Study of the Concentration of Polycyclic Aromatic Hydrocarbons and Sundry Parameters of Refinery Oil on Eleme River, Port-Harcourt, Nigeria

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Abstract: The Polycyclic Aromatic Hydrocarbons (PAHs) once formed can be transported into an aquatic environment through a number of pathways including fossil fuel distribution, petroleum spillage, sewage and waste water effluents. The aim of this study was to determine the presence of PAHs and other contaminants as a result of oil refinery effluent on the Eleme River in Port Harcourt, Rivers State, Nigeria. Water samples were collected from three (3) different stations along the water course of the river, Station A is the upstream, Station B is the point of effluent discharge and Station C, the down-stream. The PAHs concentrations were determined using Gas Chromatography-Mass Spectrometry (GC-MS) instrumentation. Using standard methods, physiochemical parameter were also analyzed. The result showed the presence of the following PAH ions, Phenanthrene, pyrene, chrysene, fluoranthene and benzo(a)pyrene. For the other parameters; the temperature (37^{o}C), conductivity (656.21, us/cm), Chemical Oxygen Demand (COD)-41.19, were higher than the other two stations and all exceeded the maximum permissible limits of federal ministry of environment standards. The mean of Biological Oxygen Demand (BOD)-3.59 and Dissolved Oxygen (DO)-7.43 are lower than the standard acceptable limits. However, the statistical analysis showed that there was no significant difference ($P>0.05$) in the values of all the parameters of the different stations. The results of this study justified that the Eleme River is highly contaminated and this could lead to acute and long term effects on human and aquatic health. Therefore, effluents emanating from the oil and gas refinery must be properly treated and tested for compliance before being discharged into the receiving water body to avoid environmental health hazards.

Keywords: PAHs, Refinery Effluents, Contamination, Water body.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic components that are mostly colorless, white or pale yellow solids. Generally PAHs enter the environment through various routes and are usually found as a mixture containing two or more of these compounds e.g Soot (CCME, 2010). They are a ubiquitous group of several hundred chemically related compounds, environmentally persistent with various structures and varied toxicity (Armstrong *et al.*, 2004). Thus, PAHs are commonly detected in air, soil and water (Latimer and Zheng, 2003). PAHs can be formed both during biological processes and as products of incomplete combustion from either natural combustion sources (forest and bush fires) or man-made combustion sources (automobile emissions and cigarette smoke). Environmental pollution has become a serious problem confronting scientists and regulators around the world. It is a problem both in developed and developing countries. Industrialization and population growth are key factors that invariably place greater demands on the environment and stretch the use of resources to the maximum (Okereke *et al.*, 2016). In the past, human and other animals enjoyed clean water and air but industrial revolution in the 19^{th} century and its perfection in 20^{th} century, gradually caused air water, and soil to become polluted by the activities of man (Udensi *et al*, 2017). The contamination of fresh waters with wide range of pollutants has become a matter of concern over the last few decades (Vutukuru, 2005). The problem can be attributed to the process of rapid urbanization and industrial development over least decades and these have been a subject of environmental concern. Rivers worldwide serve as recipient of great quantities of waste discharged by agricultural, industrial and domestic activities (Mimosa, 2007). The occurrence of PAHs in the aquatic ecosystem has been the subject of significant investigation across many industrialized cities (Opuene, 2005). PAHs can reach surface waters and sediment in different ways including atmospheric deposition, urban run-off, municipal and industrial effluents and oil spillage or leakage (Gogou *et al.*, 2000). Owing to their low aqueous solubility and strong hydrophobic nature, these contaminants tend to associate with particulate material in the aquatic environments with the underlying sediments as their ultimate sink. They have been shown to cause carcinogenic and mutagenic effects and are potent immuosuppressants (Rajendran *et al.*, 2013). Contamination of aquatic ecosystems by PAHs has been recognized as a major public health risk (Okafor and Opuene, 2007). Also several of the PAHs, including benz(a)anthracene, benzo(a)pypene, benzo(b)floranthene, benzo(j)floranthene, benzo(k)fluoranthene chrysene, dibenz(ah)anthracene and indeno[1,2,3-c,d] pyrene, have caused tumors in laboratory animals when they are exposed to these substances via several exposure pathways (Ana, *et al*, 2011).

The point sources of emissions of reportable size of polycyclic aromatic hydrocarbons include petroleum refineries, sites dealing with the production of coal tar, coke, bitumen, and asphalt, paper, wood products and aluminum, industrial machinery manufacture and power production from fossil fuels. Non point sources may include aerial fallout, inadvertent oil spills and marine oil spillage (Eddy and Cherrie, 1994). The Niger Delta area is the hit of environmental destruction arising from oil production. Port Harcourt metropolis, the study area in the Niger Delta region of Nigeria is the fourth largest urban centre in the country. The Niger Delta is host to three of Nigeria four refineries which generate large quantities of effluents daily. Though the compositions of the effluents are regulated by various laws, it is not known whether they comply with legally accepted toxicant levels for refineries in Nigeria. The present situation and the worsened environmental status are worrisome.

