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Estimation of Heavy Metals and Polycyclic Aromatic Heavy Metals in Harvested Plantains from Bodo, Rivers State

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Abstract

A Plantain harvested from Bodo community, Gokana L.G.A Rivers state were analyzed for heavy metals and Polycyclic Aromatic Hydrocarbons (PAHs) concentrations. Physicochemical properties of the agricultural soil used for the plantain cultivation showed the following: pH (5.7) while the control experiment was seen at 7.4. Soil conductivity of 721 and 398 were obtained for both the test and control experiments, respectively. Soil mineral contents: Potassium (6.88 mg/g), phosphorus (2.63 mg/g), Magnesium (12.42 mg/g), chloride ions (1021.21 mg/g). Heavy metal analysis of the soil showed a greater proportion of copper and iron in while Hg, As and Cd were below detectable limit in both tested samples. Pb was found relatively in lower concentrations of 24.12 mg/g in the test sample, 6.23 mg/g in the control experiment. Total Oxidizable Carbon Content (TOC) and Total Petroleum Hydrocarbon (TPH) content of the soil were observed at 104.12 and 2567 mg/g respectively in the tested sample. The control experiment showed TOC and TPH concentrations of 42.85 and 1094 mg/g. Heavy metal analysis of harvested plantain from Bodoh community showed the presence of the following: Lead (Pb), Iron (Fe) and Copper (Cu) in the following order: Cu>Fe>Pb in the test sample while in the control experiment, iron (Fe) was seen greater than copper (Cu). Heavy metals of mercury, cadmium and arsenic were below detectable limit at in both the harvested plantain from Bodo community and those of the control experiment, respectively. Bioaccumulation factor of all the heavy metals identified were <1. PAHs of Acenaphthalene, Acenaphthene, chrysene, pyrene and fluranthene were not detected in the control experiment while only chrysene was not detected in the test samples. Naphthalene,methyl naphthalene, acenaphthalene, acenaphthene, benzo (k) fluranthene and flourene were relatively high in concentration than pyrene and flouranthene in the test samples. Naphthalene, methylnaphthalene, flourene and benzo(k) flouranthene were only recorded in the control experiment. Acenaphthalene (0.034 mg/g) was seen as the highest PAHs in bioaccumulation in the test sample while flourene (0.005 mg/g) recorded the highest in the control experiment.

Keywords: Heavy metals • PAHs • Bioaccumulation • Plantain

Introduction

Enormous quantities of noxious pollutants have been released into our ecosystem over the last few decades. Among these pollutants, heavy metals (HMs), polycyclic aromatic hydrocarbons (PAHs) and Total Petroleum Hydrocarbons (TPH) represent the major pollutants of our environment. During exploration, production, refining, transport and storage of petroleum and petroleum products, some accidental spills may occur. The threat of petroleum pollution not only from natural sources such as seeps but also from anthropogenic activities such as spillages from effluent treatment plants and other emissions, endangers ecological biodiversity [1,2].

In our country Nigeria, the Niger Delta region is known to produce more than eighty percent (80%) of the country's crude oil [3]. There is presently an unprecedented increase in the upstream and downstream activities of oil and allied industries in this oil rich area [4,5]. Over the years, these oil companies and their allied have generated myriad of pollutants in the form of gaseous emissions, oil spills, effluents and solid wastes [6] that have polluted the environment beyond sustainability. An investigation of the polycyclic aromatic hydrocarbon (PAHs) concentrations in some Niger Delta sediment carried out by Ezemoye and Ezemoye revealed an elevated level of these pollutants in the sediments studied.

With the increasing human population there has been increased need for food supply. This with the need for quality food has increased the demand for supplement foods [7]. Plantain (Musa paradisiaca) is a common crop cultivated commonly in the southern part of Nigeria, although it is commonly eaten all around the country. Plantain can be served alone in a variety of processed forms and can also be used to garnish many other foods like rice, yam, beans, etc.

