Scientia Africana, Vol. 17 (No. 2), December 2018. Pp 90-96
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IDENTIFICATION AND QUANTIFICATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND TRACE METAL ANALYSES IN SOILS AROUND THE DONALD EKONG LIBRARY CAR PARK, UNIVERSITY OF PORT HARCOURT

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Received:03-04-18
Accepted:23-04-18

ABSTRACT
The outcome of analysis of the levels of PAHs and trace metal in soils around Donald Ekong library car park at University of Port Harcourt shows that its heavy metal contents is high relative to the DPR standard in soils. With the exception of Vanadium, all other selected heavy metal in mg/kg was detected in the soil samples. The selected trace metals and concentration in mg/kg are Cd (0.15), Pb (13.10), Zn (34.75), Fe (30.73), Cr (5.73), and Ni (9.45) relative to their respective Department of petroleum resources standards (mg/kg) which are 0.01, 0.05, 1.0, 1.0, 0.03 and 0.10 respectively. Twelve PAHs were detected while four PAHs were not detected. The carcinogenic and high molecular weight PAHs were all detected while some of the low molecular weight PAHs were not detected or were detected at very small concentration. The higher solubility and volatility of the lower molecular weight PAHs are responsible for this trend of PAHs distribution. There is need to use proper soil remediation strategy for restoration of the soil in line with the appropriate permissible limits for heavy metal and PAHs in soil, which are both (as they are) above their respective permissible limit.

Key Words: PAHs, Soil, Heavy Metal, Quantification

INTRODUCTION
PAHs are neutral, non-polar molecules. They are found in fossil fuels (oil and coal) and in tar deposits, and are produced, generally, when insufficient oxygen or other factors result in incomplete combustion of organic matter (e.g., in engines and incinerators, when biomass burns in forest fires, etc.). The simplest PAHs are phenanthrene and anthracene and are not generally considered to contain hetero-atoms or carry substituents [1].
Trends in the molecular weight of PAHs invariably affect the solubility of PAHs, which in turn, affect their hydrophobicity, characteristics, effects and distribution in the environment matrix and biological media. The lower molecular weight PAHs, i.e. PAHs with three or lesser rings, are reported to have significant acute toxicity to aquatic organisms while high molecular weight PAHs i.e. PAHs with four to seven rings are not. However some of these high molecular weight groups are known to be carcinogenic [2][3][4]. PAHs are non-polar and lipophilic. Most PAHs are not soluble in water and persist in the environment. Aqueous miscibility of PAHs decreases approximately logarithmically as molecular mass increases [5]. Because many PAHs are miscible in water to an extent, PAHs in the environment are found

primarily in the soil, sediment, oily substances, and particulate matter suspended in air. Two-ring PAHs, and to a lesser extent three-ring PAHs, dissolve in water, making them more available for biological uptake and degradation [6]. Furthermore, two to four-ring PAHs volatilize sufficiently to appear in the atmosphere predominantly in gaseous form, although the physical state of four ring PAHs can depend on temperature. PAHs are also found in cooked foods. Studies have shown that high levels of PAHs are found, for example, in meat cooked at high temperatures such as grilling or barbecuing, and in smoked fish [7].

The toxicity of PAHs is structure-dependent. Isomers (PAHs with the same formula and number of rings) can vary from being nontoxic to extremely toxic. One PAH compound, benzo[a]pyrene, is notable for being the first chemical carcinogen to be discovered (and is one of many carcinogens found in cigarette smoke). PAHs are known for their carcinogenic, mutagenic and teratogenic properties [8].
The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the World health organization (WHO) [9].

Essential heavy metals exert biochemical and physiological functions in plants and animals. However, an excess amount of such metals produce cellular and tissue damage leading to a variety of adverse effects and human diseases.
This paper describes the levels of Poly cyclic Aromatic Hydrocarbons (PAHs) in soil samples taken from the Donald Ekong library car park and using the data to determine the toxic potentials of the cPAHs in the soil sample. The article as well reports the levels of heavy metals in the soil and their potential human health hazards.

