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ASSESSMENT OF HEAVY METALS CONCENTRATION IN CRUDE OIL CONTAMINATED WATER SAMPLES OF THREE COMMUNITIES OF IKPOKPO, ATANBA, AND OKPELE-AMA OF GBARAMATU KINGDOM, ALONG THE ESCRAVOS RIVER IN WARRI SOUTH WEST LOCAL GOVERNMENT AREA OF DELTA STATE, NIGERIA

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ABSTRACT: *Background**:** Water plays a significant role in maintaining the human health and welfare. Increase in industrialization and various human activities have recently increased the pollution of surface water and ground water (WHO, 1997). The aim of this study was to carry out the analysis of the specified heavy metals present in the crude oil contaminated water samples obtained from six different crude oil contaminated sites of three communities of Ikpokpo, Atanba and Okpele-ama of Gbaramatu Kingdom along the Escravos River in Warri South West L.G.A of Delta State, Nigeria, and to determine their health effects on the affected communities aforesaid. Standard analytical method (Atomic Absorption Spectrophotometer – (AAS) Analyst 400 model) was used to carry out the analysis. Table 1, presents the WHO maximum permissible limits of some specified heavy metals in normal drinking water sources. Also, the results of the two samples analysed were all being presented from table 2 to 5 as being indicated in a tabular form. Upon comparison, between the mean values of the crude oil contaminated samples (table 5), with the WHO permissible values (table 1) and normal water samples analysed (table 3), It was found out that the crude oil contaminated water samples values were all above the WHO maximum permissible limits of heavy metals concentrations in normal drinking water sources (WHO, 2003, 2005 and 2011).Therefore, there is need for remediation of the crude oil contaminated water samples to the level of WHO standard guidelines.*

KEYWORDS: heavy metals analysis, water quality, WHO, crude oil spills, contamination.

INTRODUCTION

There is no widely agreed criterion-based definition of a heavy metal. Different meanings may be attached to the term, depending on the context. In metallurgy, for example, a heavy metal may be defined on the basis of density, whereas in physics the distinguishing criterion might be atomic number, and a chemist or biologist would likely be more concerned with chemical behaviour (*Bradl, 2002*). Density criteria range from above 3.5 g/cm^3 to above 7 g/cm^3. Atomic weight definitions can range from greater than sodium (atomic weight 22.98); greater than 40 (excluding s- and f-block metals, hence starting with scandium); or more than 200, i.e. from mercury onwards. Atomic numbers of heavy metals are generally given as greater than 20 (calcium); sometimes this is capped at 92 (uranium) (*Fergusson, 1990*). Definitions based on atomic number have been criticised for including metals with low densities (*Fergusson, 1990*). For example, rubidium in group (column) 1 of the periodic table has an atomic number of 37 but a density of only 1.532 g/cm^3, which is below the threshold figure used by other authors (*Fergusson, 1990*). The same problem may occur with atomic weight based definitions. The United States Pharmacopeia includes a test for heavy metals that involves precipitating metallic impurities as their coloured sulphides." In 1997, Stephen Hawkes, a chemistry professor writing in the context of fifty years' experience with the term, said it applied to "metals with insoluble sulphides and hydroxides, whose salts produce coloured solutions in water and whose complexes are usually coloured" (*Pacyna, 1996*). On the basis of the metals he had seen referred to as heavy metals, he suggested it would useful to define them as (in general) all the metals in periodic table columns 3 to 16 that are in row 4 or greater, in other words, the transition metals and post-transition metals. The lanthanides satisfy Hawkes' three-part description; the status of the actinides is not completely settled (*Pacyna, 1996*).

In biochemistry, heavy metals are sometimes defined—on the basis of the Lewis acid (electronic pair acceptor) behaviour of their ions in aqueous solution—as class B and borderline metals. In this scheme, class A metal ions prefer oxygen donors; class B ions prefer nitrogen or sulphur donors; and borderline or ambivalent ions show either class A or B characteristics, depending on the circumstances *(Stern, 2010).* Class A metals, which tend to have low electro negativity and form bonds with large ionic character, are the alkali and alkaline earths, aluminium, the group 3 metals, and the lanthanides and actinides. Class B metals, which tend to have higher electro negativity and form bonds with considerable covalent character, are mainly the heavier transition and post-transition metals *(Stern, 2010).* Borderline metals largely comprise the lighter transition and post-transition metals (plus arsenic and antimony). The distinction between the class A metals and the other two categories is sharp. A frequently cited proposal to use these classification categories instead of the more evocative name *heavy metal* has not been widely adopted *(Patlolla, 2009*).

List of heavy metals based on density: A density of more than 5 g/cm^3 is sometimes mentioned as a common heavy metal defining factor and, in the absence of a unanimous definition, is used to populate this list and (unless otherwise stated) guide the remainder of the article(*Goyer, 2001*). Metalloids meeting the applicable criteria–arsenic and antimony for example—are sometimes counted as heavy metals, particularly in environmental chemistry, as is the case here Selenium (density 4.8 g/cm^3) is also included in the list. It falls marginally short of the density criterion and is less commonly recognised as a metalloid but has a waterborne chemistry similar in some respects to that of arsenic and antimony (*Goyer, 2001*).

