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Determining Heavy Metals in Soil and Water in a Bioremediating Area in Nkeleoken-Alode Eleme Community Rivers State.

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Abstract
The study aims at determining the concentration of heavy metals in soil and water undergoing bioremediation in the Nkeleoken-Alode community of Eleme Local Government Area, Rivers State, carried out on both soil and aquatic sites undergoing bioremediation in the area. Soil and water samples were collected from three sites: unpolluted, polluted unremediated and polluted remediated sites. 50g of soil sample was collected using sterile aluminium foil, and water samples were collected in 250ml sterile containers. Samples were assayed using an Atomic Absorption Spectrophotometer which measures the concentrations of elements in a liquid sample. The absorption is proportional to the concentration of the elements present in the samples. Results showed a significant difference ($p<0.05$) in the concentration of lead and chromium in soil samples from polluted remediated sites compared to soil samples from unpolluted sites and polluted unremediated sites. Arsenic, cadmium and nickel did not show a significant difference when soil samples from the polluted remediated site were compared to unpolluted and polluted unremediated sites ($p>0.05$). Furthermore, there was a significant difference ($p<0.05$) in the concentrations of cadmium, nickel and chromium in water samples, when water samples from the polluted remediated site were compared to unpolluted and polluted unremediated sites. Lead and arsenic in water samples from polluted remediated sites did not show any significant difference ($p>0.05$) when compared to unpolluted and polluted unremediated sites. The concentrations of heavy metals in the soil and water samples showed a significant increase ($p<0.05$) in the heavy metal concentrations between the test and control sites. The various areas in the region that have been exposed to pollution pose a serious risk of heavy metal toxicity to occupants of the Niger Delta as a result of crude oil spillage. An immediate bioremediation strategy should be adopted in order the restore lost vegetation and aquatic life.

Keywords: heavy metals, soil, water, bioremediation, pollution, Nkeleoken-Alode community.

Introduction
The continuous construction and expansion of industries and production factories in our surroundings, have led to a considerable discharge of industrial waste into the environment (soil and water). Action such as this has resulted in the accumulation of heavy metals. Within our environment, heavy metals are naturally occurring elements that are found throughout the earth's crust, most environmental pollution and human exposure occur as a result of human – anthropogenous activities such as mining, industrial activities and the use of chemicals for domestic and agricultural purposes (He *et al.,* 2005). Heavy metals are defined as metallic elements found to have a relatively high density compared to water; these metals find their way into soil and water resulting in major health concerns as a result of their indiscriminate release into our environment.

For hundreds of years, external factors such as wind erosion and oceanic spray have contributed to the exposure of heavy metals in the environment (Asgari *et al.,* 2017). The pollution of toxic heavy metals is an important environmental issue that has been facilitated as a result of the impact of human activities due to changing industrial activities. Pollutants released into the environment can be introduced and built up through anthropogenic activities such as domestic waste, vehicles emission, industrial processes (e.g., electroplating, dyeing, and mining) as well as indiscriminate disposal of industrial wastes; agricultural by-products such as fertilizers, pesticides; sewage sludge, and waste treatment plants (Tchounwou *et al.,* 2012). In addition, heavy metals may be present at high levels in aquatic and soil ecosystems as compared with the atmosphere (e.g., vapours or particulate) Wintz *et al.,* (2002); this is because some regions are exposed to lots of degradation and as a result of this impact, there is an exposure to heavy metals which remains dangerous to many ecosystems. The source of heavy metals may be either natural or due to human activities, which eventually leads to their presence in soil, water, and air (Szyczewski *et al.,* 2009).

In many parts of the world where crude oil exploration takes place, there is usually a tendency for oil spillage. Oil spills are a source of heavy metal pollution of aquatic and terrestrial environments, especially in oil-producing regions (Egbe and Thompson, 2010) of which the Nkeleoken-Alode Eleme Community of Rivers State is among. Crude oil is a complex mixture of hydrocarbon and non-hydrocarbon compounds (including heavy metals) found in subsurface deposits worldwide (Chinedu and Chukwuma, 2018). Oil spillage results in the release of oil into the natural environment resulting in adverse effects on the environment; as a result of various activities like extraction, refining, transportation and storage of crude oil there is the likelihood of oil spillages. Spillage also results from accidents, lack of maintenance of engineering equipment and deliberate acts (including oil bunkering and sabotage which is experienced at a high frequency in the Niger Delta region).

Natural disasters such as flooding, earthquakes and hurricanes can also cause damage to oil facilities resulting in a spillage (Egbe and Thompson, 2010). Due to the presence of heavy metals in crude oil, whenever there is a spillage it automatically results in the contamination of the environment with heavy metals. The Niger Delta region experiences a high number of oil spill incidents because it is the seat of crude oil activities in Nigeria. It remains important that exploration companies take into cognisance the dangers associated with exposure to heavy metals during an oil spill as well as ensure quick remediation.

Exposure to contaminated soil and ground waters put human health at risk through direct or indirect contact with contaminated food products which are grown and harvested in polluted areas. Also, in many parts of the world where there has been excessive environmental exposure to heavy metals, man and animals can come in direct contact with these environmental contaminants through drinking polluted water and the inhalation of dust (Lasat, 1999).

Heavy metals such as arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, zinc and many others cannot be disintegrated into non-toxic forms; many of them cause detrimental health impacts even at very low concentrations, by acting as cytotoxic agents, carcinogens or mutagens (Salem *et al.,* 2000). Plants require a little number of metallic elements for their growth and development; however, at increased levels they become toxic to their survival.

Environmental Contamination of Ogoni Land

The Ogoni land remains one of the regions in Nigeria that has contributed massively to the economic stability of Nigeria for over five decades (PIND, 2019). As a result of the over-dependence of the Nigeria economy on crude oil exploration especially in the Niger Delta region, many of these regions have been greatly affected by crude oil spillage leading to the contamination of the environment by high exposure to heavy metals and several agitations on remediation processes (Uduji *et al.,* 2020).

The Ogoni region covers around 1,000 km2 in Rivers State, southern Nigeria; Ogoniland has been the site of oil industry operations since the late 1950s. The region has an enormous crude oil deposit; however, it is plagued with a tragic history of pollution from oil spills and oil well fires, although no systematic scientific information has been provided to report the level of environmental degradation. The United Nations Environment Programme saw the need to assess the level of environmental pollution in the regions which led to the publication of the Environmental Assessment of Ogoniland in 2011 (UNEP, 2011).

There have been lots of controversies surrounding oil exploration in Ogoniland which comprises several communities including the Nkeleoken-Alode Eleme community of Rivers state. The majority of concerns in the regions have been concerning the impacts of the high level of environmental pollution which has resulted in the loss of economic opportunities for the indigenous people of the region as a result of polluted farm lands and water bodies such as rivers and streams (UNEP, 2011). Also, the livelihood of the people has been gravely affected due to high levels of exposure to contaminants such as heavy metals and deleterious organic compounds resulting in numerous health complications.

Ogoniland is widespread and severely impacting many components of the environment. Although the region has been dormant for many years when it comes to crude oil exploration for over two decades, the oil spills that occurred several years ago continue to be a growing concern to the people of the region every day. As a result of the high rainfalls that the region experiences, the level of remediation processes has been slow coupled with a lack of political commitment (UNEP, 2011).