Bodo is at the epicentre of several pipelines that collect oil from nearly 100 wells in Ogoni district and there have been plenty of minor spills in and around the communities over the years [8]. Two oil spills caused by Shell in 2008 have triggered on-going social and economic problems for the 69,000 people who live in the vicinity of Bodo. Within the swamped community of Bodo are featured with farmers and fishermen [9]. Appropriately to say, most food items and local delicacy of the people is centred on plantain and its variety garnishing; the demand for this food item has increased the efforts of the farmers locally within this place to maximize their productions. Evidently within the farmland in Bodo community is petroleum hydrocarbon recalcitrant, investigation of accumulation of various fractions of the crude oil in most commonly cultivated perennial crops in this community will expose the risk assessment adjourning with the consumption by the local inhabitants [8].

Materials and Methods

All chemicals/reagents and equipments used in the present were of analytical grade and products of the following companies: BDH chemical limited (England), Merck (Germany), May and Baker limited (England), Riedel-DeHaenHannaves (Germany), Hopkins and Williams Essex (England), Fluka chemical company (Germany), Kermel chemicals (China) and Lab. Tech Chemicals, Avighkar (India).

Plant source

The plantain fruits were harvested from a farmland in Bodo City, Gokana LGA, Rivers State. Gokana is a Local Government Area in Rivers State with

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an area of 126 km² and a population of about 228,828 at the 2006 census (Figure 1).

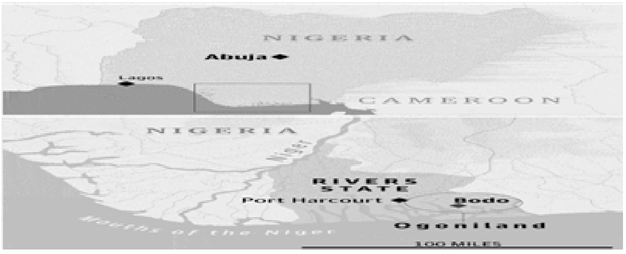

Figure 1. Geographical location of Bodo community within the suburb shells of Gokana L.G.A, Rivers State. use below the detectability limit.

The plantain fruit (control) was harvested from a farmland at Ngor-Okpala, Owerri west Local Government Area in Imo State, Nigeria.

Preparation of sample

This was carried out as described by Oparaji et al. The large leaves of the plantain were removed using sharp table knife from the suckers [10]. The remaining suckers were washed in distilled water to remove all loose silt and dirt. The samples were then sliced in distinct small sizes and air dried for several days before they were taken to the laboratory for analyses. After drying, the samples were blended using a high speed blender. All samples were labeled and transferred to the laboratory for analysis.

Determination of soil physicochemical chemicals

Bodo soil physicochemical properties were determined as described by the Journal of agency of toxic substance and disease registry (ATSDR) [11]. The following soil parameters was determined and they include: pH, conductivity, heavy metals, mineral contents, total petroleum hydrocarbon (TPH), total oxidizable carbon (TOC) and total organic matter contents (TOM).

Determination of heavy metals constituents of the harvested plantains

Heavy metal constituents in the prepared plantains from Bodo and that of the control were determined using atomic absorption spectra machine as described by Oyibo et al. [12]. Heavy metals Lead, Mercury, Chromium, Cadmium, Iron, Zinc, Copper, Arsenic was estimated in the plantain samples, respectively. Prior to the spectrophotometer analysis, the samples were digested in a concentrated acid solution (10 ml of aqua regia which constitute 3:1 of HCL and HNO_3) in a fume cupboard followed by high temperature treatment. After the preparation of the standard solutions, the concentrations of the heavy metals in each of the studied samples were estimated using Atomic Absorption Spectrophotometer (Schimadzu AA-670, Japan).

Bioaccumulation Factor (BF) was calculated here with: concentration of metal in plant÷ concentration of metal in the soil.