Heavy Metals Toxicity and the Environment: Although heavy metals are naturally occurring elements that are found throughout the earth's crust, most environmental contamination and human exposure result from anthropogenic activities such as mining and smelting operations, industrial production and use, and domestic and agricultural use of metals and metal-containing compounds (*Goyer, 2001*). Environmental contamination can also occur through metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals, sediment re-suspension and metal evaporation from water resources to soil and ground water (*Goyer, 2001*). Industrial sources include metal processing in refineries, coal burning in power plants, petroleum combustion, nuclear power stations and high tension lines, plastics, textiles, microelectronics, wood preservation and paper processing plants (*Goyer, 2001*). It has been reported that metals such as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn) are essential nutrients that are required for various biochemical and physiological functions. Inadequate supply of these micro-nutrients results in a variety of deficiency diseases or syndromes (*Goyer, 2001*). Heavy metals are also considered as trace elements because of their presence in trace concentrations (ppb range to less than 10ppm) in various environmental matrices. Their bioavailability is influenced by physical factors such as temperature, phase association, adsorption and sequestration. It is also affected by chemical factors that influence speciation at thermodynamic equilibrium, complexation kinetics, lipid solubility and octanol/water partition coefficients. The essential 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. Copper for example serves as an essential co-factor for several oxidative stress-related enzymes including catalase, superoxide dismutase, peroxidase, cytochrome c oxidases, ferroxidases, monoamine oxidase, and dopamine β-monooxygenase. Hence, it is an essential nutrient that is incorporated into a number of metalloenzymes involved in haemoglobin formation, carbohydrate metabolism, catecholamine biosynthesis, 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 used by cuproenzymes involved in redox reactions. However, it is this property of copper that also makes it potentially toxic because the transitions between Cu (II) and Cu (I) can result in the generation of superoxide and hydroxyl radicals. Also, excessive exposure to copper has been linked to cellular damage leading to Wilson disease in humans. 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 including chromium and copper, there is a very narrow range of concentrations between beneficial and toxic effects. 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 (*Goyer, 2001*). 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 (*Goyer, 2001*). 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. Several studies from our laboratory have 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, lead, and mercury. Because of their high degree of toxicity, these five elements rank among the priority metals that are of great public health significance. They are all systemic toxicants that are known to induce multiple organ damage, 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 are also 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(*Goyer, 2001*). Heavy metal-induced toxicity and carcinogenicity involves many mechanistic aspects, some of which are not clearly elucidated or understood. However, each metal is known to have unique features and physic-chemical properties that confer to its specific toxicological mechanisms of action. This review provides an analysis of the environmental occurrence, production and use, potential for human exposure, and molecular mechanisms of toxicity, genotoxicity, and carcinogenicity of arsenic, cadmium, chromium, lead, and mercury (*Goyer, 2001*).

Prospects: A comprehensive analysis of published data indicates that heavy metals such as arsenic cadmium, chromium, lead, and mercury, occur naturally. However, anthropogenic activities contribute significantly to environmental contamination. These metals are *(Nriagu, 1989).* Systemic toxicants known to induce adverse health effects in humans, including cardiovascular diseases, developmental abnormalities, neurologic and neurobehavioral disorders, diabetes, hearing loss, hematologic and immunologic disorders, and various types of cancer. The main pathways of exposure include ingestion, inhalation, and dermal contact *(Nriagu, 1989).*The severity of adverse health effects is related to the type of heavy metal and its chemical form, and is also time- and dose-dependent. Among many other factors, speciation plays a key role in metal toxicokinetics and toxicodynamics, and is highly influenced by factors such as valence state, particle size, solubility, biotransformation, and chemical form. Several studies have shown that toxic metals exposure causes long term health problems in human populations *(Nriagu, 1989).* Although the acute and chronic effects are known for some metals, little is known about the health impact of mixtures of toxic elements. Recent reports have pointed out that these toxic elements may interfere metabolically with nutritionally essential metals such as iron, calcium, copper, and zinc *(Nriagu, 1989).* However, the literature is scarce regarding the combined toxicity of heavy metals. Simultaneous exposure to multiple heavy metals may produce a toxic effect that is additive, antagonistic or synergistic *(Nriagu, 1989).*

A recent review of a number of individual studies that addressed metals interactions reported that co-exposure to metal/metalloid mixtures of arsenic, lead and cadmium produced more severe effects at both relatively high dose and low dose levels in a biomarker-specific manner. These effects were found to be mediated by dose, duration of exposure and genetic factors. Also, human co-exposure to cadmium and inorganic arsenic resulted in a more pronounced renal damage than exposure to each of the elements alone. In many areas of metal pollution, chronic low dose exposure to multiple elements is a major public health concern. Elucidating the mechanistic basis of heavy metal interactions is essential for health risk assessment and management of chemical mixtures. Hence, research is needed to further elucidate the molecular mechanisms and public health impact associated with human exposure to mixtures of toxic metals *(Verkleji, 1993).*

Hydrocarbons: Hydrocarbon (HC) group of compounds consist of hydrogen and carbon in their structure. As petrochemical industries are flourishing worldwide, Hydrocarbon contamination has become one of the major environmental problems faced globally (Nwilo and Badejo, 2001). Petroleum exploration and production in the Nigeria's Niger Delta region and export of oil and gas resources by the petroleum sector has substantially improved the nation's economy over the past five decades (Hyne and Norman, 2001). However, activities associated with petroleum exploration, development and production operations have local detrimental and significant impacts on the atmosphere, soils and sediments, surface and groundwater, marine environment, biologically diversity and sustainability of terrestrial ecosystems in the Niger Delta (Nwilo and Badejo, 2001).Discharges of petroleum hydrocarbon and petroleum–derived waste streams have caused environmental pollution, adverse human health effects, detrimental impact on regional economy, socio–economic problems and degradation of host communities in the 9 oil–producing states in the Niger Delta region. Although there are other potential anthropogenic sources of pollution, some of the major environmental consequences such as air pollution, global climate change and oil spills in the Niger Delta may be regional or global in scale (Diaz and Eduardo, 2008). Apart from other anthropogenic emission sources, atmospheric pollution in the region is associated with emissions from flaring and venting of petroleum associated natural gas by petroleum industries (Nwilo and Badejo, 2001). Atmospheric contaminants from anthropogenic activities can be categorized into (i) gaseous pollutants, (ii) persistent organic pollutants, (iii) particulate matter and (iv) trace elements and/or heavy metals (Nwilo and Badejo, 2001). Release of petroleum hydrocarbons into the environment, whether accidentally or due to anthropogenic activities, is a major cause of controlled water and soil pollution and may also contribute to regional atmospheric pollution (Nwilo *et al.*, 2001).