As a result of the high rainfall experienced in the regions, crude oil found on the surface of the land is washed away, traversing farmland and almost always ending up in the creeks. When oil reaches the root zone, crops and other plants begin to experience stress and can die, and this is a routine observation in Ogoniland. At one site, Ejama-Ebubu in Eleme local government area (LGA), the study found heavy contamination present 40 years after an oil spill occurred, despite repeated clean-up attempts (UNEP, 2011).

Furthermore, an assessment carried out by the United Nations Environmental Programme revealed that overlap between authorities and ministries, as well as a lack of resources within key agencies, has seriously impacted the cleaning-up progress. This has seriously affected environmental management on the ground, including enforcement. Remote sensing showed that over the years, there has been a rapid proliferation in the past two years of artisanal refining, whereby crude oil is distilled in crude facilities (UNEP, 2011). The act of carrying out these local and illegal ways of petroleum refining has also contributed to the huge environmental degradation of the Ogoniland and neighbouring communities which include the study area – Nkeleoken-Alode Eleme Community Rivers State.

Crude oil exploration in Ogoniland and the negligence of petroleum companies to provide and protect the normal flora and fauna of the environment have resulted in a high deposit of heavy metals in various host communities where crude oil exploration takes place. This is also evident in the United Nations Environment Programme (UNEP) report on the Ogoniland clean-up. Bioremediation programmes have been set up, using various technology tools for the removal of heavy metals and recovery of the heavy metals in polluted water and lands (UNEP, 2011); however, the process of remediation has slowed due to the lack of political willingness and commitment.

Hazards of Petroleum Hydrocarbon Contamination

When there is high environmental exposure to petroleum primary biological damage occurs by blocking the supply of water, nutrients, oxygen, and light, affecting soil fertility, plant growth and germination (Onwurah *et al.,* 2007; Fuentes *et al.,* 2014). As a result of environmental degradation due to petroleum exploration, petroleum hydrocarbons are mainly found in soil and sediment at various concentrations causing significant environmental damage (Dong and Lee, 2009).

When petroleum hydrocarbon mixes with water, they tend to seep dip into the ground, where they persist, reducing the quality and productivity of the soil and making it unsuitable for agricultural activities such as farming and investment (Ou *et* *al.,* 2004). Furthermore, when it concerns the fauna population, petroleum hydrocarbons are found to be poisonous at low concentrations and they can be carcinogenic or mutagenic to wildlife and humans. Uptake of such recalcitrant chemicals from contaminated soil may occur through ingestion, inhalation or dermal contact with contaminated soil or dust (Eman and Andrew, 2017) leading to various health complications including dermal keratosis.

Since recent studies have proven that petrogenic hydrocarbons persist in the ecosystem for long periods, they can accumulate in animals and plant tissue, passing from one to the next through the food chain causing death or genetic mutations in animals and humans (Chandra *et al.,* 2013).

Frequent exposure to sub-lethal doses of heavy metals can cause several health complications such as physiological impairments, leading to several health impacts including liver damage, haemolytic anaemia, weight decline, gastrointestinal dysfunctions, impaired immune system and reduced productivity (Paruk and Adams, 2016). Accumulated exposure to aliphatic hydrocarbons can affect the nervous system coordination, and also cause dizziness, headaches, fatigue and limb numbness, tremors, temporary limb paralysis and unconsciousness at high concentrations (Adgate *et al.,* 2014).

In both animals and humans (biological systems in general), it is found that heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondrial, endoplasmic reticulum, lysosome, nuclei, and some enzymes involved in, detoxification, metabolism and damage repair (Wang and Shi, 2001). Numerous research conducted on some of the effects of heavy metals on biological systems suggest that heavy metals interact with cell components such as DNA and nuclear proteins, causing serious DNA damage and conformational changes that may lead to significant changes in cell cycle modulation, transcriptional process, carcinogenesis or cell death (Beyersmann and Hartwig, 2008).

From the report of Tchounwou *et al.,* (2012) on the "Heavy metals toxicity and the environment", it is has been demonstrated that reactive oxygen species (ROS) production and oxidative stress play a key role in the toxicity and carcinogenicity of metals such as arsenic, cadmium, chromium, aluminium, lead and mercury (Sutton *et al.,* 2002). Due to the high degree of toxicity of these elements, they rank among the priority metals that are of great public health significance. These heavy metals are all systemic toxicants that are known to induce multiple organ severity, even at lower levels of exposure. According to the United States Environmental Protection Agency (U.S. EPA), and the International Agency for Research on Cancer (IARC), these metals classified as either "known" or "probable" human carcinogens based on epidemiological and experimental studies showing an association between exposure and cancer incidence in humans and animals (Tchounwou *et al.,* 2012).

The presence of aliphatic hydrocarbons can also negatively affect soil microflora and structure producing oil films and slicks and decreasing the interchange of oxygen and nutrient in the soil (Militon *et al.,* 2010). Aliphatic hydrocarbons may also affect the nervous system, causing

Remediation of Petroleum-Polluted Sites

Remediation processes form an integral part when it bothers restoring a polluted environment to a normal state. In a research study carried out by Adesina and Adelasoye (2014) on the "Effect of crude oil pollution on heavy metal contents, microbial population in the soil, and maize and cowpea growth"; they identified that crude oil spills resulted in the deposition of heavy metals such as nickel, chromium, zinc and several other heavy metals (Adesina and Adelasoye, 2014). Heavy metals are often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity (Duffs, 2001). The need to carry out remediation on polluted regions remains a necessity for restoring vegetation for the cultivation of crops.

It has been observed that the pollution caused by heavy metals not only results in adverse effects on various parameters relating to plant quality and yield but also causes changes in the size, composition and activity of the microbial activities (Yao *et al.,* 2003). The microbial community which is an important component of the eco-system is also greatly affected resulting in various inhibitory activities and structural modifications due to the biochemical interactions these metals have on biochemical molecules that constitute an integral component of these microbes. The changes observed in the affected microbial community are influenced by the type of metal, the nature of the medium and microbial species (Goblenz *et al.,* 1994).

Several techniques have been designed to aid with remediation processes. These processes involve the use of various methods such as the use of physical, physicochemical and biological methods like biosorption and/or bioaccumulation for the removal of heavy metals may be an attractive alternative to physicochemical methods (Hussein *et al.,* 2003).

Physical Methods

The use of a physical method for remediation processes remains perhaps one of the easiest, quickest and safe methods in remediation processes. However, it is not a sophisticated and cheap method. After excavation of affected regions is done; the contaminated soil is removed and transported to an appropriate landfill for disposal. Soil sample testing is further carried out; samples are collected from the bottom and sidewalls of the excavated area to check if the site is clean or not (Barnes, Laderach, and Showers, 2002; Olstein *et al.,* 2005; Ellerman *et al.,* 2009).

Another physical method that can be employed is the washing of contaminated soil. Washing of contaminated soil is carried out with organic solvents such as ethanol-water mixture and ethyl acetate-acetone-water mixture; this method is provided to significantly remove hydrocarbons from the contaminated soil (Khodadoust *et al.,* 1999). This process does not alone removes hydrocarbon from polluted oil but also aids in the removal of heavy metals from the soil. The efficiency of washing can be enhanced by the addition of surfactants. Research studies have shown that both artificial and natural surfactants are helpful in the removal of petroleum.

