Comparative Study of Heavy Metal Concentration across Artisanal Crude Oil Refining Sites in Some States in South-South, Nigeria

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ABSTRACT

Nigeria has had an abundance of oil since 1956, but the nation is still unable to meet its citizens' fuel needs. The country's refineries have little production capacity and are almost all moribund. As a result, there is a proliferation of unconventional refineries across the oil-producing states of the South-South region of Nigeria, despite its attendant environmental and health challenges. The purpose of this study was to compare the concentration of heavy metals across some artisanal crude oil refining sites in South-South Nigeria. The results show that Rivers state has the most polluted soil, and that the concentration of heavy metals decreases with distance from the production site. The concentration of heavy metals in mg/kg, with distance from the production sites decreased with distance from the site of production. This study concludes that, while improving the production process of artisanal refining in the study area, it is also important to remediate the already destroyed environments

Keywords: Heavy metals, Artisanal, crude oil, Concentration, Comparative, South-South

INTRODUCTION

Petroleum, also referred to as crude oil, is a naturally occurring mixture of volatile liquid hydrocarbons, mostly composed of carbon and hydrogen, though it also contains some nitrogen, sulphur, and oxygen. Amangabara and Njoku, (2012). state that when these hydrocarbons are present in large quantities, they pose a serious threat to the environment. Exploration, production, transportation, and use of petroleum products are continuously carried out globally and have recently increased, despite certain negative consequences on the environment. Petroleum prospecting in Nigeria's southern coastal area stretches back to the pre-independence era. Nigeria's oil reserves were projected to be over 37 billion barrels, and in 2019 the country produced over 2.4 million barrels of oil per day (OPEC, 2020).

The South-South region's natural environment, which the populace depends on for existence and survival is becoming worse every day. The extraction and refinement of the South-South's vast crude oil deposits has resulted in detrimental environmental contamination in areas that are in close proximity to artisanal refineries and crude oil flow stations. The artisanal refineries uses heat from an open fire to process enormous barrels of crude oil into refined products using basic and primitive methods. Spills resulting from artisanal refining, which are now frequent in South-South villages, have gravely damaged the aquatic ecology. This process of Artisanal refining involves transforming crude oil through distillation into various products over a specific range of boiling points to produce kerosene, fuel, and diesel.

This has been a common way to make money in the South-South Region of Nigeria for a while now, but it has also significantly exacerbated socio-economic issues and environmental degradation in the area recently. Surface water bodies are being destroyed by the artisanal refineries that are springing up everywhere in the South-South (Imoobe & Aganmwonyi, 2021). In addition, there has been a decrease in the quality of the air in the areas that artisanal refineries are located (Onakpohor et al. 2020). In addition, pollution from gas and crude oil is causing the mangroves in the area to disappear quickly (Onyena & Sam 2020).

Crude Oil

Crude oil is a complex mixture of various hydrocarbon chains (Nandy et al., 2020; Fingas, 2011) that is frequently combined with mineral suspension and emulsified water (Fetter et al., 2019). It is a yellow-black liquid that is typically found in underground reservoirs (Eneh, 2011); it is one of the most significant energy resources that humans have access to (Luo et al., 2020). Yasin et al., (2013), Groysman (2017), and Chinenyeze & Ekene (2017) have all stated that the main components of crude oil are hydrocarbons, metals, nitrogen, and sulfur in their natural states. However, Groysman (2017) has proposed that crude oil also contains contaminants that are present as dissolved gases, solids, and liquids. Metals are uncovered in trace concentrations in crude oil as inorganic salts (Fetter et al., 2019). In its raw form, crude oil is a fossilized mass found below the earth's surface as a geological formation (Vempatapu & Kanaujia, 2017). Crude oil contains all normal Alkanes from C1 to C120 (Yasin et al., 2013). Also, it contains hydrocarbon deposits and organic materials including aromatic hydrocarbons, alkanes, and cycloalkanes with toxic, hazardous, and carcinogenic potentials (Maamar et al., 2020). Also, Chinenyeze and Ekene (2017) asserted that crude oils are hydrocarbon compounds going from pentane to pentadecane (C5 – C15). Table 2.2 shows crude oil fractions and their various applications. Crude oil has an elemental composition distributed between carbon (85%-90%), hydrogen (10%- 14%), sulphur (0.2-3%), nitrogen (<0.1-2%), oxygen (1-1.5%), and organometallic compounds (vanadium, nickel, lead, arsenic, and other trace metals) (Vempatapu and Kanaujia, 2017).