MATERIALS AND METHODS

Sample Collection

The top soil samples were collected at Donald Ekong Library car park and stored in different bottles. The area's geographical coordinates are Longitude $4^0 54^I 13.5^0$N Latitude $6^0 55^I 15.5^0$E. The Donald Ekong car park serves as a parking lot for Library users, the Fine Arts building and the Ofrima building within the University of Port Harcourt premises.

Sample Preparation and Heavy Metal Analysis

3g of air dried well sieved top soil sample was collected in and kept in a beaker and digested with Nitric acid in a fume hood until the digestion is complete. The beaker was rinsed with distilled water and the content filtered through What man No. 44 filter paper directly into a 50ml volumetric flask and made up to 50ml mark with distilled water. Then aliquots of the filtrate were used to analyze for the various metals. Metal analysis was carried out using Atomic Absorption Spectrophotometer model (Agilent 55B SPECTRAA) with hollow cathode lamp and resonance wavelength of the metals. The concentrations of the various Heavy Metals (Ni, V, Cd, Pb, Zn, Fe, and Cr) in the soil samples are expressed in mg/kg.

Sample Preparation for PAHs Analysis

The soil samples were mixed with analytical grade anhydrous sodium sulphate and extracted using an appropriate solvent (a solvent mixture of Acetone and Hexane (ratio 1:1) in a soxhlet extractor.
The soil samples extract were passed through a polypropylene column chromatography. The polypropylene column was prepared by placing a glass wool at the base of the column that supported the 10g silica gel, which was baked at 105^0C and

Scientia Africana, Vol. 17 (No. 2), December 2018. Pp 90-96
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packed in the column which served as the stationary phase. 10 mls of the soil samples were slowly introduced into the column already filled with prepared eluents and 60ml of n-hexane was used to elute the aliphatic saturated hydrocarbon and the eluent collected with a conical flask. 40ml of dichloromethane (DCM) was used to elute the PAHs. The eluents were collected differently with other conical flask and concentrated using rotary evaporator at 60^{o}C. The different fractions were later analyzed with GC-FID, Agilent 6890 model with Chemstation 32 software. These processes were repeated trice for each sample and the mean value recorded [10] [4]