Examples of surfactants that help with the washing process of different fractions of petroleum include the followings artificial surfactant sodium dodecyl sulfate (SDS) removed aliphatic hydrocarbons while natural surfactants saponin and rhamnolipid removed polycyclic aromatic hydrocarbons from the contaminated soil (Urum and Pekdemir, 2004). This method has proven to be simple and very efficient; however, aside from the tremendous benefit of this, there are still challenges centred on time consumption and cost.

The conveyance of contaminated soil to the disposal site is another big problem in the area of logistics, and also surfactants might be dangerous due to their possibility of adhesion to soil particles.

Thermal Methods

The process of thermal remediation simply involves the roasting of contaminated soil to a temperature between (200- 1000 °F) which is known as thermal stripping or low-level temperature heating. This increases the vaporization and separation of low boiling point contaminants from the soil. Through this process, organic contaminants can be completely or partially decomposed depending upon the thermal stripping temperature and organic compounds present in the soil (Ndimele *et al.,* 2018). This method proves to be very effective and has the potential of removing approximately 90% of the contaminants but it is very costly and not environmentally friendly.

Another method used is incineration which is also a thermal process that involves high temperatures, unlike thermal stripping which involves low temperatures. The process of incineration uses high temperatures of (1600-2500°F) (Ezeji *et al.,* 2007). This process is not also environmentally friendly like thermal stripping; this is because volatile and flammable compounds present in crude oil will cause environmental pollution.

Phytoremediation

The use of phytoremediation remains one of the best environmental methods in effectively restoring lost soil and water bodies as a result of crude oil pollution leading to the accumulation of heavy deposits of heavy metals in the environment. This strategy is an effective, solar-driven and low-cost strategy that uses plants for the removal of contaminants from the soil of the large contaminated area. Some plants can grow in contaminated soil by simply metabolizing or accumulating the harmful compounds in their roots or shoots (De Boer and Wagelmans, 2016).

The selection of plants for remediation is extremely important for this process. Plants with extended root systems, minimum water requirement, adaptability to a variety of environmental conditions and fast growth rate are best for this purpose (Escobar Alvarado *et al.,* 2018). Phytoremediation efficiency depends on several factors such as plant species selection, environmental conditions and rhizobacteria (Farraji *et al.,* 2016).

Different mechanisms are devised by plants for the removal of contaminants i.e., phytoaccumulation which is a process of absorption of contaminants into the roots or shoots; phytodegradation which is a process of degradation of pollutants by utilization of plant enzymes such as laccase, oxygenase and nitroreductase; phytovolatilization which involves the release of volatile metabolites into the atmosphere, and phytostabilization (decrease the movement of contaminants) (Ding *et al.,* 2020). Alagić *et al. (*2014) and Nguemté *et al. (*2018) reported that two plant species i.e., *Eleusine indica* and Cynodon dactylon significantly eliminated some low to medium molecular weight Polycyclic Aromatic Hydrocarbons from the soil by phytoextraction process, indicating their use in the removal of Polycyclic Aromatic Hydrocarbons.

In a review of some plants that can play important roles when it comes to remediation, maize plants showed enhanced biodegradation in association with Cynanchum leave. This symbiotic relationship between maize roots and Cynanchum leaves degraded 4-6 rings more Polycyclic Aromatic Hydrocarbons efficiently than any other treatment (Garcia *et al.,* 2017).

Another plant that plays important role in phytoremediation is Vetiver grass which belongs to the Poaceae family, it is a perennial grass. It decontaminates the soil by extracting hydrocarbons and other toxins from the soil and accumulating them in the roots and shoots. This plant showed a negative effect on its growth and other physical activities when grown on soil contaminated with diesel (Dudai *et al.,* 2018). The *Mirabilis jalapa* is also considered a good candidate for phytoremediation processes, investigations after testing revealed that *Mirabilis jalapa* can remove 41-63% of saturated hydrocarbons within 127 days when compared with the natural attenuation process.

Biological Methods for Environmental Remediation

Bioremediation is a traditional method that involves the use of living organisms (bacteria, fungi and plants) to degrade harmful substances present in the environment. Bioremediation of crude oil from the soil and also water bodies has grown to become one of the best methods for the removal of heavy metals as well as hydrocarbons from polluted regions. This method has proven to be a very efficient, cheap and environmentally friendly solution. The effectiveness of this method is depended on hydrocarbon and heavy metal concentration, soil characteristics and composition of pollutants (Balba *et al.,* 1998).

In another definition, bioremediation is the use of biological systems to destroy or reduce the concentrations of hazardous wastes from contaminated sites. Such systems have potentially broad-spectrum site applications including groundwater, soils, lagoons, sludge and process waste streams, and it has been used in very large-scale applications such as the shoreline clean-up efforts in Alaska, resulting from the oil tanker “Exxon Valdez” oil spill in 1989 (Caplan, 1993).

Polycyclic Aromatic Hydrocarbons (PAH) are the most resistant and toxic group of soil pollutants present in crude oil. In addition to this, the presence of heavy metals mixed with these hydrocarbons makes them difficult to remove because of their ability to get trapped in the soil pores after they enter into the soil and are retained by the soil matrix (Safdari *et al.,* 2018).

Microbial degradation of petroleum hydrocarbon compounds is carried out by a range of microbial groups capable of decomposing a wide range of target constituents present in oil-contaminated environments. A biodegradation pathway involves a slow and gradual transformation of organic contaminants into intermediates of the central intermediary metabolism (Koshlaf *et al.,* 2017).

Most of the frequently used active microorganisms used in bioremediation belong to the genera *Acinetobacter*, *Actinobacter*, *Alcaligenes*, *Arthrobacter*, *Bacillus*, *Berjerinckia*, *Flavobacterium*, *Methylosinus*, Mycobacterium, Mycococcus, Nitrosomonas, Nocardia, Penicillium, Phanerochaete, *Pseudomonas*, *Rhizoctonia*, *Serratia*, *Trametes*, and *Xanthobacter (*Okoh, 2001; Barth, 2003; Lliros *et al.,* 2003; Chaillana *et al.,* 2004).

In recent times several strains of fungi and actinomycetes were also confirmed to be important agents for the bioremediation of hydrocarbon-contaminated sites (April *et al.,* 2000; Zhang *et al.,* 2006). Soil fauna have also been implicated in bioremediation as they redistribute microbes or help reintroduce them from less contaminated soil layers. Particularly, worms of various sizes also mix the soil and make it more porous; the increase in porosity also provides for improved aeration (Romantschuk *et al.,* 2001) which is necessary for effective bioremediation.

Furthermore, bioremediation processes most times employ the use of microorganisms such as *Arthrobacter spp*, *Pseudomonas veronii*, and *Bacillus cereus* (Kanmani *et al.,* 2012) that adopt different detoxifying mechanisms such as biosorption, bioaccumulation, biotransformation and biomineralization that can be utilized for bioremediation either ex situ or in situ (Lim *et al.,* 2013).