Determination of the polycyclic aromatic hydrocarbon contents

Polycyclic aromatic hydrocarbons that were analyzed included Naphthalene, 2-methylnaphthalene, Acenaphthalene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a) anthracene, Chrysene, Benzo (a) pyrene, Benzo (k) fluoranthene. This was done as described by Schwab et al. [13]. Five grams of prepared sample was weighed using analytical weighing balance into a 100 ml beaker and 50 ml of acetone and dichloromethane (1:1 v/v) was used as the extracting solvent. The beaker with the content was placed on magnetic stirrer and shaken for about 10 min at 65°C. The extracted solution was decanted into a clean round-bottom flask. Five grams of anhydrous sodium sulphate was added to the solution to remove water. The solution was concentrated to 5 ml with rotary evaporator maintained at 20°C. Then 1.5 ml of the concentrated extract was loaded on a silica gel column. Each of the silica gel beds was equilibrated with 40 ml of HPLC-hexane to remove any organic contaminant. 30 ml of dichloromethane was tilted into the column to elute the polycyclic aromatic hydrocarbon contents into 100 ml beaker. Then 2 g of anhydrous sodium sulphate was added to remove any traces of water left in the extract. The fractions were concentrated using rotary evaporator to about 2 ml for gas chromatographic analysis.

Gas chromatography analysis

This was carried out as described by Oyibo et al. [12]. For the gas chromatography analysis, each extract transferred to 1.5 ml vial was loaded into a gas chromatography system Agilent 6890 series model G1530 A, with flame ionization detector (FID), and cold on-column injection. Exactly 1 µL portion of the sample was injected and analyzed for PAHs (C9-C36). A HP-5 (cross-linked pH ME siloxane) column having the dimensions 30 m × 0.25 mm 1.d with a stationary phase thickness of 0.25 µm was used for analytical separation. The carrier gas was purified nitrogen held at a flow rate of 5 ml/min. The operating temperature program was started at 60°C for 2 min and then increased at a rate of 10°C/min to 300°C for 10 min (API 1968). The injector and detector temperature were maintained at 250°C and 300°C respectively. The minimum detection limit for all the compounds analyzed was 0.1 µg/kg wet weight

Quality control and assurance

For the reference solution preparation, a stock solution of 1 mg/ml was prepared in Hyper Performance Liquid Chromatography (HPLC) grade Dichloromethane (DCM) and stored in the refrigerator at 8°C. Standard solution was prepared at each day of experiment using the appropriate dilution factorials. For the internal standard stock solution preparation, 1 ml of n-hexane was taken and transferred into 100 ml volumetric flask, dissolved and diluted to volume using HPLC grade DCM. For method validation specificity (selectivity), the selectivity of the GC method was checked by comparison of chromatograms obtained from samples and the corresponding standard. The precision of the method was determined in terms of repeatability or reproducibility and intermediate precision studies. The accuracy of the method was evaluated by spiking different known concentration of hydrocarbon into the gas chromatograph and the closeness of the results to the true value was determined.

Results

Physicochemical properties of Bodo soil spilled with petroleum hydrocarbons showed the following as shown in Table 1. Revealing in the table is the presence of heavy metals like Pb, Cu and Fe while Cd, Hg and As were below detectable limit. High chloride content and relatively acidic compared with the control experiment.

Physiochemical parameters	Control experiment	Soil sample
pH	7.4	5.7
Soil conductivity	398	721
Chloride ion (mg/g)	393	1021.21
Phosphorus (mg/g)	1.86	2.63
Magnesium (mg/g)	24.27	12.42
Potassium (mg/g)	7.42	6.88
Calcium (mg/kg)	32.23	21.28
SO_4 (mg/g)	7.39	23.64
Iron (mg/g)	6.55	32.1
Cadmium (mg/g)	BDL	BDL
Mercury (mg/g)	BDL	BDL
Arsenic (mg/g)	BDL	BDL
Lead (mg/g)	6.23	24.12
Copper (mg/g)	14.28	34.72
Total Organic Carbon (TOC) (mg/g)	42.85	104.12
Total organic matter (mg/g)	51.66	126.31

Total Petroleum Hydrocarbon (TPH) (mg/g)	1094	2567
Soil temperature	34.5°C	37.0°C
Note: N=2 * BDL: Below Detectable Limits		

Table 1. Physicochemical properties of Bodo soil.

Estimation of heavy metals content from the prepared suckers of plantain from Bodo soil showed the presence of the following heavy metals as shown in Table 2. Adding to the table is the pH contents of the harvested prepared extracts.