Crude oils are complex but mainly paraffinic, naphthenic, and aromatic, (Yasin et al. 2013, Chinenyeze and Ekene 2017) and play a key role in today's world economy because they are the main source of energy (Mabood et al., 2017). Crude oil is one of the world's main energy sources, however its extraction and subsequent refining have an influence on the environment, according to Ali and Kumar (2017). Countries have begun using biofuel as an alternative fuel for engines to increase energy efficiency. However, Nigeria has not taken any significant steps to diversify away from the use of fossil fuels, leaving its citizens with no choice but to use products that have been refined from fossil fuels due to government policy and economic benefits. According to Adewuyi (2020), the obstacles impeding the growth of biofuel in Nigeria include inadequate government regulations, high production costs, the land tenure structure, and rivalry between food and feedstock for biofuel.

Crude Oil Refining in Nigeria

Four crude oil refineries in Nigeria, believed to have a combined refining capacity of 445,000 barrels per day (Kadafa 2012; NNPC 2016; Majekodumi 2013), are all in a condition of disrepair (Adegbite 2013). Two refineries make up the Port Harcourt Refining Company. The first was built with an on-stream capacity of 60,000 barrels of light crude per day and was put into service in 1965. The second refinery was built with a refining capacity of 150,000 barrels of crude oil per day and was put into service in 1989 (Odeyemi & Ogunseitan 1985; NNPC 2016; Kadafa 2012). Each of the two refineries, the Warri and Kaduna refining companies has an installed capacity of 110,000 and 25,000 barrels of crude oil per day, respectively (NNPC 2016).

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Artisanal Refining of Crude Oil in Nigeria

Fuel quality is the deciding factor in whether or not it may be sold since adulterants might lead to operational challenges (Torres-Jimenez et al., 2011). Nwajiaku-Dahou (2012) and Networks (2013) define artisanal refining as the process of crude oil refining into gasoline, kerosene, and diesel in very modest volumes for local markets using unconventional means. Since crude oil is the feedstock for artisanal refineries, these facilities are constructed in close proximity to communities that have flow stations for crude oil and pipelines that pass through them in the south. In Nigeria, artisanal refined products like kerosene and diesel are sold in towns and villages (Ogbuefin 2014). According to Networks (2013) artisanal refining camps along the riverbanks, store crude oil in locally-made drums, or in large holes dug in the ground covered in plastic and other synthetic materials to prevent any leakages. Likewise, EIA (2016) reported that artisanal refineries in the South-south swampy bushes refine crude oil, and by-products from the refined crude oil such as diesel, kerosene, and petrol are sold domestically and regionally at low cost when compared to government recognized retail outlets.

Heavy Metals across Artisanal Refining sites

The life of plants and animals depends on the quality of the soil and water. The most common methods for evaluating the quality of water are pH and heavy metal content. The degree and effects of pollution in an environment are assessed using the pH range of that environment (RPI, 1985). Certain heavy metals are harmful to both humans and aquatic life when they are found in the soil or water. Inorganic substances known as heavy metals have densities five times greater than those of water, and they cannot be degraded and naturally occurring elements of the crust of the planet. These metals enter living organisms through food or by being close to sources of emissions, as they enter, they accumulate in the living system. There are three major heavy metals, mercury, lead and cadmium “called the big three” as a result of their major impact on the environment (Volesky & Prasetyo, 1994).

Table 1: The Maximum contaminant Level standards for the most hazardous heavy metals.

HEAVY METAL	TOXICITIES	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhoea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system and nervous system	0.00003

Source: (Babel & Kurniawan, 2003)

The primary factor influencing the adsorption of metal ions from waste water is the solution’s pH. The species of adsorbate, the degree of ionization, and the surface charge of the adsorbent can all be affected by pH. Most metal adsorption is boosted in a certain pH range, rising to a set value before decreasing as pH rises higher. Both the metal chemistry of the solution and the surface functional groups on the walls of the biomass cells can be linked to the dependency of metal adsorption on pH (Sheng et al., 2004).