Implications of high levels of heavy metals in the environment and their effects on humans

Heavy metals are regarded as trace elements because of their presence in minute concentrations (ppb range to less than 10ppm) in various environmental measurements (Kabata-Pendia, 2001). Their bioavailability is affected by both chemical and physical factors. The most commonly associated physical factor that influences heavy metals are temperature, phase association, adsorption and sequestration; while chemical factors have impact on their speciation at thermodynamic equilibrium, complexation kinetics, lipid solubility and octanol/water partition coefficients (Hamelink *et al.,* 1994). It is also very important to note that biological factors such as species characteristics, trophic interactions, and biochemical/physiological adaptation, also play an important role in affecting the bioavailability of heavy metals.

A number of heavy metals have been found to be carcinogenic to the human body. Some of these carcinogenic metals include arsenic, cadmium, chromium, and nickel. These metals have all been associated with DNA damage through base pair mutation, deletion, or oxygen radical attack on DNA (Landolph, 1994). A number of research studies done using animal models also suggest that heavy metals demonstrated reproductive and teratogenic effects. Furthermore, a number of minute epidemiologic studies have noted an inverse relationship between cadmium in cord blood; maternal blood or maternal urine and birth weight and length at birth (Nishijo *et al.,* 2004; Zhang *et al.,* 2004).

Animals and plants both suffer greatly from the impact of crude oil spillage; this can also be said about humans as well. The ingestion, skin contact, and inhalation of the other constituents of spilled crude oil also have some immediate and long-term health implications. In Ordinioha and Seiyefa (2013) research on some of the impacts of crude oil pollution in the Niger Delta region of Nigeria, they both found out that although the acute manifestations of the exposures were often mild and transient, there was also severe exposures as reported in younger children as well, children who were as little as 2-year-old.

The resultant effect of hydrocarbon or crude oil exposure could result to acute renal failure (Otaigbe and Adesina 2005), or even hepatoxicity (Eyong *et al.,* 2004) and haemotoxicity (Sunmonu and Oloyede, 2007) as reported in the animal studies. The period prevalence of the symptoms reported in the Niger delta region were noted to be higher than the prevalence reported in the grounded oil tankers which indicated a high level of exposure in the Niger delta region. Also, as reported by some research on the impact of crude oil on children, it was also noted that there was a significantly high prevalence of diarrhoea in the Niger delta; this however was attributed to the consumption of contaminated fishes and animals killed by the spill.

Heavy metals are present in our soil and water bodies, as previously highlighted the common ones in our environment include: arsenic, cadmium, chromium, selenium, copper, lead, mercury, nickel, silver, zinc etc. They are not only cytotoxic but also carcinogenic and mutagenic in nature (Salem *et al.,* 2010). It has been observed that the presence of high levels of heavy metals is of significant concern for ecological, evolutionary, nutritional and environmental reasons (Jaishankar *et al.,* 2013).

Essentially, some heavy metals play very important roles in maintaining the optimal functioning of both plants and animals. This is because some heavy metals exert biochemical and physiological functions in plants and animals. They are important constituents of several key enzymes and play important roles in various oxidation-reduction reactions (WHO, 1999). For example, copper is important in animals because it serves as an essential co-factor for several oxidative stress-related enzymes such as catalase, superoxide dismutase, peroxidase, cytochrome C oxidases, ferroxidases, monoamine oxidase, and dopamine β-monooxygenase Stern (2010); ATSDR (2002). These enzymes play significant roles in the regulation of oxidative stress as well as its generation.

Also, copper serves as an essential nutrient that is incorporated into a number of metalloenzymes involved in haemoglobin formation, carbohydrate metabolism, catecholamine biosynthesis, and they form cross-link with body collagen, elastin, and hair keratin. The ability of copper to cycle between an oxidized state, Cu(II), and reduced state, Cu(I) makes it an essential element in haemoglobin that constitutes part of the erythrocytes not forgetting its redox reactions Stern (2010); ATSDR (2002). However, the redox reaction property of copper also makes it potentially toxic because the transitions between Cu(II) and Cu(I) can result in the generation of superoxide and hydroxyl radicals (Stern, 2010). Also, excessive exposure to copper has been linked to cellular damage leading to Wilson disease in humans (Tchounwou *et al.,* 2008). Similar to copper, several other essential elements are required for biologic functioning; however, an excess amount of such metals produces cellular and tissue damage leading to a variety of adverse effects and human diseases.

For some other metals like chromium there is little to no beneficial impact it plays in the human body and also to animals (Chang *et al.,* 1996). Other heavy metals such as aluminium (Al), arsenic (As), beryllium (Be), barium (Ba), cadmium (Cd), gallium (Ga), germanium (Ge), gold (Au), indium (In), lead (Pb), lithium (Li), mercury (Hg), nickel (Ni), platinum (Pt), silver (Ag), titanium (Ti), vanadium (V) and uranium (U) do not have any proven and established biological functions as such considered as non-essential metals (Chang *et al.,* 1996).

Arsenic is a well-known heavy metal which is ubiquitous in nature and detected at low concentrations in virtually all environmental matrices (ATSDR, 2000). Arsenic occurs in many forms in nature, the major inorganic forms of arsenic include the trivalent arsenite and the pentavalent arsenate. Some of the organic forms occur as methylated metabolites such as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide.

One of the major ways by which arsenic gets exposed to the external environment is through environmental pollution. Natural occurrences such volcanic eruptions and soil erosion, and anthropogenic activities (i.e., activities carried out by man such soil tillage, crude oil exploration and mining) (ATSDR, 2000). There are a number of arsenic-containing compounds are produced by man (industrially), and have been used to manufacture finished-products with agricultural applications such as insecticides, herbicides, fungicides, algaecides, sheep dips, wood preservatives, and dye-stuffs.

Aside from their agricultural applications, arsenic is also used in veterinary medicine for the eradication of tapeworms in animals such as sheep and cattle (Tchounwou *et al.,* 1999). Arsenic compounds have also been used in human medicine for the treatment of several pathogenic infections for at least a century such as the treatment of syphilis, yaws, amoebic dysentery, and trypanosomaiasis caused by the bite of tsetse fly (Centeno *et al.,* 2005; Tchounwou *et al.,* 1999). In recent times, the utilization of arsenic-based drugs are still used in treating a number of tropical diseases such as African sleeping sickness caused by trypanosomaiasis and amoebic dysentery, and in veterinary medicine to treat parasitic diseases, including filariasis caused by filarial worms in dogs and black head in turkeys and chickens (Centeno *et al.,* 2005).

Apart from its importance in the treatment of parasitic infections in humans, recently, arsenic trioxide has been approved by the United States Food and Drug Administration as an anticancer agent in the treatment of acute promeylocytic leukaemia (Rousselot *et al.,* 1999). In its role as an anticancer agent, it has been found that arsenic plays a significant role in the induction of programmed cell death (apoptosis) in leukaemia cells (Tchounwou *et al.,* 2012).

Arsenic which is an example of heavy metal has been found to cause harm to the environment and humans as previously elaborated in previously. It is toxic and available in the form of oxides or sulphides or as a salt of iron, sodium, calcium, copper, etc. (Singh *et al.,* 2017). It is estimated that millions of people are exposed to arsenic chronically throughout the world, especially in countries like Bangladesh, India, Chile, Uruguay, Mexico, Taiwan and Nigeria where the ground water is contaminated with high concentrations of arsenic. In Nigeria, exposure to arsenic is because of crude oil exploration and spillage especially in the Niger Delta region. Also, there is evidence that suggests that people who reside at the North Western part of Nigeria where gold mining takes place may be exposed to large concentrations of arsenic.

