Original Research Article

DETERMINATION OF HEAVY METALS AND TOTAL HYDROCARBON CONTENT IN *NYPA FRUITICANS* OBTAINED ALONG THE SHORES OF QUA IBOE RIVER, AKWA IBOM STATE, NIGERIA

ABSTRACT

This study ascertains the amount of heavy metal and hydrocarbon content in an area exposed to crude oil exploration and exploitation activities. The study area is the Qua Iboe River in the Niger Delta region of Nigeria and the study samples were Nypa palm (*Nypa fruiticans*) leaves obtained along the shores of the river. The concentration of Pb, Cd, Cu and Ni in the leaves were determined using the Atomic Absorption Spectrophotometer while Total Hydrocarbon Content was determined using Gas Chromatography, coupled with the flame ionization detector (GC-FID). Results obtained showed that in site I, Pb mean concentration was 1.068±0.014 mg/kg, Cd (0.017±0.003 mg/kg), Cu (2.390±0.204 mg/kg), Ni (0.012±0.001 mg/kg) and THC (124,.361.7±1120.502 mg/kg) while for site II: Pb (1.076±0.025 mg/kg), Cd (0.028±0.003 mg/kg) Cu (0.037±0.007 mg/kg) Ni (2.049±0.024 mg/kg) and THC (311,813.4±2950.291 mg/kg). Heavy metal concentration in the study sites were largely within the WHO permissible limits with the exception of Cd in site II. Generally, the amount of heavy metals and THC were higher in the study sites than in the control site, which was an area with negligent oil exploitation and industrial activities. Therefore, the elevated concentration of heavy metals and THC in the study sites may be attributed to the various industrial activities sited in the area.

Keywords: *Heavy Metal, Total Hydrocarbon, Nypa Fruiticans.*

1.0 INTRODUCTION

The southern region of Nigeria is characterized by a large number of oil and gas fields. The increasing explorative activities of oil companies and transportation of the crude oil to their refining/storage depots have led to a number of incidental discharges or spills into the environment. The oil spills can be attributed to various reasons ranging from failure of production equipment to operational mishaps, or intentional damage to production facilities, otherwise known as sabotage (Iwegbue *et al.*, 2007). One of the methods of determining the incidence of crude oil pollution in an area is by estimating

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the total hydrocarbon content (THC) and heavy metals in impacted soil. The increased use of metal-based fertilizer in agricultural revolution of government could result in continued rise in concentration of metal pollution in fresh water reservoir due to water run-off (Ubong *et al.*, 2015). As human population increases, the intensity of anthropogenic threat exerted on the environment increases as a result of industrialization and agricultural activities (Ubong *et al.*, 2020a) Apart from soil environment and aquatic ecosystem, atmospheric inorganic contaminants of natural origin or anthropogenic sources that contained heavy metals and/or trace elements such as Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Nickel (Ni), Lead (Pb) and Zinc (Zn) at high concentrations could led to serious ecological consequences and pose human health risks (Ite *et al.*, 2016). Heavy metals are potentially hazardous to humans and various ecological receptors because of their toxicity, persistence, bioaccumulative and nonbiodegradable nature add reference. Therefore, monitoring and evaluation of heavy metal concentrations in soils, groundwater and atmospheric environment is imperative in order identify hazards to human health, to prevent bioaccumulation in the food chain and further degradation of the ecosystem (Ite *et al.*, 2016) .

Organic contaminants are mostly human-induced chemicals entering into natural fresh water through pesticide use, industrial chemicals, and as by-products of degradation of other chemicals and persist long enough in the environment to cause harmful effects. They tend to accumulate in reservoirs such as water, soil, sediments etc. From these reservoirs, they are remobilized through various processes, switch form or speciation and become available to the biological food chain. In this way, these contaminants tend to bio accumulate and bio magnify exhibiting toxicity and other related outcomes – mutagenicity, carcinogenicity and teratogenicity - resulting into chronic and acute disorders (Barnes *et al.*, 2008) . Records of THC and heavy metals, taken seasonally would enhance the ability to confirm the extent of pollution, especially by comparing the data from virgin areas or available baseline data from regulatory bodies. Usually, when oil spills on shore or near shore, it inevitably affects the soil ecosystem, a prime factor in agricultural productivity. This is particularly problematic because most of the terrestrial ecosystems and shorelines in the oil producing communities encompass important agricultural land and are under continuous cultivation (Ribes *et al.*, 2003) . Soil contact with oil may result in the damage of soil properties and plant communities, as well as microorganisms present in the soil.