MATERIALS AND METHOD

Research Design

The study adopted the analytical research approach following the analysis of samples of soil and water in the study area to unravel the heavy metals in the study area. A pilot survey was carried out on some artisanal refining sites in Rivers, Bayelsa and Delta States to obtain water and soil samples at the refining sites. These States among the other States of the region are known for the abundance of artisanal refineries due to the large oil installations and samples were collected purposively

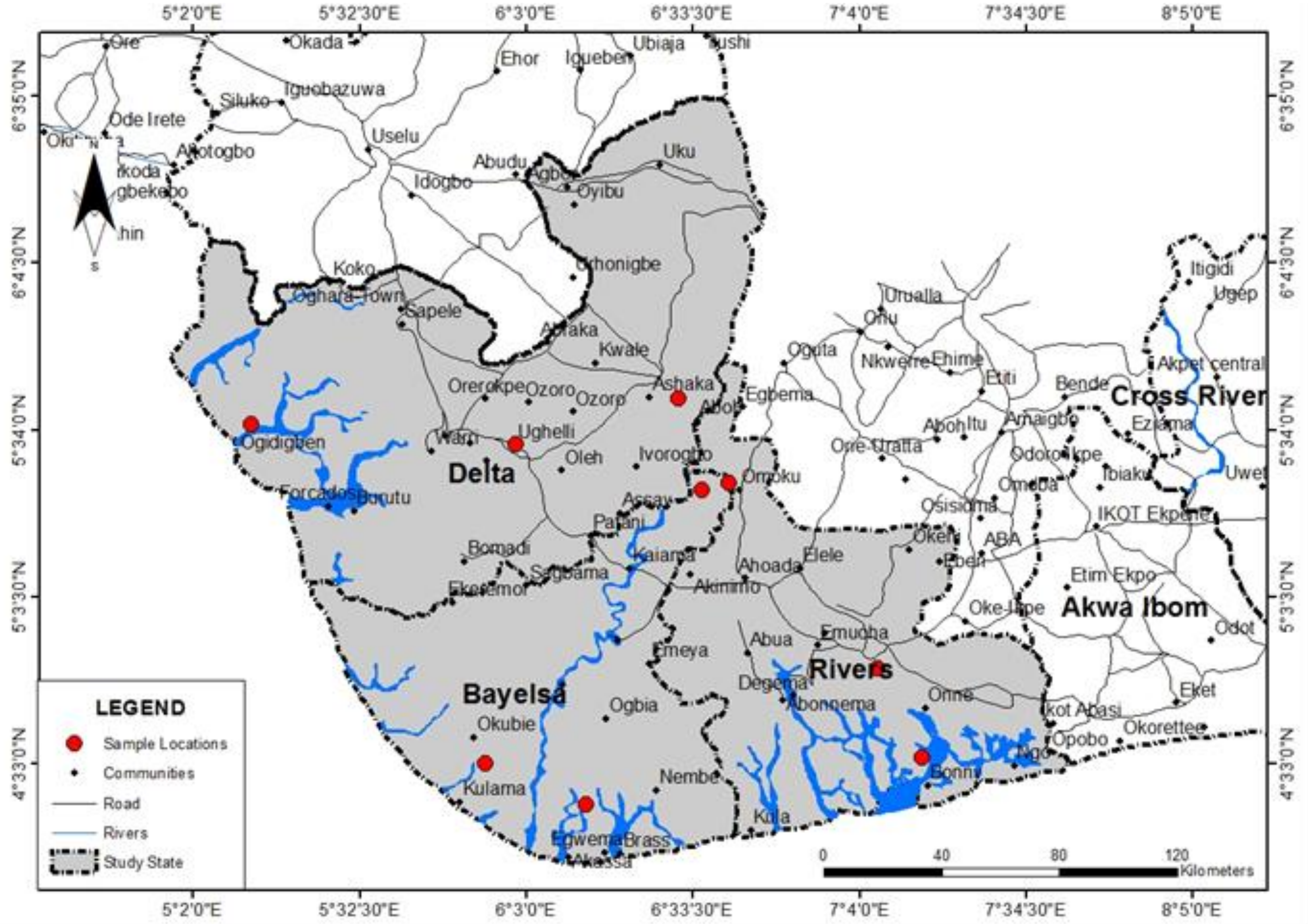

Fig1: Sample Location Map of the Study Area (GIS Dept. Uniport)