Environment: Environment is particularly being contaminated with accidental releases of petroleum products. Some of the Hydrocarbon compounds can prove carcinogenic and neurotoxin to different life forms. Crude oil extracted from oil fields may have a considerable amount of heavy metals such as cadmium, nickel, zinc, manganese, vanadium, copper, chromium, lead, arsenic and mercury etc as part of the impurities present. This is largely dependent on the mineral bearing rocks where the crude oil was formed. During oil spill, such heavy metals are bound to soil with large chain hydrocarbon compounds after volatile constituents of the oil have vaporized into the atmosphere. In the remediation of contaminated soil, much attention is given to the petroleum hydrocarbons and other related compounds while less or none is given to the associated heavy metals in such contaminated environment. Heavy metals due to their non biodegradable nature can remain bound in soil for a long time; can bioaccumulate into soil biota, leached into underground water and pose a considerable threat to the environment, biodiversity and public health (*Bautista and Rahman, 2016).*

Oil Spills: An oil spill is the release of a liquid petroleum hydrocarbon into the environment, especially marine areas, due to human activity, and is a form of pollution. The term is usually applied to marine oil spills, where oil is released into the ocean or coastal waters, but spills may also occur on land. Oil spills may be due to releases of crude oil from tankers, offshore platforms, drilling rigs and wells, as well as spills of refined petroleum products (such as gasoline, diesel) and their by-products, heavier fuels used by large ships such as bunker fuel, or the spill of any oily refuse or waste oil *(Gundlach, 1987)*.

Oil spill and the Niger Delta (Southern Part of Nigeria): The South region are the principal oil-rich region comprising the states of Akwa Ibom, Bayelsa, Cross River, Delta, Edo and Rivers, while the three remaining oil-rich states are from South West (Ondo) and South East (Abia and Imo) – all can lightly be referred to as the Niger Delta region, even though the core Niger Delta states are Bayelsa, Delta and Rivers. Since the advent of oil and its exploration in the Niger Delta, the region has been neglected in Nigeria's schemes of development compared to its economic contribution. Or put more clearly, the Nigerian government has over the years focussed on oil (exploration) without much consideration for the (development of the) Niger Delta, which is the source of the oil. The region's once green vegetation and adoring blue waters were turned black from the oil exploration activities of the black gold leaving the people unemployed as a result of the destruction of the economic activities in farming and fishing, as well as reduced means of food production and with increased health risk. From an historical perspective, the United Nations Development Programme (*UNDP; 2006*) says that, before the Second World War, a delicate balance existed between the human populations of the Niger Delta and its fragile ecosystem. The exploitation of natural resources did not go beyond the search for medicinal herbs, fuel, game, fish, and construction materials.' The situation is different today as ambitious economic aspiration has destroyed the region's heritage and pillar of livelihood. The Niger Delta region stretches over an approximate 70,000 square kilometres with more than 50 ethnic groupings. The oil companies' operations extend beyond 60% of the land mass so close to the communities with variable impacts on the homes, farmlands and water sources of these people (*UNDP; 2006*). The socio-economic livelihoods of the inhabitants are disrupted by the pollutants from the operations of these oil companies with their main economic sources of fishing and agriculture negatively impacted. Oil spillage is a common occurrence in the Niger Delta and is caused by poor infrastructure maintenance, human error, and intentional vandalism or theft of oil resulting in spills or leaks during processing and transportation. Over the years from 1976 to 1996, spill incidents in total of 4,835 were recorded with 1.897 million barrels of oil lost as pollution to the environment *(Orimoogunje, Oluwagbenga and Ajibolas, 2013).* UNDP (2006) estimates that between 1976 and 2001, an approximate 6,800 spills totalling 3 million barrels of oil were recorded in the Niger Delta region. From Table 1 (below), oil spill cases appear to be increasing over the years. This can be attributed to increased oil production and the lack of enforced regulatory control regarding environmental relations. The estimated barrels of crude oil spilled annually in the Niger Delta over surface and ground waters as well as vegetation and air is 240,000 *(Orimoogunje, Oluwagbenga and Ajibola, 2013).* The health effects of these pollution activities include contamination and poisoning of water, food and the environment resulting in ill health and death (World Health Organization (*WHO, 2003*). Oteh and Okpo *(2012)* gave account of oil spills in the Niger Delta in the past fifty years at an average 1.5 million tons, fifty times more than the volume of oil recorded in 1989 in Exxon Valdez oil spill in Alaska, with corrosion accounting for 50% of the spills, 28% due to sabotage, and 22% to oil production drills and operations. The severity of these frequent and collectively massive spills is only amplified by other environmental problems in the region like seasonal floods and a limited land space which does not allow for human resettlement thus constraining development (*UNDP, 2006*). This is also more critical in the case of a serious spill as people are not able to relocate to another nearby place for development due to the shortage of land. While economic gains exist in the exploration of oil in the Niger Delta, the losses due to hazards appear to exceed the benefits for the residents of the region and oil workers who are both at risk due to exposure and are directly affected from the negative impact of oil spills in the region, which are evident in the damages done to the region's ecosystem (*UNDP, 2006*). These impacts include soil contamination, affecting terrestrial lives (*Akpomuvie, 2011*). The oil spills kill plants, organisms and animals and in the process, the food chains are disrupted while aquatic productivity is also decreased. Otaigbe and Adesina (*2005*)'s medical case report aptly emphasized the risk of oil exposure to human health. Oil spill accounts for the major source of pollution in the Niger Delta with threats to human and the ecosystem, with the damages evident on streams and farmlands greatly affecting the livelihood of the people. As Osuji (*2004*) explains, environmental pollution as a continuous act in the region creates the impact over the long-term, having not been tracked and assessed as the incident occurs. Thus today, the Niger Delta region is devoid of its pre-oil era with the telling negative impacts of oil operations evident in its life expectancy which used to be close to 70 years but now below 40 years; once a net food exporter but now imports about 80% of its food, with dilapidated infrastructure and visible signs of being sickly on its populace (Ecumenical Council for Corporate Responsibility (ECCR, *2010*). According to Osuji, (*2004)*, an oil spill as a form of pollution is a product of human activities which occur in the form of a release of a liquid petroleum hydrocarbon into the environment, occurring over both lands and marine. The inorganic chemicals hold a greater portion as contaminants in drinking water in comparison to organic chemicals. Parts of inorganics are in mineral form of heavy metals. Heavy metals tend to accumulate in human organs and nervous system and interfere with their normal functions. In recent years, heavy metals such as lead (Pb), arsenic (As), magnesium (Mg), nickel (Ni), copper (Cu), and zinc (Zn) have received significant attention due to causing serious health problems. Moreover, the cardiovascular diseases, kidney-related problems, neurocognitive diseases, and cancer are related to the traces of metals such as cadmium (Cd) and chromium (Cr) as reported in epidemiological studies. The Lead (Pb) is known to delay the physical and mental growth in infants, while Arsenic (As), Selenium (Sn) and mercury (Hg) can cause serious poisoning with skin pathology and cancer and further damage to kidney and liver, respectively (*Goyer, 2001*). Oil spill accounts for the major source of pollution in the Niger Delta with threats to human and the ecosystem, with the damages evident on streams and farmlands greatly affecting the livelihood of the people (ECCR, *2010*).