Qua Iboe river in the Niger Delta of Nigeria is located in an area of intense oil exploration and exploitation activities (Ikpe *et al*., 2020). Nypa palm (*Nypa fruticans*), which is an ubiqiutous mangrove along the shores of Qua Iboe River, are constantly affected by heavy metals and hydrocarbon pollution; therefore, they are used as bio-indicator to assess the damage caused by oil spill in the ecosystem (Ikpe *et al*.,2020). Accordingly, the present study examines the concentrations of hydrocarbons and heavy metals in Nypa palm at Qua Iboe River, Nigeria.

2. MATERIALS AND METHODS

Study area and Sampling Site

Qua Iboe River Estuary, the relief is characterized by the Atlantic Ocean shoreline and surf beach. It falls within Latitudes 4° 39'N and Longitudes 7° 56'E. The region is also characterized by mangrove swamp and river floodplains mostly found around the Qua Iboe Estuary and the floodplains in Akwa Ibom State, Nigeria. The river measures about 158.18 kilometers in length and inundates about 7,000 hectares of fresh water floodplains once a year.

The samples were collected from three different sites; two sites were at Nditia community, Ibeno L.G.A with latitude between $04^0$34'56.74"N and $04^0$34'02.6"N and longitude between $07^0$54'50.96E and $07^0$58'25.9E respectively, while the third site was at Ikot Ibok, Etinan L.G.A between latitude $4^0$47'0.50"N and a longitude of $7^0$52'55.80"E, which was the control.

Fig. 1 Map showing the Study area

Sample collection and preservation

The *Nypa Fruticans* leave samples were collected from the three sampling sites, washed with distilled water to remove dust particles and dried in an oven (105˚C) for 24 hrs. The dried leave samples were crushed using mortar and pestle. Finally, the powder was stored in tightly closed clean sample bottles until analysis.

Determination of Heavy Metals in *Nypa fruiticans*

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The grounded samples were digested after drying according to– (Lee, (1995). The concentration of Pb, Cd, Cu and Ni were determined using bulk scientific model 210VGP (variable giant pulse) atomic absorption spectrophotometer with different hollow cathode lamp at different wavelength. All reagent used were of analytical grade and deionized water was used in all preparations. The digestion procedure was as follows; the samples (1 g) was weighed into digestion flask and 10_ml nitric acid (HNO_3)/ perchloric acid ($HClO_4$) acid mixture (3:1 ratio) was added to the sample; the suspension was swirled and allowed for some minutes for any reaction to subside. The digestion flask was mounted on a heating mantle and heated at 70 C until appearance of whitish dense fumes;–digestion ended when a clear solution was obtained. The digestion flask was removed and allowed to cool. 50_ml of deionized water was added to the digest filtered and made up to mark of 100_ml standard volumetric flask with deionized water. Each of the standard flasks with the digest was corked labeled and refrigerated for AAS analysis (Ogbeifun *et al*., 2019).