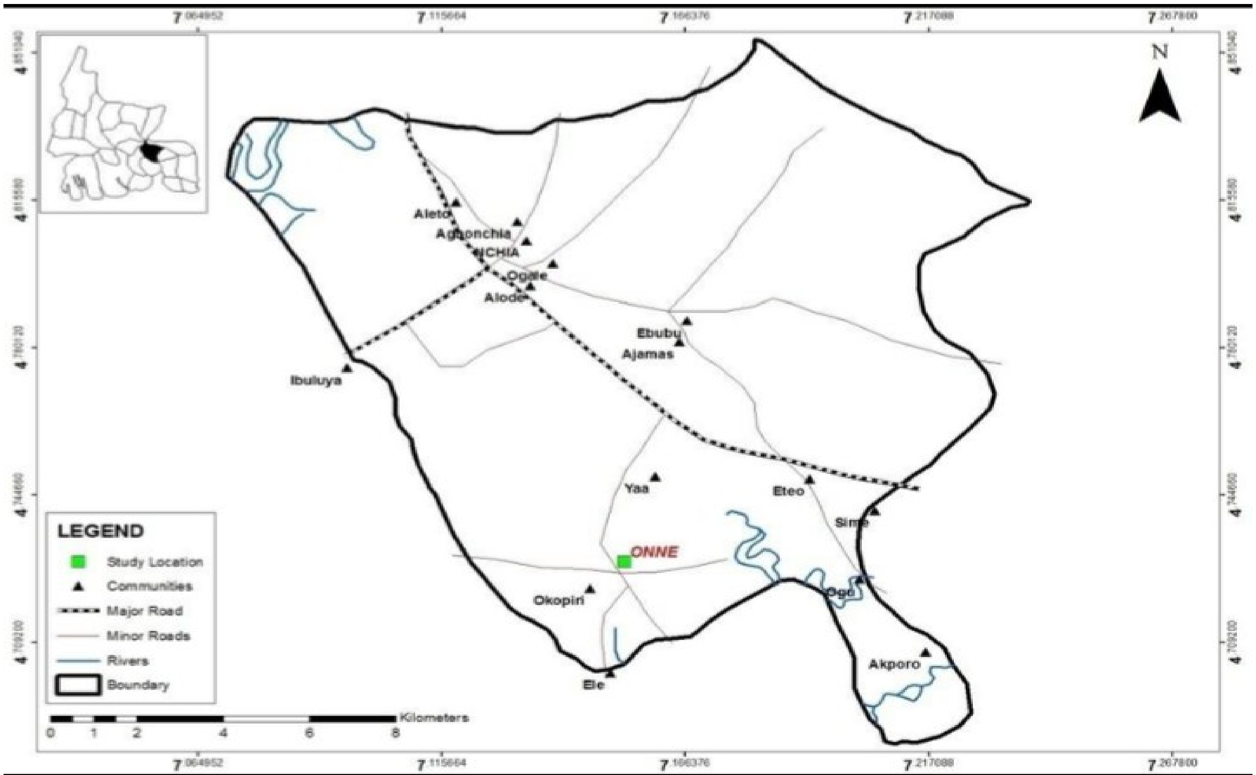
The present study was designed to provide an insight into the current scenario of Polycyclic aromatic hydrocarbons contamination in selected points in recipient water body (environment) where the refinery effluent/runoff are discharged (Marcus and Ekpete, 2014).

MATERIALS AND METHOD

Study Area

Eleme is a Local Government Area (LGA) in Port Harcourt , Rivers

State, Nigeria. It is located east and it is part of the Greater Port Harcourt metropolitan area. It covers an area of $138km^2$ and at the 2006 census had a population of 190,884. The territory known as Eleme constitutes one LGA of the 23 that make up Rivers State and is located between longitude 7^1 and 7^1 $35^{''}$(Seven degrees thirty five minutes) East of the Meridian and latitudes 4^1 $60^{''}$and 4^1 $35^{''}$(four degrees sixty minutes and four degrees thirty five minutes) North of the equator. The discovery in 1957 of abundant reserves of oil & gas in the area has attracted over one hundred companies that are engaged in the upstream and downstream sectors of exploration, with the Onne port complex serving as the pivot for Sub-Saharan Africa. The Eleme Community is the home to a number of industries including petrochemicals, oil refining, paint and fertilizer industries.