Justification: Reports on the extent of the oil spills vary.

The Department of Petroleum Resources estimated 1.89 million barrels of petroleum were spilled into the Niger Delta between 1976 and 1996 out of a total of 2.4 million barrels spilled in 4,835 incidents. (Approximately 220 thousand cubic metres). A UNDP report states that there have been a total of 6,817 oil spills between 1976 and 2001, which account for a loss of three million barrels of oil, of which more than 70% was not recovered. 69% of these spills occurred off-shore, a quarter was in swamps and 6% spilled on land (*UNDP, 2006*).

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The Nigerian National Petroleum Corporation places the quantity of petroleum jettisoned into the environment yearly at 2,300 cubic metres with an average of 300 individual spills annually. However, because this amount does not take into account "minor" spills, the World Bank argues that the true quantity of petroleum spilled into the environment could be as much as ten times the officially claimed amount. Recently, several oil spills have been reported in press in August and September 2016. All of these spills have had a devastating impact on the water, agriculture, environments and general well-being of the local communities in Delta State (NOSDRA, 2016). The largest individual spills include the blowout of a Texaco offshore station which in 1980 dumped an estimated 400,000 barrels (64,000 m^3) of crude oil into the Gulf of Guinea and Royal Dutch Shell's Forcados Terminal tank failure which produced a spillage estimated at 580,000 barrels (92,000 m^3).

MATERIALS AND METHODS

Site location of crude oil contamination: Crude oil spills have been reported in the press in August and September 2016. All of these spills have had a devastating impact on the drinking water, agriculture, environments and general well-being of the local communities. In Delta State, Ten Ijaw communities along the Escravos River in Warri South West Local Government Area of Delta State have been affected by a crude oil spill from a Nigerian National Petroleum Corporation (NNPC) facility. The spill occurred on August 17th 2016, and journalists in the area were told that it was traced to a crude oil trunk line from the Pipelines and Products Marketing Company (PPMC), the products marketing and distribution subsidiary of the NNPC. The communities that were affected were the Tebujor/**Okpele-Ama**,**Ikpokpo**, Okerenkoko-Gbene, Opuedebubor, Opuede, Opuendezion, **Atanba,** Oto-Gbene, Meke-Ama Communities in Gbaramatu Kingdom, along the Escravos River in Warri South West Local Government area of the state.

Sourcing for crude oil contaminated water: Samples of untreated produced water were collected from three different locations of crude oil polluted areas of Ikpokpo, Okpele-ama and Atanba communities, in Gbaramatu Kingdom on 12th of April, 2019, along the Escravos River in Warri South West local Government Area of Delta State, Niger Delta Region of Federal Republic of Nigeria, using ten 5 litres chemically clean amber glass bottles and properly covered with Teflon-lined lids in such a way as to completely protect all the water samples from any external contamination. All the bottles containing the untreated produced water samples were properly labelled for identification and transferred to the laboratory, in ice boxes, for laboratory analyses targeted at detecting and quantifying the concentrations of heavy metals in the samples *(Musliu and Salawudeen, 2012)*.

Chemicals and Reagents: All chemicals and reagents to be used for this research project are of analytical grades.

Sterilization of Glass wares and other working equipments: Materials which included conical flasks, funnels and test tubes were sterilized in a hot air oven at 160°C for about 1 hour. All pipettes and other heat-resistant glassware's were wrapped in Aluminium foil to protect the items from recontamination during handling and storage before sterilization was done at 160°C for 1hr in the hot air oven. Water was used to wash all the equipment's, detergents were used where necessary and 70% ethyl alcohol which is bactericidal was used to swab the top of the working bench in the laboratory where the inoculations were done.