Sample and Sampling Techniques

The target population comprised of artisanal refinery sites across the various states of the study area. The number of household that constitute the target population from which the appropriate samples were selected. The Taro Yamane equation (equation 1) was deployed and sample sizes of artisanal sites were derived (307) as presented in Table 2. To avoid bias, the determine Taro Yamane sample was proportionally distributed for the artisanal refineries across the states of the study area (see Tables 2).

Yamane formula as follows:

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$$n = \frac{N}{1+N(e)^2} = \quad n = \frac{1324}{1+1324\,(0.05)^2} = 307 \qquad \text{………..equ (3.1)}$$

where: n = sample size

N = Population size (owners of artisanal refineries)

1 = Constant

e = error limit or margin of error or level of significance (accepted error set at 5% i.e. 0.05)

Table 2: Artisanal Refining sites across the states

States	Number of Artisanal Refining	Sample Size
Rivers	521	121
Bayelsa	721	167
Delta	82	19
Total	1324	307

Source: Researcher's Computation, 2024

RESULTS

Table 3. Concentration of soil heavy metal (mg/kg) with distance in the study area

State	Distances	Pb	Ni	V	Cd	C	Zn	Mo	Cu
Rivers	100	21.01	552	902	0.65	95	261	2.3	156
	200	18.02	508	798	0.52	81	242	2.1	199
	300	17.51	478	697	0.51	57	215	1.9	184
	400	14.1	233	455	0.51	32	175	1.9	123
Bayelsa	100	17.25	306	1248	1.02	97	426	4.8	485
	200	15.15	244	1126	0.47	80	325	3.7	456
	300	14.01	269	956	0.45	68	115	3.2	238
	400	13.33	238	535	0.36	56	100	2.3	156
Delta	100	22.5	317	867	0.93	87	335	3.8	574
	200	20.05	292	947	0.62	72	260	2.6	299
	300	18	283	1808	0.57	52	120	2.8	248
	400	16.01	213	1009	0.27	47	137	2.8	197

Source: Researchers Computation, 2024.

N:B: Pb-Lead; Ni-Nickel; V-Vanadium; Cd-Cadmium; C-Carbon; Zn-Zinc; Mo-Molybdenum; Cu-Copper.

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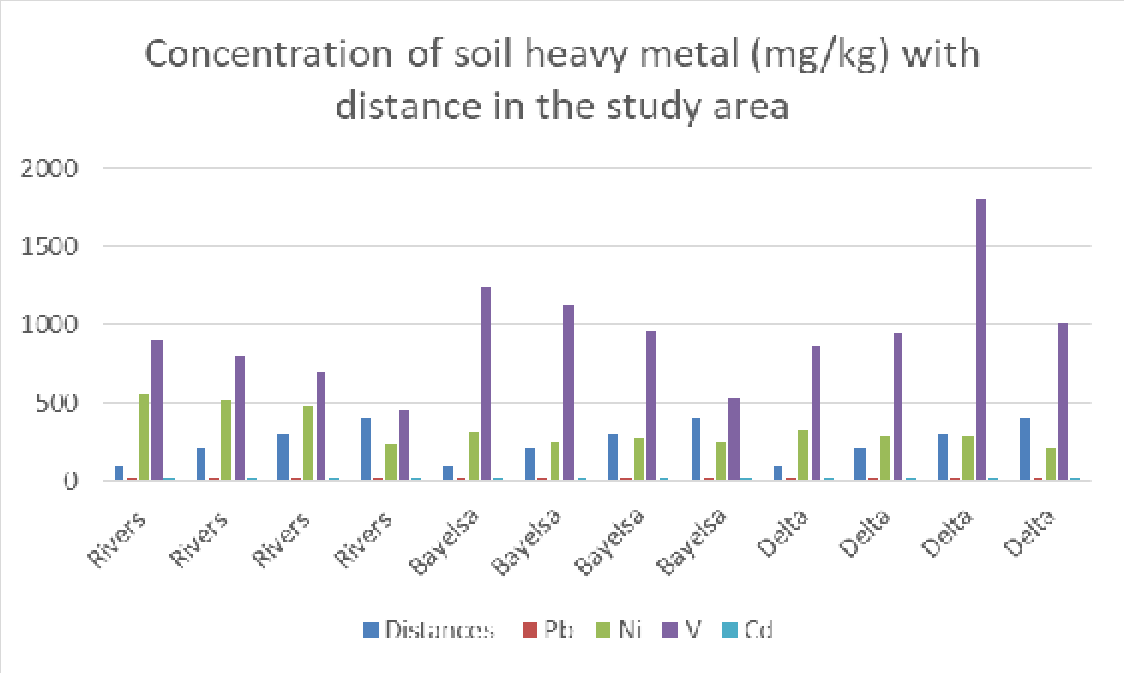