Determination of Total Hydrocarbon Contents (THC) in *Nypa fruiticans*

Total hydrocarbon contents (THC) were determined using Gas chromatography fitted with flame ionization detector (GC-FID). The samples were cut into pieces and then crushed using mortar and pestle. The extraction method outlined by (Schwab *et al.*, (1999);(Ekanem *et al*.,2019) -was applied to the samples as follows; 10g of each of the crushed samples were weighed into a 100ml beaker and 60ml of THC extraction mixture (250ml of acetone and 250_ml of dichloromethane) was then added. The beaker with its contents was placed on a magnetic stirrer (with heater) and shaken for about 25 min. at 70^0C. The extract was later decanted into a flask. 30ml of fresh extraction solvent was added and the process of shaking on the magnetic stirrer repeated. 5g of anhydrous sodium sulphate was used to remove water from the extract, which was concentrated to 3ml with rotary evaporator maintained at 20^0C. Subsequently, 1.5_ml of the concentrated extract was loaded on silica gel column. The silica gel was prepared by loading a 2g glass wool followed by a 30g chromatography silica gel onto a chromatography column (2cm internal diameter and 10cm long). Each of the bed was conditioned with 40ml HPLC-hexane to remove any contaminant. The concentrated was eluted with 30ml HPLC-hexane into a well labeled 100ml beaker to get the aliphatic hydrocarbon components in the sample. Thereafter, 30ml of chloromethane was added to elute the aromatic hydrocarbon contents into another labeled 100ml beaker. 2g of anhydrous sodium sulphate was added to remove any traces of water left in the extract. The extract were re-concentrated using rotary evaporator to about 2ml. 1ml of extract was taken and transferred into a well labeled chromatography vial read for gas chromatography analysis. The samples were stored at temperature of 4^0C until GC analysis.

Moisture Content Determination

Water content in *Nypa Fruticans* leaves ~~sample~~ was determined by drying a known weight (1 g) in an oven to a constant weight at a suitable temperature of ~~105^0C~~105˚C. The loss in weight was due to moisture loss and calculated in terms of percentage weight of the samples (1 g of the fresh sample).

$$\% \text{ Moisture} = \frac{W_1 - W_2}{W_1} \times 100$$

Where W_2= weight of sample after drying

W_1= weight of sample before drying

Ash Content Determination

The ash content of the samples was determined by burning the dry samples in an enclosed muffle furnace at temperature of ~~500^0C~~500˚C, for 4 hours until the samples turned to ash. The organic matter was obtained by subtracting the amount of the ash from the dry samples and the value expressed in terms of dry weight of the samples.

3.~~0~~ RESULTS AND DISCUSSION

Table 1. Proximate analysis

SAMPLE	pH	TEMPERATURE (~~⁰C~~˚C)	MOISTURE CONTENT	ASH CONTENT
Nypa Palm	6.46±0.01	27.01±0.06	65.023±0.02	4.02±0.05

Table 2. Levels of Heavy metals in *Nypa fruiticans* leaves

SITES	METALS	RANGES (mg/kg)	MEAN CONCENTRATIONS (mg/kg)	STANDARD DEVIATIONS
SITE I	Pb	1.051-1.076	1.068	0.014
	Cd	0.014-0.019	0.017	0.003
	Cu	1.001-3.09	2.390	0.204

	Ni	0.011-0.012	0.012	0.001
SITE II	Pb	1.048-1.094	1.076	0.025
	Cd	0.025-0.031	0.028	0.003
	Cu	0.029-0.042	0.037	0.007
	Ni	2.031-2.076	2.049	0.024
SITE III (control)	Pb	0.012-0.029	0.023	0.010
	Cd	BDL	BDL	BDL
	Cu	0.001-0.007	0.002	0.001
	Ni	0.007-0.007	0.007	0.000

Detection Limit (DL) of metals studied: Pb (0.25), Cd (0.025), Cu (0.078), Ni (0.125)

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Table 3. Levels of Total Hydrocarbon Contents in *Nypa friuticans* leaves

SITE	RANGE (mg/kg)	MEAN CONCENTRATION (mg/kg)	STANDARD DEVIATION (mg/kg)
SITE I	123240 - 125481	124361.7	1120.502
SITE II	310009.1 - 315218.11	311,813.4	2950.291
SITE III (control)	1489.00 - 1502.13	1488.08	14.532

Table 4. WHO recommended limits in plants (Organization-, 1996) (WH0 1996)