Laboratory Analyses:

Heavy Metal Determination in the crude oil contaminated water samples:

Wet Digestion: In order to determination the heavy metals concentrations all collected samples were prepared. In this respect, the digestion of water samples with aqua regia (HNO3 67%: HCl 37% = 3:1) was achieved. Acid mixture (HNO3 67%:H2SO4 98%: HCl 37%: HF 40% = 2:1:1:1) for mud samples digestion was used. Mineralization of samples was performed by using a Berghof MWS-2 microwave digester *(Azcue and Mudroch, 1994).*

Heavy Metals analysis Using Atomic Absorption Spectrophotometer (AAS): Atomic Absorption Spectrophotometer (AAS) Analyst 400 model used in determining the content of heavy metals in the previously digested water samples. The nitrous oxide, acetylene gas and compressor were fixed and compressor turned on and the liquid trap blown to rid of any liquid trapped *(AOAC, 1990).* The Extractor and the AAS control were turned on. The slender tube and nebulizer piece were cleaned with purifying wire and opening of the burner cleaned with an arrangement card. The worksheet of the AAS programming on the joined PC was opened and the empty cathode light embedded in the light holder *(Haswell, 1991).* The light was turned on, beam from cathode adjusted to hit target zone of the arrangement card for ideal light throughput, at that point the machine was touched off. The fine was set in a 10 ml graduated chamber containing deionised water and yearning rate estimated *(AOAC, 1990).* The analytical blank was prepared, and a series of calibration solutions of known amounts of analyte element (standards) were made. The blank and standards were atomized in turn and their responses measured. A calibration graph was plotted for each of the solutions, after which the sample solutions were atomized and measured. The various metal concentrations from the sample solution were determined from the calibration, based on the absorbance obtained for the unknown sample *(Haswell, 1991).*

RESULTS

Table 1: WHO permissible limits of Heavy Metals concentrations of normal drinking water.

S/N	HEAVY METALS	WHO PERMISSIBLE LIMIT (mg/L)
1	Copper (Cu)	2
2	Zinc (Zn)	5
3	Magnesium (Mg)	50
4	Iron (Fe)	0.3
5	Cadmium (Cd)	0.003
6	Chromium (Cr)	0.05
7	Lead (pb)	0.01
8	Mercury (Hg)	0.006
9	Arsenic (As)	0.01
10	Selenium (Sn)	0.01

KEY: WHO- World Health Organization. **S/N**- Serial Number. **mg/L:** - Milligram per litre.

Table 2: Heavy metals concentration analysis of Normal water samples collected from six different locations within Kano Metropolis, Kano State, Nigeria.

		Heavy Metals Concentrations (mg/L) of normal water samples									
S/N	Crude oil contaminated water samples	Cu (mg/L)	Zn (mg/L)	Mg (mg/L)	Fe (mg/L)	Cd (mg/L)	Hg (mg/L)	Cr (mg/L)	Pb (mg/L)	As (mg/L)	Sn (mg/L)
1	SDH-1	1.7	4.3	45	0.21	0.0003	0.00002	0.0015	0.0024	0.00003	0.0028
2	SDH-2	1.3	3.8	39	0.17	0.0004	0.00001	0.0014	0.0016	0.00002	0.0043
3	SDH-3	1.9	4.1	34	0.24	0.0003	0.00002	0.0013	0.0025	0.00003	0.0033
4	JMB-4	1.6	2.9	48	0.26	0.0001	0.00001	0.0012	0.0017	0.00002	0.0012
5	JMB-5	1.8	3.7	42	0.20	0.0002	0.00001	0.0013	0.0018	0.00001	0.0014
6	JMB-6	1.4	3.4	40	0.14	0.0001	0.00001	0.0012	0.0015	0.00001	0.0012

KEY: SHD & JMB: - Normal Water sample collected from Sharada Industrial area and Jambulo Residential area **S/N**: - Serial Number, **mg/L**: - Milligram per litre. **TSS:** - Total Suspended Solids, **TDS:** - Total Dissolved Solids.

Table 3: The mean, range and standard deviations of heavy metals concentrations (mg/L) of normal water samples collected from six different locations within Kano Metropolis, Kano State, Nigeria.

Heavy Metals	**Cu**	**Zn**	**Mg**	**Fe**	**Cd**	**Hg**	**Cr**	**Pb**	**As**	**Sn**
Mean values ±Standard Deviations	1.67 ± 0.582	3.7 ± 0.502	41.3 ± 4.86	0.20 ± 0.044	0.0002 ± 0.00012	0.00001 ± 0.000005	0.0013 ± 0.00012	0.0019 ± 0.00043	0.00002 ± 0.000009	0.0024 ± 0.0013
Range values	1.3-1.9	2.9-4.3	34-48	0.14-0.26	0.0001-0.0004	0.00001-0.00002	0.0012-0.0015	0.0015-0.0025	0.00001-0.00003	0.0012-0.0043

Table 4: Heavy metals concentration analyzed from the crude oil contaminated water samples collected from six different locations within the crude oil contaminated sites in three communities of Ikpokpo, Okpele-ama and Atanba in Gbaramatu Kingdom, along the Escravos River in Warri South West L.G.A of Delta State, Nigeria.

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Heavy Metals Concentrations (mg/L) of crude oil contaminated water samples

S/N	Crude oil contaminated water samples	Cu	Zn	Mg	Fe	Cd	Hg	Cr	Pb	As	Sn
1	ND-1	7	10	65	0.91	0.017	0.019	0.29	0.09	0.2I	0.28
2	ND-2	5	11	71	0.78	0.028	0.021	0.24	0.06	0.24	0.35
3	ND-3	9	10	69	0.97	0.013	0.023	0.31	0.05	0.23	0.33
4	ND-4	10	9	60	0.79	0.016	0.018	0.33	0.07	0.29	0.32
5	ND-5	8	10	67	0.88	0.014	0.024	0.25	0.08	0.27	0.29
6	ND-6	10	15	70	0.94	0.015	0.026	0.28	0.09	0.26	0.31

KEY: ND$_n$: - Crude oil contaminated water samples obtained from Niger Delta, (n-serial numbering from1-6).
S/N: - Serial Number**. mg/L**: - Milligram per litre.

Table 5: Mean, Standard Deviations and Range values of crude oil contaminated water samples collected from six different locations within the crude oil contaminated areas in three communities of Ikpokpo, Okpele-ama and Atanba in Gbaramatu Kingdom, along the Escravos River in Warri South West L.G.A of Delta State, Nigeria.