Fig 2: chart showing Concentration of Pb, Ni, V and Cd(mg/kg) in soil, with distance in the study area

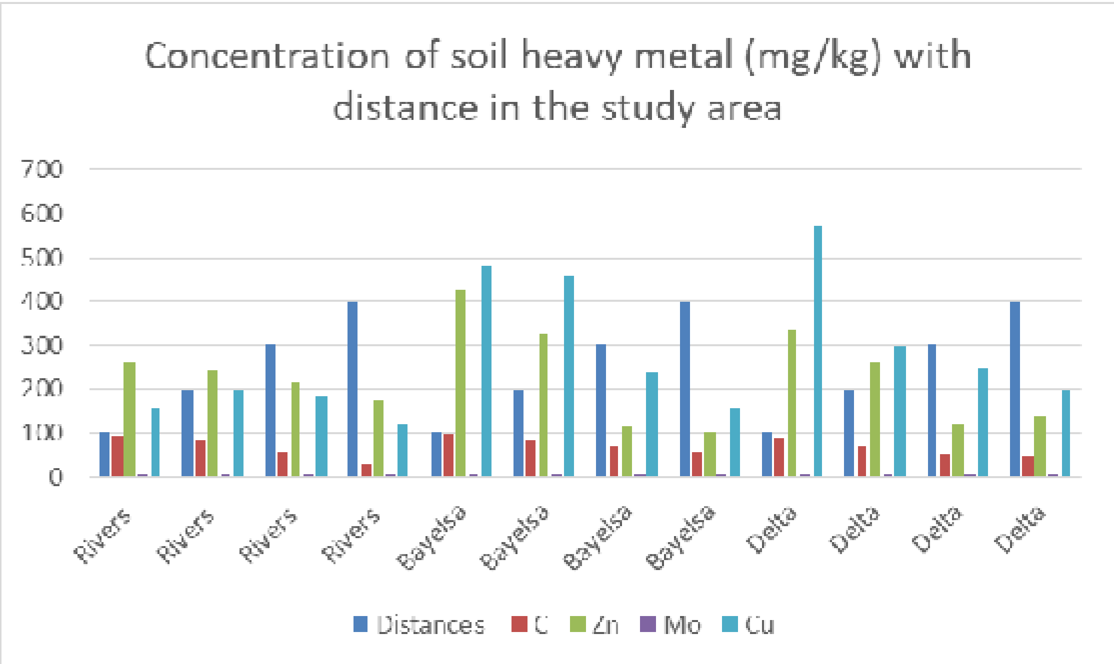

Fig 3: chart showing Concentration of C, Zn, Mo and Cu (mg/kg) in soil, with distance in the study area

Table 3 showed the concentration of heavy metals in mg/kg, with distance from the production sites. Samples were collected from 100m, 200m, 300m and 400m respectively. All the heavy metals detected in the samples decreased with distance from the site of production. This does also imply that areas affected are highly contaminated with heavy metals. Also, the metals detected were higher than the WHO standard and by implication very toxic for human health. The dangers of the presence of these heavy metals in water, fish or crop is highly hazardous for humans. However, the contamination of heavy metals in Rivers state

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appeared to be higher than Bayelsa and Delta States. The finding here therefore puts clear that, within 400m leeward off artisanal refining sites, plants and animals won't be able to survive, because of heavy metal poisoning.