Heavy metals (mg/g)	Control experiment	Bodo sample
pH	5.2	4
Lead	0.8	2.34
Iron	5.6	6.8
Arsenic	BDL	BDL
Copper	4.9	7.2
Cadmium	BDL	BDL
Mercury	BDL	BDL
Note: N=2 * BDL: Below Detectable Limits		

Table 2. Heavy metals concentrations in the harvested Bodo plantain.

Estimation of Bioaccumulation Factor (BF) of heavy metals in the prepared suckers of plantain from Bodo soil. From the table it is seen that the heavy metal bioaccumulation quotient in the plant samples were all <1.

Estimation of polycyclic aromatic hydrocarbon contents from the prepared suckers of plantain from Bodo soil showed the presence of the following heavy metals as shown in Table 3 and Table 4.

Heavy metals (mg/g)	Control experiment	Bodo sample
Lead	0.128	0.1
Iron	0.855	0.213
Copper	0.343	0.21

Table 3. Bioaccumulation factor of heavy metals in the harvested Bodo plantain.

PHAs (mg/g)	Control experiment	Bodo plantain
Naphthalene	0.004	0.016
2-methylnaphthalene	0.003	0.023
Flourene	0.005	0.015
Acenaphthalene	ND	0.034
Acenaphthene	ND	0.025
Pyrene	ND	0.002
Chrysene	ND	ND
Benzo (k) flouranthene	0.001	0.031
Fluoranthene	ND	0.002
Note: N=2 ND: Not detected.		

Table 4. Polycyclic aromatic hydrocarbon contents harvested Bodo Plantain.

Discussion

Oil especially from petroleum hydrocarbons spills are considered as the most significant pollutant in recent time. Petroleum hydrocarbons contain hundreds or thousands of aliphatic, branched and aromatic hydrocarbons among other sub component compounds like heavy metals. The benzene presence components of crude oil and some heavy metals are said to be toxic to living organisms. Significantly, crude oil renders the environment unsightly and constitutes a potential threat to humans, animals and vegetation.

This study looked at estimation of heavy metals and polycyclic aromatic hydrocarbon content of plantain harvested from Bodoh community, Rivers state. From the present study, results obtained from the soil analysis contaminated with crude oil showed pH of 5.7 while the control experiment was seen at 7.4. soil conductivity of 721 and 398 for the test and control experiments respectively. The relative lower pH of the test sample can be attributed to the nature of the contaminant in the soil such as oil which can contain higher acidic contents (PAHS) as stated in the proceedings of the ASTDR. Other contents of the soil upon analysis showed potassium (6.88 mg/g), phosphorus (2.63 mg/g), Magnesium (12.42 mg/g), chloride ions (1021.21 mg/g). The presence of Potassium, magnesium and chloride ions in higher concentration (Mg/g) revealed the level of pollution of the soil with the petroleum hydrocarbons. This showed a significant different from the control soil sample which upon analysis showed a lower concentration of K, P, Mg and Cl ion in the following order respectively: 7.42, 1.86, 24.27, 393 mg/g. Chikere et al. [4] in their study at Eleme petrochemical jetting port site reported a similar correlation of ions concentrations in the contaminated Eleme port soil. Their revealed a higher concentrations of the mineral ions in the following order 2.28, 1.84, 5.22 and 1789.22 mg/g respectively for K, nitrate, magnesium and chloride ions. Upon analysis of heavy metal (Fe, Pb, Cu, Hg, As and Cd) contents of the contaminated soil showed a greater proportion of copper and iron in the soil while Hg, As and Cd were below detectable limit in both tested samples. Pb was found relatively in lower concentrations of 24.12 mg/g in the test sample, 6.23 mg/g in the control experiment. Total Oxidizable Carbon Content (TOC) and Total Petroleum Hydrocarbon (TPH) content of the soil were observed at 104.12 and 2567 mg/g respectively in the tested sample. The control experiment showed TOC and TPH concentrations of 42.85 and 1094 mg/g. This showed a strong significant different from the control experiments in the tested samples. A similar result in their research on microbial diversities in a spent engine polluted site at Mgbuka, Onitsha Anambra state with Total petroleum hydrocarbon and total organic matter contents showing the highest in concentrations (114.06 and 1765.21 respectively).