Exposure to arsenic typically occurs via the oral route (ingestion), inhalation, dermal contact, and the parenteral route to some extent (ATSDR, 2000). Arsenic concentrations in air range from 1 - 3 ng/m^3 in remote locations (away from human releases), and from 20 to 100 ng/m^3 in urban regions. 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 (Morton and Dunnette, 1994). Drinking water may get contaminated by the use of arsenical pesticides, natural mineral deposits or inappropriate disposal of arsenical chemicals. This metal causes malfunctioning in cellular respiration, cell enzymatic activities and mitosis (Mazumder, 2018).

Human exposure to arsenic also results in pigmentation and keratosis of the skin (Martin and Griswold, 2009). Lower levels of arsenic exposure can cause nausea and vomiting, reduced production of erythrocytes and leukocytes, abnormal heartbeat, pricking sensation in hands and legs, and damage to blood vessels. Long-term exposure can lead to the formation of skin lesions, internal cancers, neurological problems, pulmonary disease, peripheral vascular disease, hypertension and cardiovascular disease and diabetes mellitus (Smith *et al.,* 2010).

Lead is a metal that occur naturally; by nature, it has a bluish-grey colouration and present in small amounts in the earth's crust. Although lead occurs naturally in the environment, the various human activities such as fossil fuels burning, mining, and manufacturing contribute significantly to the release of high concentrations.

Lead is a highly toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. The sources of lead were gasoline and house paint, which has been extended to lead bullets, plumbing pipes, pewter pitchers, storage batteries, toys and faucets (Thürmer *et al.,* 2012). Lead causes toxicity by increasing the level of oxidative stress, which is a condition caused by an elevation in the concentration of free radicals, and a reduction in the activities of antioxidants. Reactive oxygen species (ROS) present due to oxidative stress may cause structural damage to cells, proteins, nucleic acid, membranes, and lipids, resulting in a stressed situation at a cellular level (Mathew *et al.,* 2011).

It has been also observed that the uptake of lead in plants reduces their survival rates, thereby reducing biomass and quality. Lead treatment was found to cause huge instability in ion uptake by plants, which in turn leads to significant metabolic changes in photosynthetic capacity and ultimately in a strong inhibition of plant growth (Mostafa *et al.,* 2012). Exposure to lead can result in different effects depending on if it is acute or chronic exposure. There are a number of ways through which humans gets in contact with lead. One of major forms of exposures is mainly via inhalation of lead-contaminated dust particles or aerosols, and ingestion of lead-contaminated food, water, and paints (ATSDR, 1999).

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 concentration in the skeleton represents the major body fraction (Flora *et al.,* 2006). When it bothers on lead, the nervous system is the most vulnerable target of lead poisoning causing a number of health abnormalities such as headache, poor attention spam, irritability, loss of memory and dullness are some of the early symptoms of the effects of lead exposure on the central nervous system (CDC, 2001).

One of the most common mechanisms by which lead carries out its toxic effect is through biochemical processes that include lead's ability to inhibit or mimic the actions of elements like calcium and to interact with biological compounds like proteins (ATSDR, 1999). In the human body the skeletal system which is composed on mainly bones has the highest deposit of calcium; however, when lead gets into the body system it has the potential of incorporating itself with other minerals in place of calcium. Lead binds to biological molecules and thereby interfering with their function by several mechanisms. For example, lead binds to sulfhydryl and amide groups of enzymes, altering their configuration and diminishing their activities.

This heavy metal also has the ability when in systemic circulation to compete with essential metallic cations for binding sites, inhibiting enzyme activity, or altering the transport of essential cations such as calcium (Flora *et al.,* 2007). Many researches carried out lead have shown that lead intoxication induces a cellular damage mediated by the formation of reactive oxygen species (ROS) (Hermes-Lima, Pereira and Bechara 1991). Reactive oxygen species are simple compounds that are very unstable in nature, they can react with biological molecules and as a result of this causing both cellular and tissue damage to vital structures of the body (Ben-Chioma *et al.,* 2020). In addition, Jiun and Hseien (1994) both demonstrated that the levels of malondialdehyde (MDA) in blood had very strong correlation with lead concentration in the blood of exposed workers.

A number of research studies have also shown that the activities of antioxidant enzymes that are involved in the removal radicals and reactive oxygen species (ROS) such as superoxide dismutase (SOD), and glutathione peroxidase in erythrocytes of workers exposed to lead are remarkably higher than that in non-exposed workers (Bechara et al 1993). In a series of investigations carried out by Tchounwou and Colleagues (2012) they found out that lead-induced toxicity and apoptosis in human cancer cells involved several cellular and molecular processes including induction of cell death and oxidative stress (Yedjou and Tchounwou, 2008), transcriptional activation of stress genes, DNA damage, externalization of phosphatidylserine and activation of caspase-3 (Yedjou *et al.,* 2010).

Acute exposure can cause loss of appetite, headache, hypertension, abdominal pain, renal dysfunction, fatigue, sleeplessness, arthritis, hallucinations and vertigo. Chronic exposure to lead can result in mental retardation, birth defects, psychosis, allergies, dyslexia, weight loss, hyperactivity, paralysis, muscular weakness, brain damage, and kidney damage and may even cause death (Martin and Griswold, 2009).

Since the late 1970's, human exposure to lead has decreased significantly because of multiple efforts including the removal of lead in gasoline, and the reduction of lead levels in paints used for residential apartments, food and drink cans, and plumbing systems (ATSDR, 1999). In the United States a number of federal programs (ATSDR, 1999) implemented by various tiers of government both state and local health governments have not only focused on banning lead in gasoline, paint and soldered cans, but have also supported screening programs for lead poisoning in children and lead abatement in housing (CDC, 1991). Even with the tremendous efforts in trying to reduce exposure to lead, human exposure continuous to remain a serious health problem (Pirkle *et al.,* 1998). Lead is the most systemic toxicant that affects many organs in the body including the kidneys, liver, central nervous system, haematopoietic system, endocrine system, and reproductive system (ATSDR, 1999).

Mercury is a naturally occurring metal which is a shiny silver-white, odourless liquid and becomes colourless and odourless gas when heated. Mercury is very toxic and exceedingly bio-accumulative. Its presence adversely affects the marine environment and hence many studies are directed toward the distribution of mercury in a water environment. Most of the mercury pollution has come from human activities such as mining, agricultural activities, and industrial wastes (Chen *et al.,* 2012).

Experimental studies on the effects of mercury using animal models have shown that mercury exposure has a pathological effect on the brain causing marked cellular degeneration and necrosis (Patrick, 2012). The brain remains the target organ for mercury, yet it can impair any organ and lead to the malfunctioning of nerves, kidneys and muscles. It can disrupt the membrane potential and interrupt intracellular calcium homeostasis. Mercury vapours can cause bronchitis, asthma and temporary respiratory problems.