SOURCE: (Onyebade and Buochuama 2016)

MAP OF ELEME COMMUNITY

Materials

Autoclave, bijou bottles, Bunsen burner, clover slips, durham tubes, electronic weighing balance, glass slides, incubator, microscope, nail hardener, paraffin wax, pasteur pipette, petri dishes, sterilized inoculating loop, test tubes tryptophan broth, one mercury thermometer with calibration between point 0-100^{o}C, an ice chest, a pair of hand gloves, three 2.5 liter white can, measuring tape, masking tape, aluminum foil, BOD and COD bottles.

Reagents

Kovac's reagent, lactophenol blue, malachite green potassium hydroxide, mercury chloride solution, crystal violet (primary stain), Gram's iodine (Mordant), Ethanol/alcohol(decolorizer), Safranin (counter stain).

Sample collection

Three sampling stations were judiciously selected along the River. These stations are Station A (SA), Station B (SB) and Station C (SC). Station A is located upstream of the creek, north of the out fall or the refinery discharge point. Station B is located at the point of impact, which is the point where the refinery waste water enters the creek. Station C is located downstream of the point of impact. Station A was used as the control for the analysis. This was due to the fact that it was located upstream from the outfall and therefore contained less pollutants. Composite water samples were collected at low tide with a 2.5 litre white laboratory container. The samples were collected in directions opposite the Greek flow. The sample bottles were filled to the brim to ensure that no air was trapped in them. This was done by tilting the bottle and inserting the stopper with a quick thrust inside the water. Prior to the collection of water from each sample from each station, the sample bottles were rinsed with water samples of the point of collection.

Laboratory Analysis

Gas Chromatography-Mass Spectrometry Instrumentation and Conditions. An Agilent 6890N GC equipped with an Agilent 7683B injector, a 30m, 0.25mm i.d. HP-5ms capillary column coated with 5% phenyl-methyIsiloxane (film thickness 0.25um) and a Agilent 5975 mass selective detector (MSD) was used to separate and quantify the PAH compounds. The samples were injected in the splitless mode at an injection temperature of 300^{o}C. The transfer line and ion source temperatures were 280^{o}C and 200^{o}C. The column temperature was initially held at 40^{o}C for 1min, raised to 120^{o}C at the rate of 25^{o}C/min, then to 160^{o}C at the rate of 10^{o}C/min and finally to 300^{o}C at the rate 5^{o}C/min held at final temperature for 15 min. Detector temperature was kept at 280^{o}C. Helium was used as a carrier gas at a constant flow rate of 1 ml/min. Mass Spectrometry was acquired using the electron ionization (EI) and selective ion monitoring (SIM) modes.

Method

Hexane, dichloromethane and acetone was used as solvents to determine the PAHs. A standard mixture containing 16 priority PAHs dissolved in an acetone/benzene mixture (V/V 1:1) in individual concentrations of 2000ug/ml was used to calibrate the device. Deuterated Pyrene (pyrene-d10) was used as internal standard. Results on the analysis of this sample indicate both a satisfactory convergence and accuracy of data obtained. Water samples were frozen using a freeze dryer. A solution of internal standard was added to the frozen samples weighing 2g, the samples were subsequently extracted in a Soxhlet apparatus for with 50ml of dichloromethane: methanol (V\V 3:1) mixture. The recovery factor was calculated on the basis of the internal standard which was 80-95%. Concentrations of PAHs in Eleme River, as a rule 2-3 order of magnitude lower than that compared with aliphatic hydrocarbons therefore the extract was fractionated on a column filled with a sequence of consisting silica gel, aluminum oxide and sodium sulphate. The fraction containing mainly polycyclic aromatic hydrocarbons was eluded with 30ml of hexane-dichloromethane (9:1 V\V). The fraction containing PAHs was evaporated under a weak (flow) of nitrogen to 1ml and it's subjected to qualitative and quantitative analysis on GC/MS Agilent 7890/5975C. The following analytical conditions were used: Capillary column HP-5ms (30m, 0.32mm, 25 microns) rate of the carrier gas-1, 2, cm^3/min, input method-PTV, sample volume-1ul, injector temperature-300^{o}C temperature program-initial temperature 70^{o}C, 1min, heating rate-10^{o}C min-1, first isotherm-190^{o}C for 1min, heating rate-4^{o}C min-1, second isotherm-280^{o}C for 20min, ionization-E+70 eV,-data collection method-SIM, interface temperature-285^{o}C, temperature of source-230^{o}C, temperature of quadrupole-150^{o}C.

RESULTS AND DISCUSSION

Table 1: THE RESULTS OF GC/MS DETERMINATION OF PAHS IN ELEME RIVER.