Table 4 presents the concentration of heavy metals in surface water in the component states of the study area. The detected heavy metals in water were Lead (pb), which ranged from 14.9 mg/m^3 in Delta to 19.1 mg/m^3 in Rivers State; Nickel (Ni) which ranged from 264.3 mg/m^3 in Delta State to 442.8 mg/m^3 in Rivers State; Vanadium (V) ranged from 713.0 mg/m^3 in Delta State to 1157.8 mg/m^3 in Rivers State; cadmium (Cd) and carbon (C) were relatively same across the study sites in the study area. Same can be said of Zinc (Zn) and Molybdenum (Mo). However, Copper (Cu) ranged from 165 mg/m^3 in Delta State to 333.8 mg/m^3 in Rivers State. The heavy metals in water were also higher than minimum standard by World Health Organisation (WHO).

Table 4: Concentration of water heavy metal (mg/m^3) in the study area

States	Pb	Ni	V	Cd	C	Zn	Mo	Cu
Bayelsa	17.7	276.3	966.3	0.6	66.3	223.3	3	333.8
Delta	14.9	264.3	713	0.6	64.5	213	2.1	165.5
Rivers	19.1	442.8	1157.8	0.6	75.3	241.5	3.5	329.5

Source: Researchers Computation, 2024.

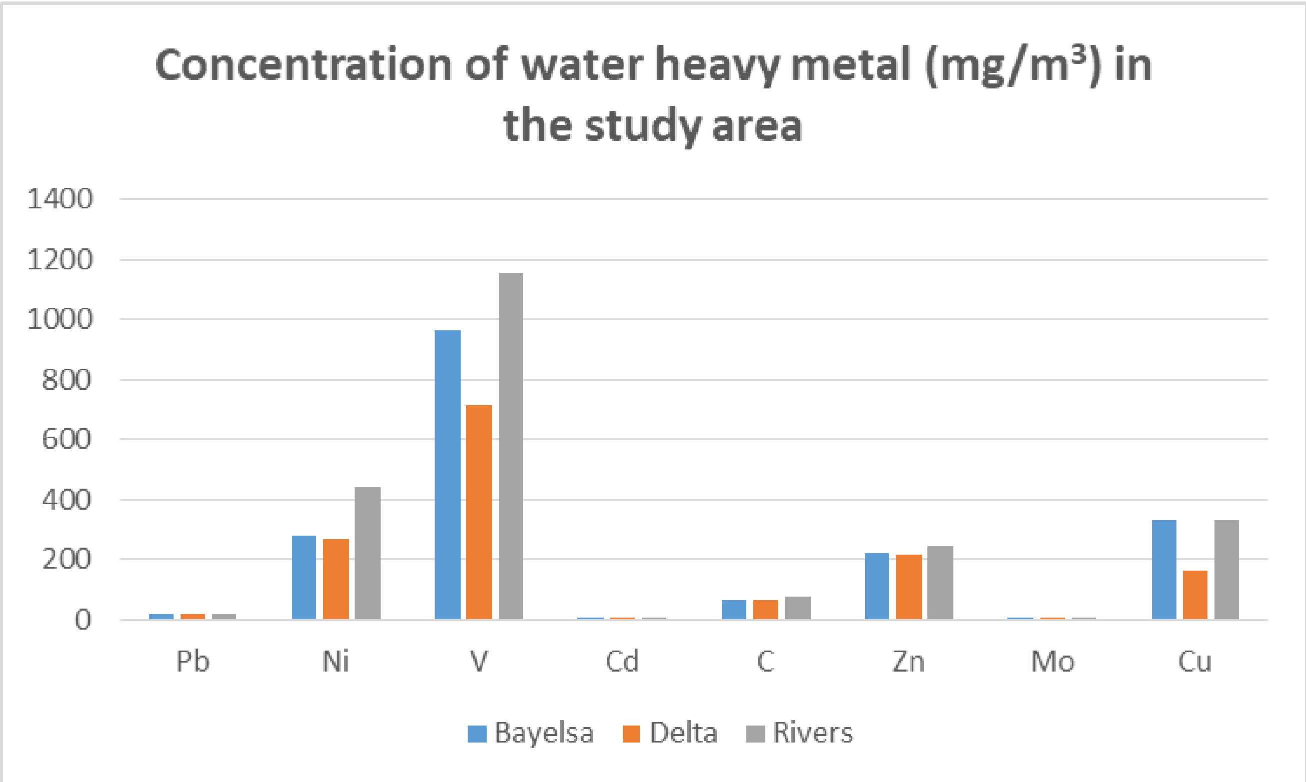

Fig 4: Concentration of water heavy metal (mg/m^3) in the study area

Heavy metals pollution across the artisanal refining sites in the study area

In this study one of the major intent was to establish the rates of soil and water pollution by looking at the heavy metal pollutions in soil and water across the study location and to compare the concentration of the heavy metals in the different states sampled. To establish this, samples were also collected at varying distances from the artisanal refining sites. In all, the soil properties appeared to depreciate as one moved close to the artisanal sites. Also, Rivers state had the most polluted soil followed by Bayelsa and Delta States

DISCUSSIONS

The detected heavy metals in water were Lead (pb), which ranged from 14.9 mg/m3 in Delta to 19.1 mg/m3 in Rivers State; Nickel (Ni) which ranged from 264.3 mg/m3 in Delta State to 442.8 mg/m3 in Rivers State; Vanadium (V) ranged from 713.0 mg/m3 in Delta State to 1157.8 mg/m3 in Rivers State; cadmium (Cd) and carbon (C) were relatively same across the study sites in the study area. Same can be said of Zinc (Zn) and Molybdenum (Mo). However, Copper (Cu) ranged from 165 mg/m3 in Delta State to 333.8 mg/m3 in Rivers State. The heavy metals in water were also higher than minimum standard by World Health Organisation (WHO).