Metals are said to act as stabilizers and chelators of charges, radicals etc in every chemical system including the environment (Valero, 2010). Heavy metals which are those characterized with large atomic radii generally are indications of pollutions and environmental contaminations in the ecosystems. Heavy metal analysis of harvested plantain from Bodoh community showed the presence of the following: Lead (Pb), Iron (Fe) and Copper (Cu) in the following order: Cu>Fe>Pb in the test sample while in the control experiment, iron (Fe) was seen greater than copper (Cu). Heavy metals of mercury, cadmium and arsenic were below detectable limit at the atomic absorption spectrophotometer in the harvested plantain from Bodo community and those of the control experiment. The order of their presence and bioaccumulation could be attributed to differences in uptakes, soil topography, metabolisms and detoxifications of the metals by the plantain.

These correlate with the findings of Oparaji et al. [10] on the bioaccumulation of heavy metals in aquatic faunas and sediments at Forcados river, Rivers state. Their results showed a higher proportion of Fe in all the tested species of aquatic fauna in the contaminated Eleme river while they reported Hg to be at below detectable limits (BDL) in all the tested faunas and surrounding sediments. Saeed and Shaker [14] reported that heavy metals like mercury, Arsenic are poisons which are not often seen in any environmental pollution. Mercury are mostly seen in sites located near nuclear factory, cell factory etc. which are seldom in our locality. The results from this investigation are in correlation with the work of Saeed and Shaker [14] that attributed the abundance of these metals in the fish samples to accumulation of the metals in sediments and water.

Polycyclic aromatic hydrocarbons (PAHs) are petroleum hydrocarbon compounds characterized by presence of a benzene fused ring(s) and are mostly seen in most environmental pollutions but relatively in fewer occurrences than other petroleum hydrocarbon compounds like petroleum aliphatic hydrocarbons [15]. Binelli and Provini stated that most of these PAHs are recognized mutagens and carcinogens; they went further to state that this pollutant class has been considered of "high crucial necessity" for environmental contamination evaluation [16]. In present study (Tables 3 and 4) PAHs of Acenaphthalene, Acenaphthene, chrysene, pyrene and fluranthene were not detected in the control experiment while only chrysene was not detected in the test samples. Naphthalene,methyl naphthalene, acenaphthalene, acenaphthene, benzo (k) fluranthene and flourene were relatively high in concentration than pyrene and flouranthene in the test samples. Naphthalene, methylnaphthalene, flourene and benzo (k) flouranthene were only recorded in the control experiment. Acenaphthalene was seen as the highest PAHs in bioaccumulation in the test sample while flourene recorded the highest in the control experiment. Bioaccumulation which is a process, by which a compound is absorbed by living matter, processed and exposed the finished compound [17]. Polycyclic aromatic hydrocarbons bioaccumulation in living matter is highly dependent on fatty and lipid-rich tissues and organs [18]; their bioavailability is a function of kinetics and partitioning of the contaminants in the environment. Polycyclic Aromatic Hydrocarbons (PAHs) are rated by the European Union as “priority hazardous” substances [19-22]. Low concentration of PAHs in the experimented sample can be in consonance with the findings of Antizar-Ladislao who reported that PAHs are less soluble in aqueous solutions and are fastidious in identification, he went further to state that even though they acumulate within the sediments of soil where the settle and easily associate with particles as a result of their hydrophobic characteristics.

Conclusion

The present research has shown with analysed empirical the presence of certain Heavy Metals (Hm) and their bioaccumulation index in plantain harvested from Bodo community, Rivers state, Nigeria. From the result, arrays of heavy metals were seen in relatively high concentrations when compared with that of the control experiments. Of the alarming result is the incident of lead (Pb) in the tested plantain from Bodo community. Petroleum hydrocarbon compounds of polycyclic aromatic hydrocarbons were estimated in the plantain samples. Though their (PAHs) concentrations generally were low but evident in all the tested samples except chrysene which is not detected with experimented plantains. The afore with data will provide the health and risk assessment of inhabitants of Bodo community whose major meals are plantains prepared in different delicacies more so the present study has shown the level of pollution of the community agricultural soil.

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