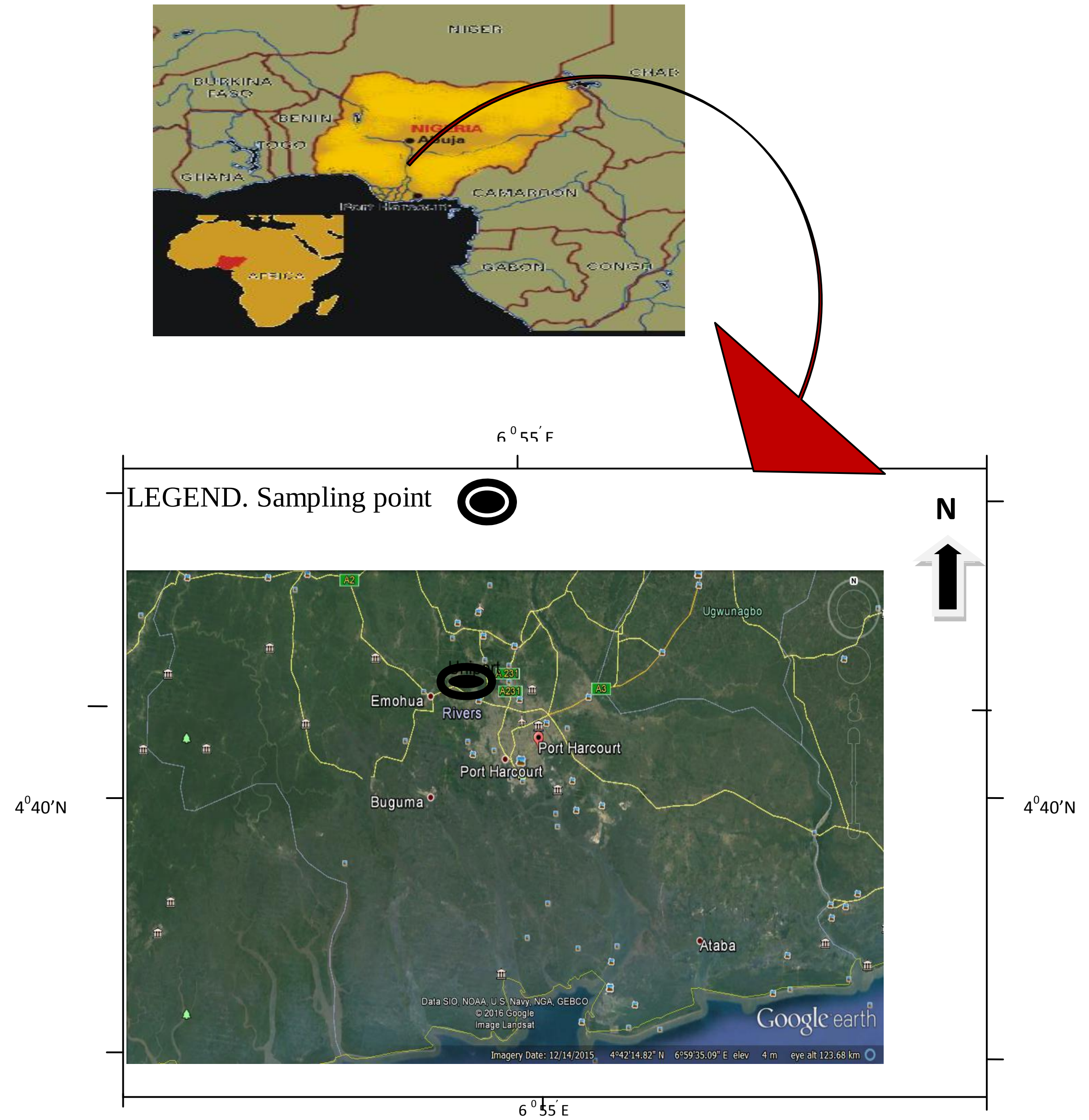

Figure 1. Map of Port Harcourt, Nigeria indicating sampling point (Uniport)

RESULTS

Tables 1 and 2 represent results of heavy metal and PAHs concentration in soil samples from the Donald Ekong Library Park.

Table 1: Mean concentration of Heavy Metals (mg/kg) in the Soil Sample and their corresponding permissible environmental limits (mg/kg)

Heavy metal	Sample	Standards
Vanadium	ND	
Cadmium	0.150	0.01
Lead	13.102	0.05
Zinc	34.750	1.0
Iron	30.730	1.0
Chromium	5.725	0.03
Nickel	9.452	0.10

ND = Not detected

This is an indicative of heavy metal contamination of the soil within the park area. The possible/probable causes of the high levels of the various metals detected may be attributable to weathering of metallic sculptures and scrap metals around the vicinity of the car park, exhaust fumes from cars, presence of petroleum products (e.g engine oil, petrol, diesel etc.) that may have leaked from packed faulty vehicles, waste water from the clothing and textile department as well as acidic rainfall in the area [11].

Table 2: Mean concentration in ppm of PAHs in the Soil Sample

Amount in ppm	PAHs Detected
-	Naphtalene
-	Acenaphthylene
-	Acanaphthene
1.7742	Fluorene
-	Phenanthrene
2.52057	Anthracene
2.22068	Fluoranthene
4.37277	Pyrene
4.43547	Benz (a) anthracene
5.65893	Benzo (b) fluoranthene
10.48042	Chrysene
14.87677	Benzo (a) pyrene
15.79145	Benzo(k) Fluoranthene
25.28736	Indeno (1,2,3-cd) Pyrene
54.69899	Dibenz (a,h)Anthracene
20.10399	Benzo (g,h,i)Perylene

The result of the soil sample analyzed indicates a total PAHs concentration of 162.2268 ppm. The USEPA permissible limits of total PAHs in soil is 40 mg/Kg [12].

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Hence, the PAHs concentration in the Donald Ekong Library Park exceeded the limit. This has tremendous health indicator.