Cadmium is another very toxic heavy metal that causes great harm when exposed to humans and animals. Once this metal gets absorbed by humans, it will accumulate inside the body throughout life. About three-fourths of cadmium is used in alkaline batteries as an electrode component, the remaining part is used in coatings, pigments and plating and as a plastic stabilizer. Humans may get exposed to this metal primarily by inhalation and ingestion and can suffer from acute and chronic intoxications (Bernard, 2008). It also causes high toxicity to plants and has been found to influence the enzymatic systems of cells, and oxidative stress and induce a nutritional deficiency in plants (Irfan *et al.,* 2013).

One of the best ways of measuring cadmium presence in the human body is simply by determining its amounts in blood or urine. Blood cadmium reflects recent cadmium exposure (from smoking, for example). Cadmium in urine (usually adjusted for dilution by calculating the cadmium/creatinine ratio) indicates accumulation, or kidney burden of cadmium (Jarup *et al.,* 1998). In the United State, reports has it that an estimate of 2.3% of the U.S. population has elevated levels of urine cadmium (>2μg/g creatinine), a marker of chronic exposure and body burden (Becker et al. 2002). Blood and urine cadmium levels are typically higher in people who smoke cigarette and acute levels in former smokers and lower in non-smokers (Mannino *et al.,* 2004). As a result of continuing use of cadmium in industrial processes, the environmental contamination and human exposure to cadmium have dramatically increased during the past century (Elinder and Järup, 1996).

The toxicity it causes in humans has not been fully understood, but studies have shown that lead causes nephrotoxicity when it encounters renal tissues. If cadmium is ingested in higher amounts, it can lead to stomach irritation and result in vomiting and diarrhoea (Chakraborty *et al.,* 2013). On very long exposure time at lower concentrations, it can become deposited in the kidney and finally lead to kidney disease, fragile bones, and lung damage (Bernard, 2008).

Several environmental agencies as well as food and drugs agencies have classified cadmium compounds as being carcinogenic to humans. According to International Agency for Research on Cancer and the United States National Toxicology Program have both concluded that there is adequate evidence that cadmium is a human carcinogen. This designation as a human carcinogen is based on very strong suggestions and repeated findings that links occupational cadmium exposure and lung cancer, as well as on very strong experimental researches using animals (rodents) data showing the pulmonary system as a target site (IARC, 1993).

According to the numerous data on cadmium and its effects on the human body, it has been shown that the lung is the most definitively established site of human carcinogenesis from cadmium exposure. Other target tissues of cadmium carcinogenesis in animals include injection sites, adrenals, testes, and the haemopoietic system which include the bones (Waalkes *et al.,* 1996; IARC, 1993). In some other research studies, occupational or environmental cadmium exposure has also been associated with development of several types of cancers such as cancer of the prostate, kidney, liver, hematopoietic system and stomach (Waalkes *et al.,* 1996).

Chromium happens to be another heavy metal that has a significant effect on both plants and animals when in contact with it. Chromium occurs in several oxidation states in the environment ranging from Cr^{2+} to Cr^{6+} (Rodríguez *et al.,* 2009). The most commonly occurring forms of Cr are trivalent- Cr^{3+} and hexavalent- Cr^{6+}, with both states being toxic to animals, humans, and plants (Mohanty and Kumar, 2013).

The release of chromium in the environment is a result of anthropogenic activities through sewage and fertilizers (Ghani, 2011). The presence of excess chromium beyond the permissible limit is destructive to plants since it severely affects the biological factors of the plant and enters the food chain on the consumption of these plant materials. Common features due to Chromium phytotoxicity are reduction in root growth, leaf chlorosis, inhibition of seed germination and depressed biomass.

Exposure to chromium occurs both through non-occupational routes and occupational routes. Non-occupational exposure occurs via ingestion of chromium containing food and water that can be seen in regions that have been heavily exposed to this metal through anthropogenic activities, whereas occupational exposure occurs via inhalation. Chromium concentrations range between 1 and 3000 mg/kg in soil, 5 to 800 µg/L in sea water, and 26 µg/L to 5.2 mg/L in water bodies such as rivers and lakes (Jacobs and Testa 2005). Chromium content in foods varies greatly and depends on the processing and preparation. In general, most fresh foods typically contain chromium levels ranging from <10 to 1,300 µg/kg.

According to the United States Agency for Toxic Substances and Disease Registry (ATSDR), people who work in chromium-related industries can be exposed to chromium concentrations two orders of magnitude higher than the general population (ATSDR, 2008). In as much as the principal route of human exposure to chromium is through inhalation, and the lung is the primary target organ as similar as reports done on cadmium, significant human exposure to chromium has also been reported to take place through the skin (Shelnutt *et al.,* 2007). For instance, the widespread incidence of dermatitis noticed among construction workers is attributed to their exposure to chromium present in cement (Shelnutt *et al.,* 2007). Occupational and environmental exposure to Cr (VI)-containing compounds is known to cause multi-organ toxicity such as renal damage, allergy and asthma, and cancer of the respiratory tract in humans (Goyer, 2001).

Exposure to chromium compounds can result in the formation of ulcers, which will persist for months and heal very slowly. Ulcers on the nasal septum are very common in the case of chromate workers. Exposure to higher amounts of chromium compounds in humans can lead to the inhibition of erythrocyte glutathione reductase, which in turn lowers the capacity to reduce methaemoglobin to haemoglobin (O'Brien *et al.,* 2001).

There have been adverse health effects caused by Cr(VI) as reported by scientists after clinical investigations in humans. Epidemiological investigations have reported respiratory cancers in workers occupationally exposed to Cr(VI)-containing compounds (Dayan and Paine 2001). Chromium plays a role in DNA strand breakage in peripheral lymphocytes and lipid peroxidation products in urine observed in chromium-exposed workers also support the evidence of Cr (VI)-induced toxicity to humans (Goulart *et al.,* 2005). One of the most supported causes of gene damage by chromium is because of oxidative reactions which causes serious chromosomal abnormalities (Wise *et al.,* 2002), and DNA strand breaks (Xie *et al.,* 2005). Aside from the lethal characteristics of chromium, it is very important to note that recent studies indicate a biological relevance of non-oxidative mechanisms in Cr(VI) carcinogenesis (Zhitkovich *et al.,* 2001). Various hypotheses have been proposed to explain the carcinogenicity of chromium and its salts; however, some inherent difficulties exist when discussing metal carcinogenesis.

Aluminium is the third most abundant element found in the earth's crust. Aluminium occurs naturally in the air, water and soil. The mining and processing of aluminium elevate its level in the environment (ATSDR, 2010). The interaction of Al3+ with the apoplastic, plasma membrane, and symplastic targets leads to toxicity and distracts the physical and cellular processes in plants.

Aluminium exposure is probably a risk factor for the onset of Alzheimer's disease (AD) in humans, as quoted by the WHO in 1997. Contact dermatitis and irritant dermatitis were seen in persons who were exposed to aluminium in their place of work. Aluminium showed adverse effects on the nervous system and resulted in the loss of memory, problems with balance and loss of coordination (Krewski *et al.,* 2007).

Iron is one of the most common and abundant metals on the earth's crust. Iron is one of the most crucial elements for the growth and survival of almost all living organisms (Valko *et al.,* 2005). The source of iron in the surface water is anthropogenic and is related to mining activities. Iron toxicity in humans comes as a result of high exposure to iron leading to the circulation of free unbound iron. This circulating unbound iron results in a corrosive effect on the gastrointestinal tract and biological fluids.