Heavy Metals	**Cu**	**Zn**	**Mg**	**Fe**	**Cd**	**Hg**	**Cr**	**Pb**	**As**	**Sn**
Mean ± Standard Deviations	8.2 ± 1.94	10.3 ± 2.14	67 ± 4.05	0.878 ± 0.078	0.017 ± 0.0055	0.022 ± 0.0031	0.283 ± 0.034	0.073 ± 0.016	0.25 ± 0.029	0.313 ± 0.026
Range values	5-10	9-15	60-71	0.78-0.97	0.013-0.028	0.018-0.026	0.24-0.33	0.05-0.09	0.21-0.29	0.28-0.35

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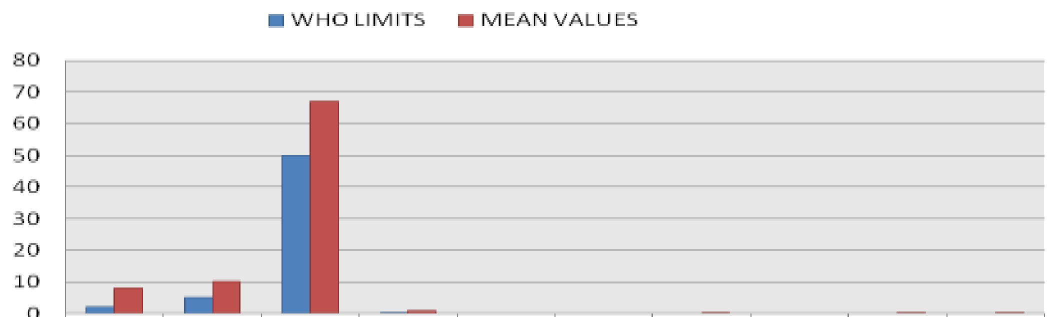
	Cu (mg/L)	Zn (mg/L)	Mg (mg/L)	Fe (mg/L)	Cd (mg/L)	Hg (mg/L)	Cr (mg/L)	Pb (mg/L)	As (mg/L	Sn (mg/L)
WHO LIMITS	2	5	50	0.3	0.003	0.006	0.05	0.01	0.01	0.01
MEAN VALUES	1.67	3.7	41.3	0.2	0.0002	0.00001	0.0002	0.0019	0.00002	0.0024

Figure 1: Comparison between the Mean concentrations (values) of the results of heavy metals obtained from table 3 with the WHO maximum permissible limits of heavy metal concentrations in normal drinking water (in table 1).



	Cu (mg/L)	Zn (mg/L)	Mg (mg/L)	Fe (mg/L)	Cd (mg/L)	Hg (mg/L)	Cr (mg/L)	Pb (mg/L)	As (mg/L	Sn (mg/L)
WHO LIMITS	2	5	50	0.3	0.003	0.006	0.05	0.01	0.01	0.01
MEAN VALUES	8.2	10.3	67	0.878	0.017	0.022	0.283	0.073	0.25	0.313

Figure 2: Comparison between the Mean concentrations (values) of the results of heavy metals obtained from table 5, with the WHO maximum permissible limits of heavy metals concentrations in normal drinking water (in table 1).

Figure 3: Aerial view of Escravos River being floated with oil spills across the communities of Gbaramatu kingdom of Warri South L.G.A of Delta State, Nigeria. Source: (NOSDRA, 2016).

Figure 4:.Aerial views of crude oil contaminated sites of some of the affected communities of Atanba, Ikpokpo and Okpele-ama of Gbaramatu Kingdom of Warri South West L.G.A of Delta State, Nigeria. Source: (NOSDRA, 2016).

DISCUSSION

World Health Organization (WHO) maximum permissible limits recommended for all the heavy metals level in drinking water were presented in table 1. In this table, the values of all the specified heavy metals were outlined in accordance with the WHO (2003, 2005 and 2011) standard guidelines. The concentrations of WHO maximum permissible limits for all metals specified for normal drinking water are: Copper (Cu):2mg/L (WHO, 2003), Zinc (Zn):5mg/L (WHO, 2003),Magnesium (Mg):50mg/L (WHO, 2003), Iron(Fe):0.3mg/L (WHO, 2003),Cadmium (Cd):0.003mg/L (WHO, 2011), Chromium (Cr):0.05mg/L (WHO, 2003) Lead (Pb):0.01mg/L (WHO, 2003), Selenium (Sn):0.01mg/L (WHO, 2011), Mercury (Hg):0.006 mg/L (WHO, 2005) and Arsenic (As):0.01 mg/L (WHO, 2011). These standard guidelines were set by WHO to checkmate quality of different water sources are that are safe for drinking and also to determine the level of heavy metals toxicity in different water sources. Table 2, presents the summary of all the results of heavy metals concentrations analysed from the normal water samples obtained from six different locations of Sharada industrial area and Janbulo residential quarters of Gwale L.G.A of Kano State Nigeria. Also, Table 4 presents the results of all the heavy metals concentrations analysed from the crude oil contaminated water samples obtained from six different crude oil contaminated sites of three communities of Ikpokpo, Atanba and Okpele-ama of Gbaramatu Kingdom along the Escravos River in Warri South West L.G.A of Delta state, Nigeria. The mean, standard derivations and the ranges of all the results of these heavy metals of the two different samples are presented in table 3 and 5 respectively. The various results of all the specified heavy metals analysed are being discussed in details below:-

Copper (Cu): Copper is found abundantly in the earth's crust. From table 3, the mean value of Cu is 1.67 mg/L, the standard deviation is ±0.582mg/L and the range is from 1.3 mg/L to

1.9 mg/L from the overall results obtained from table 2 of the normal water samples analysed. These values are within the ranges of WHO (2003), Cu maximum permissible limits in normal drinking water. Also, from table 5, the mean value is 8.2 mg/L; the standard deviation is ±1.94 mg/L. While the range is from 5mg it to 10mg/L respectively, of the overall results from table 4, of the crude oil contaminated water samples analysed. These values are above the WHO (2003) of Cu in normal drinking water. High concentrations may be due to heavy oil spilled in the crude oil contaminated water samples. The increase in Cu value in water can result in cellular damage leading to Wilson disease in humans (Goyer, 2001).