The TPH of the analyzed soil sample is 8.613ppm. According to USEPA [16], the acceptable limit of TPH in soil is 1000 mg/kg. Hence, the concentration of the TPH in the soil is within the compliance limit as recommended by USEPA. [12]

DISCUSSION

Table 1 shows the results of investigated heavy metals in mg/kg as well as the Department of Petroleum Resources (DPR) / Federal Ministry of Education (FME) permissible limits for heavy metals in soil as standards for easy correlation. The order of heavy metal concentration in the soil sample is: Zn> Fe> Pb> Ni> Cr> Cd with concentrations in mg/kg of 34.750, 30.730, 13.102, 9.452, 5.725, and 0.150 respectively. Vanadium was below the detection limit of the analytical instrument used. A comparison of the average concentrations of the six heavy metals (Cd, Zn, Pb, V, Cr, Ni) revealed that the concentrations of the heavy metals in the soil sample are higher than the permissible values for the individual metals with respect to the FME and DPR permissible limits for inland areas.

The results of the Σ16 PAHs analyzed, show that Naphthalene, Acenaphthylene, Acenaphtene and Phenanthrene were below detection limit of the analytical equipment used. The order of concentration of the PAHs are as follows: Dibenz (a,h)anthracene > Indeno (1,2,3-cd) pyrene> Benzo (g,h,i) perylene> Benzo (k) fluoranthene> Benzo (a) Pyrene> Chrysene> Benzo (b) fluoranthene> Benz (a) anthracene> Pyrene> Anthracene> Fluoranthene with respective concentrations in ppm as: 54.699, 25.287, 20.104, 15.791, 14.877, 10.480, 5.659, 4.436, 4.373, 2.221, 2.521 and 1.779.

All the carcinogenic PAHs (cPAHs) analyzed viz: Indeno (1,2,3-cd)Pyrene, Dibenzo (a,h) perylene, Benzo (k) fluoranthene, Chrysene, Benzo (b)fluoranthene, Benzo (a) anthracene and Benzo (a) pyrene were detected with concentrations in ppm as: 25.287, 54.699, 15.791, 10.480, 5.659, 4.435 and 14.877 respectively. The total concentration of cPAHs is 131.229ppm which represents 80.89% of the total PAHs (tPAHs) in the soil sample.

Benzo(a)pyrene (BaP) is the basis of estimating the carcinogenicity of cPAHs in an environment and has a permissible limit of 0.0007mg/l as stipulated by USEPA. Using this limit as a guideline for the interpretation of the result, Benzo (a) Pyrene (BaP) is 21252.53 times higher (more toxic) than the BaP standard, which represents 9.17% 0f the total PAHs. Indeno (1,2,3-cd) Pyrene is 36124.8 times higher (more toxic) than BaP standard, and represents 15.59% of the total PAHs. Dibenzo (a,h) Perylene is 78141.41 times higher (more toxic) than BaP standard, and represents about 33.72% of the total PAHs. Benzo (k) fluoranthene is 22559.21 times higher (more toxic) than BaP standard, and represents about 9.73% of the total PAHs. Chrysene is 14972.03 times higher (more toxic) than BaP standard, and represents about 6.46% of the total PAHs. Benzo (b) Fluoranthene is 8084.19 times higher (more toxic) than BaP standard, and represents about 3.49% of the total PAHs. Benzo (a) Anthracene is 6336.39 times higher (more toxic) than BaP standard, and represents about 2.73% of the total PAHs. Benzo (a) Pyrene is 21252.53 times higher (more toxic) than BaP standard, and represents about 9.17% of the total PAHs.

The results of the analyses show the levels of concentration of heavy metals in mg/kg, PAHs and TPH in ppm.

The order of heavy metal concentration in the soil sample is: Zn > Fe > Pb > Ni > Cr > Cd with concentrations in mg/kg of 34.750, 30.730, 13.102, 9.452, 5.725 and 0.150 respectively. The concentrations of the various metals analyzed were above the permissible limit of heavy metals in soil as recommended by DPR and FME except Vanadium which was below the detection limit of the analytical equipment used.