METALS	LIMITS (mg/kg)
Pb	2
Cd	0.02

Cu	10
Ni	10

Lead: High Pb concentration in environmental compartments indicates pollution from oil spill and other industrial activities. According to (Osuji & Onojake, (2004), lead is present in crude oil obtained from the Niger Delta, Nigeria. Plants grown in lead-contaminated soils accumulate low levels of lead in the edible portions of the plant from adherence of dusts and translocation into the tissues -(Finster *et al.*, 2004);(Ubong *al.*, 2020). At site I, the mean value of Lead in *Nypa fruiticans* ranged from 1.051-1.076 mg/kg with a mean value of 1.068 ± 0.014 mg/kg (Table 2), site II (1.076 ± 0.025 mg/kg) and III (0.023 ± 0.010 mg/kg). These values are all below the WHO recommended limit (Table 4), which indicates a low level of lead pollution. However, site III recorded the least concentration of lead and it may be attributed to the absence of oil exploration and other industrial activities at this site. Comparatively, these values are higher than results recorded by (Opaluwa *et al.*, (2012) -who investigated the heavy metals in plants grown around dumpsites in Lafia, Nigeria. However, the Pb concentrations in the current study are much lower than values obtained by (Deribachew *et al.*, (2015), who investigated the levels of heavy metals in plants produced through wastewater irrigation in eastern Ethiopia. Lead is a well-known neurotoxin which causes the impairment of the neurodevelopment in children. Exposure in the uterus and breastfeeding may all be responsible for the effects. Lead accumulates in the skeleton and its mobilization from bones during pregnancy and lactation causes exposure to fetuses and breastfed infants (ATSDR, 2007). The observed study disagrees with the observation of (Ubong *et al.*, (2011) on determination of heavy metals in tissues of *Callinectus latimanus* from new Calabar river, Nigeria. The results obtained from the current study show that metal concentration in male *C. latimanus* ranged as follows: Ni (93.09 – 231.17 mg/kg), Pb (2.73 – 29.76 mg/kg), Cd (0.05 – 4.10 mg/kg) while the range for female crab species were: Ni (165.63 – 313.53 mg/kg), Pb (4.77 – 37.08 mg/kg), Cd (0.26 – 4.10 mg/kg).

Cadmium: Cadmium is utilized in several industrial and agricultural activities like manufacture of herbicides and pesticides; it is also found in trace amounts in crude oil (Osuji & Onojake, 2004). Table 2 ~~shows~~ showed that the concentration of Cadmium in *Nypa fruiticans* obtained from site I ranged from 0.014 - 0.019 mg/kg while the mean values of site II 0.028±0.003 mg/kg; the amount of Cd in site III was below the detention limit (BDL) indicating a negligible degree of Cd pollution. It can be observed that only site II recorded Cd concentration above the WHO recommended limit of 0.2

mg/kg (Table 4), which implies that site B has a high degree of Cd pollution. However, all Cd concentrations recorded in this study are lower than the results by Bal *et al.*, (2013) on heavy metal accumulation in plants in urban and industrial area of Istanbul, Turkey. Cd has similar chemical properties like Zn, which may account in part for its toxicity in biological system. Zn being an essential trace element in plants and animals can be substituted with Cd and may cause the malfunctioning of metabolic processes (Campbell, 2006). Cd is very toxic to human, and specifically targets the bones and kidneys.

Copper: Cu is a micro element which is essential in plant growth and occurs naturally in soil and sediments. It is an important component of enzymes and is necessary for normal growth and development. However, anthropogenic activities may raise the level of Cu in soil above their natural background levels; this may lead to hair and skin decolourations, dermatitis, respiratory tract disease in humans (Khan *et al.*, 2008) . From Table 2, the mean values of Copper were 2.390±0.204 (Site I), 0.037±0.007mg/kg (Site II) and 0.002±0.001mg/kg (Site III), and were all below the WHO permissible limit of 10 mg/kg (Table 4). Site III recorded the least Cu concentration while site I had the highest. Sites II and III gave a lower Cu concentration than the results of Opaluwa *et al.*, (2012) on the metal concentration in plants grown around dumpsites (0.36 – 0.71 mg/kg).