Arsenic (As): Arsenic (As) is a ubiquitous element that detected in virtually all environmental matrices (Yedjou and Tchounwou, 2008). From table 3, the mean concentration is $2.0x10^{-5}$mg/L, standard deviation in $\pm 8.9x10^{-6}$mg/L, and the range is from $1.0x10^{-5}$mg/L to 3.0 $x10^{-5}$mg/L respectively of the overall results obtained from table 2 of the normal water samples analyzed. These values are all within the WHO (2011) standard guidelines. From table 5, the mean value of As is 0.25mg/L, the standard deviation is ±0.029mg/L and the range is from 0.21mg/L to 0.29mg/L of the overall results obtained from stable 4 of the crude oil contaminated limits of Arsenic in water (WHO 2011). The high concentrations of arsenic in the crude oil contaminated water may be due to large deposition of Arsenic content into the water. Consumption of these water sources with high concentration of arsenic cause serious human health effects such as cardiovascular and peripheral vascular disease developmental anomalies, neurologic and neurobehavioral disorders, diabetes, hearing loss, fibrosis, hematologic disorder (anaemia, leucopoenia and eosinophilia) and carcinoma (Yedjou and Tchounwou, 2008).

Zinc (Zn): is widely distributed in the earth’s crust. It is one of the most abundant heavy metals in the environmental matrices. From table 3, the mean concentration is 3.7mg/L, the standard deviation is ±0.0502mg/L, and the range is from 2.9mg/L to 4.3mg/L of the overall results obtained from table 2 of the normal water samples analysed. These values are within the normal range of WHO (2003), Zinc permissible limit in drinking water. The mean value of Zn is 10.3mg/L from table 5, the standard deviation is ±2.14mg/L and the range is from 9mg/L to 15mg/L of the overall results obtained from table 4 of the crude oil contaminated analysed. These values are above the WHO (2003), Zinc maximum limits in normal drinking water sources. Despite its importance in the overall function of the body, higher concentration upon consumption can lead to serious health related complications from acute adverse of its intake such as vomiting, loss of appetite, nausea, abnormal cramps, diarrhea and headache. Chronic health issues include urinary tract complications leading to kidney damage (Verkleji, 1993).

Iron (Fe): From table 3, the mean value is 0.20mg/L; the standard deviation range is from 0.14mg/L to 0.26mg/L, with the standard deviation of ±0.0 44mg/L, of the overall results obtained from table 2 of the normal water samples analysed. These values are all within that range of WHO (2003), for maximum Fe in normal drinking water sources. Also, from table 5, the mean value is 0.878mg/L, the standard deviation is ±0.078mg/L, while that of range is from 0.78mg/L to 0.97mg/L respectively, of the overall results obtained from table 4 of the crude oil contaminated water samples analysed. Upon comparison, the mean values from table 5 are above the range of WHO (2003) standard guidelines for Fe in normal drinking

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water sources. Despite its importance in tissues metabolism in the body, high concentrations of Fe can serve as a medium for the growth of bacteria and other microorganisms, as such, upon consumption can lead to serious health related illness, hemachromatosis, stomach ache, nausea and vomiting.

Magnesium (Mg): It is one of the eight's most abundant heavy metal found in the earth's crust. It is found in abundance in mineral brucite, magnesite, dolomite and carnalite. From table 3, the mean value is 41.3mg/L, the standard deviation is ±4.86mg/L and the range is from 34mg/L to 48mg/L of the overall results obtained from table 2, of the normal drinking water samples analysed. There values are within the normal range of WHO (2003) of Mg permissible limit in drinking water. Furthermore, from table 5, the mean value is 67mg/L, the standard deviation is ±4.05mg/L and the range is from 60mg/L to 71mg/L of the overall results obtained from table 4 of the crude oil contaminated water samples analysed. High concentrations of Mg in the crude oil contaminated water samples may be due to high rate of industrial activities that may have contributed to large deposition of Mg in the crude oil contaminated water. This can cause hardness of water. Upon consumptions the affected communities may develop muscle slacking, Nervous important and depression and other serious health complications.

Mercury (Hg): Mercury is a widespread environmental toxicant and pollutant. It is mostly encountered compound of the organic form found in the environment. From table 3, the mean value of Hg is 1.0×10^{-5}mg/L; the standard deviation is $\pm 5.0 \times 10^{-6}$mg/L, while the range is from 1.0×10^{-5}mg/L to 2×10^{-5}mg/L of the overall results obtained from table 2, of the normal water samples analysed. These values are all within the range of WHO (2005), standard guidelines. From table 5, the mean value is 2.2×10^{-2}mg/L; the standard deviation is $\pm 3.1 \times 10^{-3}$mg/L, whilst the range is from 0.018mg/L to 0.026mg/L from the overall results obtained from table 4 of the crude oil contaminated water samples analyzed. These values are above the WHO (2005), Hg maximum permissible limits in normal drinking water. High concentration of Hg is toxic to humans and can lead to impaired DNA metabolism, genotoxicity, and liver damage (Sutton and Tchounwou, 2007).

Chromium (Cr): Is a naturally, occurring element in the ranging from chromium (II) to chromium (VI). It enters into various environmental matrices (air, water and soil) from a release coming from exploration and industrial establishment (Verkleji, 1993). From table 3, the mean value is 1.3×10^{-3} mg/L the range is from 1.2×10^{-3} mg/L to 1.5×10^{-3} mg/L and the standard deviation is $\pm 1.2 \times 10^{-4}$ mg/L. From the overall results obtained from table of the normal water samples analyzed. There concentrations are all below the WHO (2003) standard guidelines for Cr concentration in normal drinking water. Also, from table 5, the mean value is 2.83×10^{-1} mg/L, the standard deviation is $\pm 3.4 \times 10^{-2}$ mg/L, while the range is from 2.4×10^{-3} mg/L to 3.3×10^{-3} mg/L from that overall results obtained from table 4 of the crude oil comparison higher than the standard guidelines for maximum permissible limits set by WHO (2003). Increase in chromium concentration in the contaminated water may be due to high contents of oil spills in the swampy and crude oil contaminated sites and upon consumptions can lead to high risks e.g. renal damage allergy, asthma and concern of the respiratory tract in humans (Verkleji, 1993).