All the carcinogenic PAHs (cPAHs) analyzed viz: Indeno (1,2,3-cd)Pyrene, Dibenzo (a,h) perylene, Benzo (k) fluoranthene, Chrysene, Benzo (b)fluoranthene, Benzo (a) anthracene and Benzo (a) pyrene were detected with concentrations in ppm as: 25.287, 54.699, 15.791, 10.480, 5.659, 4.435 and 14.877 respectively. The total concentration of cPAHs is 131.229ppm and represents 80.89% of the total PAHs (tPAHs) in the soil sample. The concentration of the individual cPAHs exceeded the baseline of compliance by several thousands of folds. This has inherent implications for the soil fertility, the environment and humans.

The authors are thankful to Mr. Justin Okorondu of Jawura Environmental Services, Port Harcourt, for his technical input. The Authors appreciate the initial correction of the research design by other members of our research group; Petroleum and Environmental Chemistry Research group that led to vast improvements in its current outlook.

REFERENCES

Fetzer, J. C. (2000). "The Chemistry and Analysis of the Large Polycyclic Aromatic Hydrocarbons". Polycyclic Aromatic Compounds (New York: Wiley) **27** (2): 143.doi:10.1080/10406630701268255. ISBN 0-471-36354-5.

Neff, J. M. (1979). Polycyclic aromatic hydrocarbon in the aquatic environment; source, fates and biological effects. Applied science publishers, London.

Futoma, D.J., Smith, S.R., Smith, T.E. and Tanaka, J. (1981). Polycyclic Aromatic Hydrocarbons in water systems. CRC, Boca Press Raton, FL.

Iwuoha, G.N., Nwigoo, J., Onojake, M.C (2015). Determination of Total Potency Equivalent Concentration (TPEC) of Carcinogenic Polycyclic Aromatic Hydrocarbons (cPAHs) In Soils of Bodo-City. J. Appl. Sci. Environ. Manage. Vol. 19(3), pp. 495-499.

Choi, H., Harrison, R., Komulainen, H.; Delgado Saborit, J. (2010). "Polycyclic aromatic hydrocarbons" WHO Guidelines for Indoor Air Quality: Selected Pollutants. Geneva: World Health Organization. Retrieved 2014-12-12.

Mackay, D.; Callcott, D. (1998). "Partitioning and physical chemical properties of PAHs". In A. Neilson (ed.). PAHs and Related Compounds. The Handbook of Environmental Chemistry. Springer Berlin Heidelberg. pp. 325–345. ISBN 978-3-642-08286-3. Retrieved 2015-06-23.Department of

Scientia Africana, Vol. 17 (No. 2), December 2018. Pp 90-96
© Faculty of Science, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

Petroleum Resources (1991). Environmental guidelines and standards of the petroleum industry, Lagos. Pp. 35-76

Larsson, B. K., Sahlberg, G. P.; Eriksson, A. T.; Busk, L. A. (1983). "Polycyclic aromatic hydrocarbons in grilled food". Journal of Agricultural and Food Chemistry **31** (4): 867–73.doi:10.1021/jf00118a049. PMID 6 352775.

Luch, A. (2005). The Carcinogenic Effects of Polycyclic Aromatic Hydrocarbons. London: Imperial College Press. ISBN 1-86094-417-5.

Jarup, L., Berglund, M., Elinder, C.G. (1998). Health Effects of Cadmium Exposure--A Review of the Literature and a Risk Estimate [Published Erratum Appears in Scand J Work Environ Health 1998 Jun; 24(3):240] Scand J Work Environ Health. 1998; 24(1):1.

Method for the determination of extractable petroleum hydrocarbons (EPH) (1995). Massachusetts DEP, wall experiment station.

John, Kanayo-Chukwu Nduka, Orish, Ebere Orisakwe (2010). Precipitation Chemistry and Occurrence of Acid Rain over the Oil-Producing Niger Delta Region of Nigeria. The Scientific World Journal Volume 10 (2010), Pages 528-534.

United States Environmental Protection Agency, USEPA (1993a). Integrated risk information system and assessment office.