Nickel: Ni is an essential trace element for plants and animals; according to Hjortenkrans, (2003), it is absorbed easily and rapidly by plants. However, at high concentration, Ni is toxic to humans and causes severe diseases like weight loss, loss of vision, heart and liver failures (McGrath, 1990). Nickel in Nypa fruiticans ranged from 0.011-0.012 mg/kg in site I (Table 2), 2.031-2.076mg/kg (site II) and 0.007-0.007mg/kg (site III) and were all below WHO permissible limit. Higher Ni concentration in plants was recorded by Bal *et al.*, (2013). According to Ubong *et al.*, (2020b), Ni in *Tympanotonus fuscatus* and sediments of Iko River ranged from 0.77±0.3 - 83.6±0.2 mg/kg and 2.42±0.3 - 91.6±0.2 mg/kg, respectively, which is largely higher than the amounts recorded in this study.

THC: Hydrocarbon is a family of organic compounds or a class of organic chemicals composed entirely of carbon and hydrogen atoms, which bond together as structure of the compound. It is considered to be an organic compound of simplest composition and may be thought to be the parent substance from which other compounds are derived (McDonald & Ahern, 2002) Hydrocarbons come in four structural classes namely; aromatic, aliphatic, halogenated and terpenes. This study however assessed the cumulative amount of all classes of hydrocarbons in the study area. At site I, the mean value of THC in *Nypa fruiticans* ranged from 1.23240-125,.481 mg/kg with a mean value of 124,361.7±1120.502 mg/kg (Table 3); at site II the mean value of THC ranged from 310,009.1-315,218.9 mg/kg with a mean value of 311,813.4±2950.291mg/kg and at site III (control) the mean value of THC ranged from 1489-1502mg/kg with a mean value of 1488.08±14.532 mg/kg. The THC in *Nypa fruiticans* at the different study site ~~follow~~follows the sequence: Site II > Site I > Site III. THC concentration in the study sites exceed previous study obtained by ~~(~~Numbere, (2019) on the bioaccumulation of THC in Nypa fruiticans in the Niger Delta, Nigeria. Furthermore, THC in this research ~~also~~ exceed the concentration recorded in other studies carried out in the Niger Delta as follows;(Osam *et al.*, 2011), (Okop & Ekpo, 2012) , and (Edwin-Wosu & Albert, 2010). Therefore, it implies that the area under investigation has a high degree of THC pollution, which will pose a problem to the exposed ecosystem. According to ~~(~~Udoetok *et al.*, (2011), the introduction of petroleum hydrocarbons to the Niger Delta as a result of the oil spill incident there, may have been responsible for the high level of petroleum hydrocarbons obtained at the site. This is evident by the high level of total hydrocarbon content (THC), significant concentration of total petroleum hydrocarbon fractions within the n-C12 - n-C17 range, especially the n-C13 and n-C17 fractions, the high concentration of polycyclic aromatic hydrocarbons (PAHs) and the substantial concentration of the volatile BTEX fractions. Hydrocarbon accumulation in humans leads to diverse adverse effects as outlined in different literature, which include the pulmonary and cardiovascular effects (Aitzaz *et al.*, 2019), central nervous system, gastrointestinal effects, renal effects and dermatological effects (Members *et al.*, 2009).

4.0 CONCLUSION

The findings showed that the samples under study were contaminated with heavy metal and total hydrocarbon content. The trend of heavy metal was as follows: Cu > Pb > Ni > Cd at site I, Ni > Pb > Cu > Cd at site II and Pb > Ni > Cu > Cd at site III which is the control. The heavy metals in Nypa palm were below the permissible limits of world health organization (WHO), with the exception of Cd in site II. The levels of THC in sites I and II were much higher than site III, indicating that both sites I and II are highly contaminated with THC. The heavy metals and hydrocarbon present in the environment can pose a serious environmental risk and affect crops that are grown in the area. The results from this research reveals that the flora found on the shores of Qua Iboe River in Nditia community (Ibeno LGA) have a very high level of THC, making the plants unfit for human consumption. On the other hand, heavy metals and THC in *Nypa fruiticans* in the control site (Ikot Ebok) were very low and within permissible limits; implying very minimal contamination of the area.

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