Exposure to nickel comes in various ways due to its usefulness in various products used by man, such as in the production of batteries, nickel-plated jewellery, machine parts, nickel plating on metallic objects, manufacture of steel, cigarette smoking, wire, electrical parts, etc. Also, it can be found in foodstuffs such as imitation whip cream, unrefined grains and cereals, commercial peanut butter, hydrogenated vegetable oils, as well as contaminated alcoholic beverages (Sharma *et al.,* 2014).

Materials and Methods

Study Area

The research study was conducted in the Nkeleoken-Alode community situated in the Eleme Local Government Area of Rivers State, Nigeria. Nkeleoken Alode is within the South-Eastern part of Eleme LGA. The community lies in latitudes 4◦45'N and 7◦15N and longitude 6◦50'E and 7◦25'E. It is always rainy in this area from the months of April to October with the dry season setting in later in the year (November to March). Temperatures throughout the year in the city are relatively constant, showing little variation throughout the course of the year. Average temperatures are typically between 25 °C-28 °C.

Sample Collection

Soil and water samples were collected from three (3) sites which included: Unpolluted sites, Polluted unremediated sites, Polluted remediated sites. Using a sterile aluminium foil, 50g of soil samples were collected while water samples were collected with a 250ml sterile container.

Sample Analysis

Soil and water samples collected from sites undergoing bio-remediation in Nkeleoken-Alode, polluted unremediated sites from Ejamah Ebubu and unpolluted sites in an apparent clean area within the village in Eleme Local Government were analyzed for the presence of heavy metals (Arsenic, Cadmium, Chromium, Lead and Nickel).

Method: Atomic Absorption Spectrophotometer

Principle:

Atomic Absorption Spectrophotometer measures the concentrations of elements present in a liquid sample. It utilizes the principle that elements in the gas phase absorb light at very specific wavelengths which gives the technique excellent specificity and detection limits. The absorption is proportional to the concentration of the element.

Procedure: Acid Digestion

A 5g of air-dried soil that had been well-grounded was prepared. The samples were weighed into the digestion vessels that were already well-labelled. Under the hood cupboard, 9ml of concentrated Hydrochloric acid (HCL) was measured with a 25ml graduated measuring cylinder and 3ml of concentrated HNO3 was measured into the HCL in the digestion beakers. The beaker was transferred onto a heating mantle at the temperature of 110°c. The solution was allowed to stand until a pale-yellow solution was observed, and the brown fume of HNO3 ceased to exist. At that stage, the solution was transferred from the top of the hot plate and allowed to cool before filtration took place through the 0.2mm Whatman filter paper into the measuring cylinder. Deionized water was used to rinse both the walls of the digestion vessel as well as the funnel. The filtrate solution was made up to the 100ml mark with de-ionized water. After the filtration process, the filtrate was transferred into a small plastic bottle. The filtrate was aspirated using an Atomic Absorption Spectrophotometer after an approximate hollow cathode lamp with its corresponding wavelength had been installed. All necessary standardization was carried out according to the manufacturer's instructions.

Statistical Analysis

Values of Raw data obtained were evaluated statistically using GraphPad Prism Version 9.0 (California, USA). Descriptive statistical tools used are mean and Standard Deviation (SD) of heavy metals concentration in soil and water samples. Inferential statistics were done using Turkey Multiple Comparison Test. Statistical significance was set at $p =< 0.05$. Results obtained were expressed as Mean±SD.

Limitations

Some limitations were observed during the course of this study and must be acknowledged. Few sites were sampled during the course of this study as compared to other studies where more than one site was sampled. This was due to restricted access to the sites undergoing bio-remediation.

Results

Result of Heavy Metals in Soil Sample from Polluted Remediated Unpolluted and Polluted Unremediated Sites.

Analysis was carried out on the following heavy metals: lead, arsenic, nickel, cadmium and chromium. Analysis of lead results showed significantly higher values in polluted remediated sites and polluted unremediated sites when compared to unpolluted sites. There were significant differences when polluted remediated sites were compared with polluted unremediated sites. Results obtained from the arsenic evaluation showed significantly higher values in polluted remediated and polluted unremediated sites when compared to unpolluted sites ($p<0.05$). There was no significant difference when polluted remediated sites were compared with polluted unremediated sites. Results obtained from nickel evaluation showed significantly higher values for polluted remediated sites and polluted unremediated sites when compared with unpolluted sites.

There was no significant difference when polluted remediated sites were compared with polluted unremediated sites ($p>0.05$). Results obtained from cadmium evaluation showed significantly lower values for polluted remediated sites and polluted unremediated sites when compared with unpolluted sites ($p<0.05$). There was also no significant difference when polluted remediated sites were compared with polluted unremediated sites at ($p>0.05$). The comparison of chromium results showed significantly higher values for polluted remediated sites and polluted unremediated sites when compared with unpolluted sites. There was also a significant difference when polluted remediated sites were compared with polluted unremediated sites (Table 1).

Table 1: Results of Heavy Metals in Soil Sample from Polluted Remediated, Unpolluted and Polluted Unremediated Sites

Heavy Metals	Polluted remediated site	Unpolluted Site	Polluted unremediated site	p-value	F-value	Remark
Lead (ppm)	1.283±0.859[ac]	0.016±0.001[a]	2.090±0.0193[bc]	0.0092	8.792	S
Arsenic (ppm)	0.1548±0.206	0.004±0.0004	0.123±0.004	0.3978	1.037	NS
Cadmium (ppm)	0.051±0.037	0.002±0.001	0.048±0.003	0.0770	3.592	NS
Nickel (ppm)	1.027±0.834	0.002±0.001	0.5770±0.089	0.1176	2.830	NS
Chromium (ppm)	0.803±0.422[bd]	0.002±0.001[a]	3.712±0.205[bc]	<0.0001	119.0	S

Lead: Values in the same row with different superscripts (a, b) differ significantly when unpolluted sites site was compared with polluted unremediated sites site as well as polluted remediated sites site. However, values in the same row with the same superscript (c) do not differ significantly when the polluted remediated site was compared with polluted unremediated sites site. Chromium: Values in the same row with different superscripts (a, b) differ significantly when unpolluted remediated sites site was compared with polluted unremediated sites as well as unpolluted sites. Also, values in the same row with different superscripts (c, d) differ significantly when polluted unremediated sites were compared with polluted remediated sites.

Result of Heavy Metals in Water Samples from Polluted Remediated, Unpolluted and Polluted Unremediated Sites

Analysis was carried out on the following heavy metals: lead, arsenic, nickel, cadmium and chromium. Analysis of lead results showed a statistically significant lower values in polluted remediated sites when compared to unpolluted sites and polluted unremediated sites. There were no significant differences when polluted unremediated sites were compared with unpolluted sites ($p>0.05$). Results obtained from the arsenic evaluation showed no significant difference in values in polluted remediated and polluted unremediated sites when compared together. There were no significant differences when polluted remediated sites and polluted unremediated sites were compared with unpolluted sites. Results obtained from cadmium evaluation showed statistically significant higher values for polluted unremediated sites when compared with unpolluted sites. There was no significant difference when polluted remediated sites were compared with unpolluted sites ($p>0.05$). The comparison of nickel results showed significantly higher values for polluted unremediated sites when compared with unpolluted sites and polluted remediated sites. There was also a statistically significant difference between polluted remediated sites compared with unpolluted sites. Analysis of chromium showed a significantly higher values for polluted unremediated sites when compared with unpolluted sites and polluted remediated sites ($p<0.05$) (Table 2).