The concentration of heavy metals in soil in the component states of the study area, compared to WHO standard were as follows; Lead (pb), Delta 16.03 mg/kg, Rivers State 18.63 mg/kg and Bayelsa 19.33 mg/kg and all > WHO standard of 2 mg/kg; Nickel (Ni) which ranged from 133.2 mg/kg in Delta State to 442.8 mg/kg in Rivers State were also higher than WHO standard of 10 mg/kg; Vanadium (V) ranged from 345.3 mg/kg in Delta State to 509.5 mg/kg in Rivers State and greater than WHO standard of 1.1 mg/kg; cadmium (Cd) and carbon (Co) were relatively same across the study sites in the study area but were far higher than the WHO standard of 0.02 and 0.05 mg/kg respectively. Same can be said of Zinc (Zn) and Mo. However, Copper (Cu) ranged from 453.18 mg/kg in Delta State to 604.07 mg/kg in Rivers State and higher than WHO standard of 10 mg/kg.

The problem with the presence of these heavy metals in the environment is that they stick around for a very long time, making its penetration of plants, fishes and animal very likely. The connection of these metals with diseases such as cancer, kidney disorder, renal failure, headaches, nausea etc has been established before now.

RECOMMENDATION

The effects of artisanal refineries on the environment, included oil spills on farms, water and air pollution. This in return has affected the economic activities in the study area both negatively (by reducing the number of persons involved in agriculture and fishing) and positively (by engaging youth in production of petroleum products). Also, the health of the people is being affected by the crude methods employed for production of petroleum products.

It is therefore recommended that:

1. Oil companies operating in the region in collaboration with government should increase their corporate social responsibility through the encouragement and support the development and expansion of the local economy for rural inhabitants in the state such as provision of social and welfare amenities, companies (to engage youths).
2. There is need to improve on the soil and water quality of the area, through remediation. This should be done by both government and oil companies that have installation in the area.

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