Lead (Pb): is a naturally occurring bluish-gray metal present in small amount in the earth's crust. Anthropogenic acuities such as oil exploration, fossils fuels burning and other industrial activities leading to environmental spillage contributes to the release of high concentrations (Tchounwou and Ishaque, 2001). From table 3, the mean value of is $1.9x10^{-3}$mg/L, the standard deviation is $\pm 4.3x10^{-4}$mg/L, while the range is from $1.5x10^{-3}$mg/L to $2.5x10^{-3}$mg/L. Also, from table 5, the mean value is $7.3x10^{-2}$mg/L the deviation is $\pm 1.6x10^{-2}$mg/L and the range is from 4.5mg/L to 0.09mg/L from the overall results obtained from table 4 of the crude oil contaminated water samples analysed. These values are above the WHO (2011) permissible range of Pb in normal drinking water. High concentrated of Pb in water is harmful upon consumption can cause serious health related complications such as liver disease, kidney and heart impairments, memory loss as a result of severe normal system impairment (Tchounwou and Ishaque, 2001).

Cadmium (Cd): Cadmium is a heavy metal of considerable environmental and occupational concern. It is widely distributed in the earth's crust. From table 3, the range is from $1.0x10^{-4}$mg/L to $4.5x10^{-4}$mg/L, the mean is $2.0x10^{-7}$mg/L, while the standard deviation is $\pm 1.2x10^{-4}$mg/L, respectively of the overall results obtained from table 2 of the normal water samples analysed. There values all are within the normal range of WHO (2011) maximum permissible limits of Cd in normal drinking water. Furthermore, from table 5, the mean value $1.7x10^{-2}$mg/L, the range is from $1.3x10^{-2}$mg /L to $2.8x10^{-2}$mg/L with standard deviation of $\pm$ $5.55x10^{-3}$mg/L of the crude oil contaminated water (in table 4) analysed. Upon comparison, these values are higher than both the WHO standard guidelines and the normal water value analysed. High concentration of Cadmium the water upon consumption can course long damage (Verkleji, 1993).

Selenium (Sn): From table 3, the mean value of Sn is $2.4x10^{-3}$mg/L; the standard deviation is $\pm$ $1.3x10^{-3}$ mg/L, while the range is from $1.2x10^{-3}$mg/L to $4.3x10^{-3}$mg/L of the overall results obtained from table 2, of the normal water samples analysed. More so, from table 5, the mean value is 0.313mg/L, the standard deviation $\pm 0.026x10^{-3}$mg/L, while the range is from 0.28mg/L to 0.35mg/L, of the crude oil contaminated water samples (from table 2) analysed. Despite its importance, in thyroid hormone metabolism in the body and DNA synthesis, high concentration of selenium in water can lead to serious health issues such as hepatoxicity, gastrointestinal disturbances upon consumption (Verkleji, 1993).

Effect of water quality on affected communities of the Niger Delta Region:

Diseases related to contamination of drinking-water constitute a major burden on human health. Interventions to improve the quality of drinking-water provide significant benefits to health (*WHO, 2006).* Water is essential to sustain life, and a satisfactory (adequate, safe and accessible) supply must be available to all (*WHO, 2004).* Improving access to safe drinking-water can result in tangible benefits to health. Every effort should be made to achieve a drinking-water quality as safe as practicable. The great majority of evident water-related health problems are the result of microbial (bacteriological, viral, protozoan or other biological) contamination. Excessive amount of heavy metals accumulated in drinking water sources can lead to deteriorating effects on human health. As discussed in the results, all the crude oil contaminated water sources obtained from six different locations of crude oil contaminated sites of Ikpokpo, Okpele-ama and Atanba Communities of Gbaramatu kingdom of Warri South west LGA of Delta State, Nigeria contained heavy metals analysed above the

WHO maximum permissible limits in normal drinking water sources (*WHO, 2003, 2005 and 2011).* Therefore, the present study has found out that the crude oil contaminated water sources are not suitable and safe for consumption and can have significant health impacts on residents of the affected communities within the Niger Delta region, hence there is an urgent need for the Federal Government of Nigeria to provide appropriate means to remediate the contaminated water to the level of WHO guideline standards for normal drinking water (*WHO, 1997).*

CONCLUSION

On the basis of these findings, it was concluded that all the heavy metals analysed from the crude oil contaminated water samples collected from the crude oil contaminated sites of the three communities of Ikpokpo, Atanba and Okpele-ama of Gbaramatu Kingdom of Warri South West L.G.A of Delta State, Nigeria, have concentrations values above the World Health Organization maximum permissible limits of heavy metals in normal drinking water (WHO, 2003, 2005 and 2011). Meanwhile, the normal drinking water samples obtained within Kano Metropolis that were used in benchmarking have concentrations within the World Health Organization maximum permissible limits for heavy metals in normal drinking water sources (WHO, 2003,2005 and 2011). These samples were analyzed for intended water quality, following internationally recognized and well established analytical techniques. Therefore, the present study has found out that the crude oil contaminated water sources are not suitable and safe for consumption and can have significant health impacts on residents of the affected communities within the Niger Delta region, hence there is an urgent need for the Federal Government of Nigeria to provide appropriate means to remediate the rate of crude oil spills within the Niger Delta region and also provide means of normal drinking water to the affected communities in accordance with the WHO guideline standards for normal drinking water (WHO, 2011).

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