Table 2: Result of Heavy Metals in Water Sample from Polluted Remediated, Unpolluted and Polluted Unremediated Sites.

Heavy Metals	Polluted remediated site	Unpolluted Site	Polluted unremediated site	p-value	F-value	Remark
Lead (ppm)	0.002±0.001	0.053±0.099	0.114±0.001	0.2103	1.907	NS
Arsenic (ppm)	0.007±0.004	0.002±0.001	0.007±0.001	0.4573	0.8804	NS
Cadmium (ppm)	0.001±0.0007^{ad}	0.002±0.001^{a}	0.006±0.001^{bc}	0.0003	27.03	S
Nickel (ppm)	0.035±0.031^{ad}	0.003±0.001^{a}	1.104±0.001^{bc}	<0.0001	1546	S
Chromium (ppm)	0.154±0.122^{ad}	0.025±0.002^{a}	0.538±0.081^{bc}	0.0004	23.98	S

Cadmium, Nickel and Chromium: Values in the same row with different superscripts (a, b) differ significantly when water is unpolluted sites was compared with water in polluted unremediated sites as well as water in polluted remediated sites. Also, values in the same row with different superscripts (c, d) differ significantly when water is polluted in unremediated sites were compared with water in polluted remediated sites.

Discussion

Since the advent of oil in Nigeria in 1956, the oil sector has grown to be a dominant component of the country's economy (Adejoh, 2014). In 2004, Nigeria had an average exportation rate of 2.5 million barrels of petroleum per day, the oil and gas sector accounted for about 80% of total government revenue and about 90–95% of export revenues (Aluko, 2004). According to the world's ranking, Nigeria is among the world's top ten oil-producing nations and sits comfortably at the top spot in Africa (Olokesusi, 2005).

In as much as the country has produced enormous crude oil not so much can be done in protecting the natural environment during the mining. This has, however, come at a great price to the Niger Delta region, where virtually all of the oil production in Nigeria takes place and experiences a higher rate of oil spills. The oil contains several types of heavy metals with dangerous health effects; hence oil spills result in environmental contamination with heavy metals and heavy metal toxicity, posing a health risk to people who live in this region (Chinedu and Chukwuma, 2018).

Heavy metals are metallic elements with a relative density of at least five times that of water. These elements have several toxic effects on humans, and their toxicity is almost interrelated with their heaviness. In recent times, there has been an increase in ecological and global health concerns regarding environmental pollution by heavy metals. Although these metals occur naturally and are found throughout the earth's crust in low quantities, human exposure generally results from anthropogenic activities such as smelting, mining, and agricultural and industrial activities.

This present study evaluated the toxicity of heavy metals in soil and water in Nkeleoken Alode, an oil-producing community in Eleme Local Government Area of Rivers State of Nigeria. Comparing the results of the analysis of the heavy metals obtained from the soil sample, it was seen that there was a statistically significant increase in the concentrations of lead and chromium in the soil sample obtained from the three sites. There was a statistically significant increase in the lead and chromium in polluted unremediated sites when compared to the concentration of heavy metals obtained in the other two sites (unpolluted and polluted remediated sites). The concentrations of heavy metals such as Arsenic, cadmium and nickel showed no statistical increase as shown in Table 1. This is in support of the study by Owamah (2013) which evaluated the concentration of heavy metals (Pb, Ni, Cu, Cr, Fe, Co, Cd and Hg) in soil from the Riverbanks of Ijana, Warri showed that the concentrations of heavy metals from polluted soil were higher than the control.

The findings from Chinedu and Chukwuma (2018) on "Oil Spillage and Heavy Metals Toxicity Risk in the Niger Delta, Nigeria" suggests that although a large quantity of crude oil has been released into the Niger Delta region, the concentration of heavy metals present on both soil and water bodies vary across the different communities in the Niger Delta region. The concentration of heavy metals in the aquatic and terrestrial environments in some communities may be within allowable limits but may be above allowable limits in others, elevating the risk of toxicity. However, as part of their recommendation, they suggest that a holistic evaluation of heavy metals is needed in the Niger Delta region to identify communities at risk of heavy metals toxicity and corresponding risk levels (Chinedu and Chukwuma, 2018). This recommendation is in line with our research study which is aimed at evaluating the concentration of specific heavy metals in a localized region that constitute part of the Niger Delta region.

Another study by Ogamba *et al.* (2017) which evaluated the level of heavy metals in soil and sediments from Kolo Creek reported that the concentrations of heavy metals did not show any statistically significant difference between the test and control soil and sediment samples. Analysis of heavy metal toxicity of water collected from the same region showed that there was a statistical increase in the concentrations of cadmium, nickel and chromium in the water sample obtained from the three sites (unpolluted site, polluted unremediated site and polluted remediated site). There was a statistically significant increase in the cadmium, nickel and chromium in the polluted remediated site when compared to the concentration of heavy metals obtained in the other two sites (unpolluted and polluted unremediated). The concentrations of heavy metals such as arsenic and lead showed no statistical increase as shown in (Table 2).

This is in contrast with the study by Ubiogoro and Adeyemo (2018), in which the researchers evaluated water samples from the Gbokodo river in Warri, the River Ethiope in Sapele, the Urie River in Igbide Isoko, Asaba-Ase creek, the Aragba River in Abraka, and Uzere creek and found that most heavy metals (Arsenic, copper, cadmium and chromium) showed no significant difference between the test and control water samples.

Conclusion

The concentrations of heavy metals in the soil and water samples analysed in this study showed that there was a significant increase in the heavy metal concentrations between the test and control sites. Concerning the increased concentrations of heavy metals (lead, nickel, cadmium and chromium), this current study showed that the occupants of the Niger Delta region are at risk of heavy metal toxicity because of the large amount of crude oil being spilt in the region. To minimize the level of exposure to heavy metals and the risk of toxicity in the Niger Delta region, effective strategies should be adopted to reduce the occurrence of crude oil spills. Containment and remediation of crude oil spills should be more rapid and efficient to lower human exposure, and in restoring vegetation. In addition, due to the wide range of detrimental health effects that heavy metals can elicit in humans, the government should establish a centre where the local population can be clinically assessed and given medical attention for the detoxification of heavy metals if present in their bodies.

Recommendations

As seen in this study, bioremediation carried out at some of the remediated sites had not yet returned the sites to their natural state. Therefore, it is recommended that a different bioremediation technique should be employed in remediated sites in the Nkeleoken-Alode community of Eleme Local Government Area. As a result of the health impacts the various heavy metals analysed have on the human body, it remains imperative that locals in this region as well as the Niger Delta region are clinically assessed for evaluation of toxicity because of direct or indirect exposure to these heavy metals. Further studies should be done in this area to ascertain the level of health challenges caused by indiscriminate oil exploration, and illegal oil refining to the locals of petroleum communities in the Niger Delta region.

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