hg	As	Pb	Zn
Egwa 1	Top soil	0.31±0.01	5.48±0.06	2.14±0.02	0.20±0.01	4.20±0.03
	Mid soil	0.24±0.01	4.10±0.06	2.00±0.02	0.32±0.01	3.84±0.03
	Sub soil	0.84±0.01	4.03±0.06	3.64±0.01	0.45±0.01	2.48±0.03
Kurutie	Top soil	0.93±0.01	6.31±0.08	3.47±0.04	0.43±0.01	6.34±0.02
	Mid soil	0.40±0.01	6.01±0.08	2.84±0.03	0.40±0.01	6.07±0.02
	Sub soil	0.22±0.01	5.45±0.08	5.40±0.05	0.53±0.02	4.38±0.02
Okeren koko	Top soil	0.84±0.02	4.22±0.04	2.36±0.03	0.34±0.01	5.16±0.04
	Mid soil	0.63±0.02	3.87±0.04	2.12±0.02	0.30±0.01	5.20±0.04
	Sub soil	0.50±0.02	3.40±0.04	3.96±0.02	0.46±0.02	4.23±0.04
Kurukunama	Top soil	1.11±0.01	5.80±0.04	3.10±0.02	0.53±0.01	5.44±0.03
	Mid soil	0.15±0.01	4.20±0.04	2.70±0.02	0.41±0.01	5.21±0.03

	Sub soil	0.54±0.01	3.92±0.04	3.60±0.03	0.54±0.01	4.50±0.04
Dutch Ecologist	[29]	1.10	1.90	4.50	55.00	16.00

3.1 Discussion

The mean concentrations (mg/Kg) of the analysed heavy metals [Cd, Hg, As, Pb and Zn] as they are distributed in the selected soils are represented in table1. The distribution of heavy metal in the four investigated sites does not follow a regular pattern with consideration to the concentration of each metal at the top, mid and sub soils. This suggests that the source of these heavy metals are both anthropogenic and natural. From the study of Ngele *et al.,* [30], the levels of heavy metals from the different study waste dumps generally decreased in the order: top soil> mid soil>sub soil, this suggests that the source of these metals are anthropogenic in nature. Among the heavy metals of interest [Cd, Hg, As, Pb and Zn] only Hg and As were generally above the permissible limit of heavy metals in the soil as illustrated by a Dutch Ecologist [29]. Cd, Pb and Zn were all within the permissible values. Metals are naturally occurring constituents in the environment and vary in concentrations across geographic regions. Generally, top soils from each study location proved to have higher accumulation of these metals in study. In some locations, the least amount of heavy metals was accumulated at the mid soils. Metals, unlike organic chemicals, are neither created nor destroyed by biological or chemical processes; although, these processes can transform metals from one species to another (valence states) and can convert them between inorganic and organic forms. These metals have the ability to exhibit synergism by linking with another metal such as in Cd/Ni, Cd/Zn, Cu/Cd, Cu/Zn, etc, thereby creating more hazardous effects than when they appear as individuals [31]. Certain metal compounds are known to bioaccumulate in tissues and this bioaccumulation can be related to their toxicity.

The Cadmium concentration from the four locations ranges from 0.15±0.01 to 1.11±0.01 mg/Kg as compared to the standard Cadmium concentration in soil [29]. The sub soil from Egwa 1 recorded the highest concentration of Cadmium to be 0.84±0.01 mg/Kg while the mid soil recorded the least concentration to be 0.24±0.01 mg/Kg. the top soils of Kurutie, Okerenkoko and Kurukunuame had the highest concentration of Cadmium of 0.93±0.01, 0.84±0.02 and 1.11±0.01 mg/Kg respectively, whereas the sub soils of Kurutie and Okerenkoko locations recorded the least concentrations of Cadmium as 0.22±0.01 and 0.50±0.02 mg/Kg respectively but the mid soil of Kurukunuama recorded the least Cadmium concentration of 0.15±0.01 mg/Kg. Cadmium is a heavy metal of considerable environmental and occupational concern. It is widely distributed in the earth's crust at an average concentration of about 0.1 mg/kg. The highest level of cadmium compounds in the environment is accumulated in sedimentary rocks, and marine phosphates contain about 15 mg cadmium/kg [36]. Absorption of these heavy metal by plants and under-ground water can easily find their way into human food chains causing dangerous ailments. The bio-accessibility, bio-availability, and bio-accumulation properties of inorganic metals in soil, sediments, and aquatic systems are interrelated and abiotic (e.g., organic carbon) and biotic (e.g., uptake and metabolism). Modifying factors determine the amount of an inorganic metal that interacts at biological surfaces (e.g., human digestive system, at the gill, gut, or root tip epithelium) and that binds to and is absorbed across these membranes. A major challenge is to consistently and accurately measure quantitative differences in bioavailability between multiple forms of inorganic metals in the environment.