SAMPLE	PAHs U/kg	Carc PAHs PAHs 100	LMW/HMW	B(a)Peqv, ug/kg	Total PAHs
A	329.6	40	0.52	34.9	4.92
B	1093.3	50	0.23	195.1	6.15
C	789.6	47	0.31	121.4	6.14

KEY

SA: Water Sample from Station A (Upstream)

SB: Water Sample from Station B (Point of Effluent Discharge)

SC: Water Sample from Station C (Downstream)

Table 2: THE RESULTS OF THE PHYSICO-CHEMICAL CHARACTERISTICS FROM THREE (3) DIFFERENT POINTS IN ELEME RIVER

PARAMETERS	SA	SB	SC
PH	6.22	7.01	6.40
Temperature (^{o}C)	34	37	33
Conductivity (us/cm)	153.52	656.21	131.0
Biological Oxygen Demand (BOD)	2.10	5.28	3.40
Chemical Oxygen Demand (COD)	9.40	41.19	15.44
Dissolved Oxygen (DO)	8.00	6.68	7.61
Oil and Grease	0.31	10.55	1.03
Ammonia	1.94	4.31	7.43
Nitrate	2.00	2.85	3.25
Sulphate	9.41	39.08	25.15
Phenol	0.14	0.25	0.15
Total Dissolved Solids (TDS)	38.22	250.00	91.25
Total Suspended Solids (TSS)	10.43	24.00	16.00
Iron	0.12	0.68	0.98
Zinc	7.01	21.00	16.80

KEY
SA: Water Sample from Station A (Upstream)
SB: Water Sample from Station B (Point of Effluent Discharge)
SC: Water Sample from Station C (Downstream)

Figure 1: THE AVERAGE VALUES OF THE RESULTS FROM THE ANALYSIS CARRIED OUT ON THE WATER SAMPLES FROM ELEME RIVER

Possible sources of PAHs emission into the environment can be found through the use of indices, which are the ratio of concentrations of some PAHs in the samples (Mannino and Orecchio, 2008). The physico-chemical properties of the effluent receiving body (River) in Eleme were evaluated and it was observed that the levels of various pollutants varied among the desired discharge limits and others clearly exceeded such limits. The PH mean value of the upstream was 6.90 and downstream 7.4 while that of the point of effluent discharge is 6.54. There was no significant difference ($P>0.05$) between the point of effluent discharge and both upstream and downstream sections are all within Federal Ministry of Environment, Nigeria (FmEnv) permissible limit of 6-9. The result contradicts with the findings of (Ogunlaja and Ogunlaja, 2007) and (Nduka and Orisakwe, 2007). The difference in PH could be due to evapotranspiration, rainfall, chemical and biological processes in the water. The temperature at the time of study ranged from 37^oC for point of impact, 34^oC for upstream and 33^oC downstream. The observed higher mean temperature at the point of discharge might be due to fresh effluent from refinery plants and these values pose no significant threat to the homeostatic balance of the receiving water and were in agreement with the report of (Jaji et al., 2007). Aquatic ecosystem could be adversely affected by a change in temperature. For instance, a rise in temperature could upset the ecological balance of the water course by reducing the amount of dissolved oxygen available for the survival of aquatic organisms. The temperatures recorded were slightly higher than the FmEnv standards. Decrease in DO concentration recorded, could be as a result of the breakdown of organic matter by aerobic microbes.

The oxygen required for this process is taken from the surrounding water thus diminishing its total oxygen content. (Odokuma and Okpokwasili, 1993) reported that it may be partly due to the displacement of dissolved oxygen by dissolved solids within the effluent. The decrease of DO level at the point of discharge might lead to the death of fishes and aquatic plants that live in the River. This in turn could lead to further pollution of the water body thus making the consumption of water by humans harmful to the health. Verbal evidence obtained from the local fishermen suggests that the area around the point of impact is devoid of fishes.

CONCLUSION AND RECOMMENDATIONS

The determination and identification of PAHs using GC/MS was successfully demonstrated. From the results, the presence of 16 compounds of PAHs is an indicator of oil pollution in Eleme River. The physicochemical parameters, heavy metal concentrations as well as the PAHs concentrations were relatively high at the point of effluent discharge in the River which gradually diminishes toward the downstream region. The possible source of PAHs in the River could be as a result of coal combustion from the refinery plant. This result should be useful in designing future strategies for environmental protection of the River and surrounding communities. The results of this study further showed that Eleme River is highly contaminated and this could lead to acute and long term effects on human health. Immediate and long term medical care is recommended to ensure that the potential health effects due to the exposure to the contaminated Eleme River are properly addressed. Some of the effluents did not meet the Federal Ministry of Environment Nigeria (FmEnv) and Department of Petroleum Resources (DPR) standards for the discharge of these wastes into the recipient water bodies.

Therefore, appropriate treatment of effluents must be done and tested for compliance with laid down guidelines before being discharged into the receiving environment. In addition, the use of bioremediation processes in the cleanup of affected water bodies will help to facilitate the detoxification of contaminating compounds insitu.

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