The concentration of Mercury from the four study locations ranged from 3.40±0.04 to 6.31±0.08 mg/Kg. The top soil from Kurutie recorded the highest Mercury concentration (6.31±0.08 mg/Kg) while the sub soil from Okerenkoko recorded the least Mercury concentration (3.40±0.04 mg/Kg). Humans are exposed to all forms of mercury through accidents, environmental pollution, food contamination, dental care, preventive medical practices, industrial and agricultural operations, and occupational operations [36]. The major sources of chronic, low level mercury exposure are dental amalgams and fish consumption. Mercury enters water as a natural process of off gassing from the earth's crust and also through industrial pollution [32]. Algae and bacteria methylate the mercury entering the waterways. Methyl mercury then makes its way through the food chain into fish, shellfish, and eventually into humans [38].

The Arsenic concentration from both study locations ranged from 2.00±0.02 to 5.40±0.05 mg/Kg. The mid soil of Egwa 1 and the sub soil of Kurutie showed the least and highest concentrations of Arsenic respectively. Arsenic is a ubiquitous element that is detected at low concentrations in virtually all environmental matrices [32]. Study showed that several million people are exposed to arsenic chronically throughout the world, especially in countries like Bangladesh, India, Chile, Uruguay, Mexico, Taiwan, where the ground water is contaminated with high concentrations of arsenic. Human Exposure to arsenic occurs through the oral route (ingestion), inhalation, dermal contact, and the parenteral route to some extent [32,33]. Arsenic concentrations in air range from 1 to 3 ng/m3 in remote locations (away from human releases), and from 20 to 100 ng/m3 in cities. Its water concentration is usually less than 10µg/L, although higher levels can occur near natural mineral deposits or mining sites. Its concentration in various foods ranges from 20 to 140 ng/kg [34]. Natural levels of arsenic in soil usually range from 1 to 40 mg/kg, but pesticide application or waste disposal can produce much higher values [32]. Diet, for most individuals, is the largest source of exposure, with an average intake of about 50 µg per day. Intake from air, water and soil are usually much smaller, but exposure from these media may become significant in areas of arsenic contamination. Workers who produce or use arsenic compounds in such occupations as vineyards, ceramics, glassmaking, smelting, refining of metallic ores, pesticide manufacturing and application, wood preservation, semiconductor manufacturing can be exposed to substantially higher levels of arsenic [32, 35]. Contamination with high levels of arsenic is of concern because arsenic can cause a number of human health effects. Several epidemiological studies have reported a strong association between arsenic exposure and increased risks of both carcinogenic and systemic health effects [35].

Concentrations of Pb from both study locations ranged from 0.20±0.01 to 0.54±0.01 mg/Kg. the sub soil of Kurukunama and top soil of Egwa 1 showed the highest and lowest concentrations of Pb respectively. Exposure to lead occurs mainly through inhalation of lead-contaminated dust particles or aerosols, and ingestion of lead-contaminated food, water, and paints [38, 39]. Adults absorb 35 to 50% of lead through drinking water and the absorption rate for children may be greater than 50%. Lead absorption is influenced by factors such as age and physiological status. In the human body, the greatest percentage of lead is taken into the kidney, followed by the liver and the other soft tissues such as heart and brain, however, the lead in the skeleton represents the major body fraction [40]. The nervous system is the most vulnerable target of lead poisoning. Headache, poor attention spam, irritability, loss of memory and dullness are the early symptoms of the effects of lead exposure on the central nervous system [37, 38]. Recently, exposure to Lead has significantly reduced as a result of multiple efforts including its elimination in gasoline, and the reduction of the levels of Lead in residential paints, food and drink cans, and plumbing systems

4.0 Conclusion and Recommendations

In summary, result revealed that among the heavy metals analysed [Cd, Hg, As, Pb and Zn] only Hg and As were generally above the permissible limit of heavy metals in the soil, Cd, Pb and Zn were all within the permissible values. Metals are naturally occurring constituents in the environment and vary in concentrations across geographic regions. Generally, top soils from each study location proved to have higher accumulation of these metals in study. In some locations, the least amount of heavy metals was accumulated at the mid soils. Metals, unlike organic chemicals, are neither created nor destroyed by biological or chemical processes; although, these processes can transform metals from one species to another (valence states) and can convert them between inorganic and organic forms. It will be of environmental benefit, if a complete environmental impact assessment is carried out within this environment to clearly ascertain the other causes of the current environmental pollution and the level the soils have been polluted. This monitoring should be regularly checked and possible environmental regulatory measures should be put in place.

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