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POLYCYCLIC AROMATIC HYDROCARBONS IN SOILS WITHIN SELECTED COMMUNITIES IN DELTA STATE

Ivwurie W., Emelife S.C., Sun C. and Snape C.
Department of Chemistry,
Federal University of Petroleum Resources, Effurun
Email: wivwurie@yahoo.com.uk

Abstract: Five soil samples from five different communities in Delta State were analyzed for Polycyclic Aromatic Hydrocarbons using gas chromatography-mass spectrometry. The concentrations of the polycyclic aromatic hydrocarbons ranged from 1-17mgg^{-1} with a mean concentration of 66mgg^{-1} $\pm$ 5.63mgg^{-1}. The PAH diagnostic ratio showed that all the soil samples have PAH inputs from liquid fossil fuel as a result of crude oil spillage from Shell operations in the study areas and also vehicular emissions. The high PAH concentrations show that all the soil samples had more input from exogenous sources than endogenous.

Keywords: Polycyclic Aromatic Hydrocarbon, Crude Oil Spillage, Exogenous and Endogenous Sources

INTRODUCTION

Fuel and energy are important components of man and other living entities. The discovery of fossil fuel as means of generating energy has brought about rapid development, industrialization of areas, which hitherto were underdeveloped and barren. Sophisticated plants and machinery have been successfully powered, transportation by various means has been eased and various raw materials, which served as by-products of major fuel industries, have now been used as feedstock for major petrochemical industries. While these operations have tremendously reduced the burden on man, the concomitant effects of these operations are harmful. Natural resources exploitation has caused deforestation, loss of wildlife, depletion of soil nutrients for crop cultivation as well as the discharge of toxic organic and inorganic materials into the environment. Amongst the organic species that find their way into the environment as a result of diverse industrial and domestic operations are the polycyclic aromatic hydrocarbons (PAHs). These originate from the incomplete combustion of organic materials or directly from fossils fuels, as well as from direct biogenic precursors [1]. This class of compounds in recent time has become the focus of attention for chemists, chemical engineers; and related professionals, because they have been reported to be toxic, carcinogenic and mutagenic/genotoxic [3, 7, 12].

The sources of these PAHs have been reported. They can arise from natural disasters such as volcanic eruption and combustion of biomass. Moreover, the contribution from anthropogenic activities has been reported to be a larger source [10, 11, 13]. The combustion of fuel (coal, petroleum, wood) by various industries in their routine operations has been reported to be the predominant stationary contributor of PAH emissions, while transportation, gives rise to mobile sources of PAHs. When PAHs come in contact with biological entities in particular and the environment in general, it carries negative consequences, given that they are genotoxic (have harmful effect on genes), and they could find their way into the atmosphere as aerosols or other forms in soil, water, or come directly in contact with man, other animals as well as plants. Therefore, it is highly essential to put a check to the activities carried out in the environment as these turn around to cause numerous negative impacts on lives and properties. Hence, the

objectives of this study are to determine the concentrations and distributions of the PAHs in some selected soils in Delta State and the possible sources of these PAHs.

DESCRIPTION OF STUDY AREA

The studied areas are Afioseri (NG2), Erhiemu (NG3) and Egbo-Uwherhie (NG4). Soil samples were collected from residential areas in the three different communities. These areas have been suspected to have been contaminated by oil spillage from oil industry operation. Two other soil samples (NG5 and NG6) were collected at a considerable distance (about 70 kilometres away) from an oil flow station, in a separate community called Abraka. All the aforementioned communities are in Delta State, which is in the South-South region of Nigeria. It is also worth mentioning that even in the Abraka community, oil prospecting by different oil companies has taken place from time to time. A schematic diagram of the study areas is given in Figure 1.

MATERIALS AND METHOD

Sample Preparation and Solvent Extraction

The different soils were dried at a temperature of 105°C for 3 to 4 hours and then ground to pass through a 60-mesh sieve. The samples were extracted by soxhlet extraction and refluxing techniques using redistilled dichloromethane (DCM) and dichloromethane- methanol (93:7) mixture. The weight of each sample extracted was altered to obtain sufficient amounts of PAHs analysis. 100 g of soil to 250 ml of solvent mixture was used for each extraction. When refluxing and Soxhlet extraction were completed, the slurries were filtered to obtain the extract solution. The extract of each sample was concentrated using rotary evaporator at 30°C for DCM solutions and 45°C for DCM/methanol mixtures. The extract was concentrated and dried using a stream of N_2. Open column chromatographic separation was then carried out on each extract obtained and the neutral aromatics containing the PAHs together with the aliphatics were kept for analysis.

PAH Analysis

The extract were analyzed for naphthalene, trimethylnaphthalene, fluorine, methylfluorene, phenanthrene/anthracene, fluoranthene, pyrene, methylpyrene, benz(a) anthracene/chrysene, benz(b)/(k)fluoranthene, benzo(a)pyrene, dibenz(a,h) anthracene/Inden(1,2,3-cd) Pyrene, benzo(ghi) perylene using GC-MS at the School of Chemical, Environmental and Mining Engineering, University of Nottingham. The GC-MS analysis was performed on a Fisons instruments 8000 gas chromatograph interfaced to a MD 800 mass spectrometer with a quadrupole mass analyzer (ionizing energy 70eV, source temperature 280° C). The gas chromatograph capillary column is 50 m long; i.d. is 0.32 mm and a film thickness of 0.25µm, stationary phase is polyphenylmethylsiloxane. Lab base software written by VG was used for data acquisition and Mass lynx for interpretation. The determinations were at selected ion monitoring (SIM) mode. Concentrations of the various PAHs were determined using internal standard injection. Identification of the various PAHs was achieved by comparison with authentic standards.

RESULTS AND DISCUSSION

PAH Concentration and Distribution

Table 1 shows the various PAH concentrations of each soil. From the table, the individual PAH concentrations of the different soils ranged from 1-17 mgg^{-1} dry weight, with a mean concentration of $66mgg^{-1} \pm 5.63$ mgg^{-1} dry weight. This range appears to be higher than the range of concentration (1-10μgg^{-1}) associated with endogenous soils resulting from plant

synthesis and natural fires as reported in Zhang *et al.*, 2006. The highest PAH concentration (75.5mgg^{-1}) was found at NG3 which is the Egbo-Uwherhie community which is suspected to have been contaminated by oil spillage as a result of operations at the oil flow station. The oil spillage, must have contributed to the high PAH concentration in the said area. The next to NG3 in concentration is NG5 and NG6 which have the same PAH concentrations of 65.5mgg^{-1}. These are the soil samples collected from the Abraka motor way and Abraka farm field respectively. The high concentrations must have been as a result of a combined effect of vehicular emissions and vegetation fires. The 2-3 ring PAHs (Naphthalene, trimethylnaphthalene, fluorine, methylfluorene, phenanthrene and anthracene) were highest in the NG3 (Egbo-Uwherhie) soil sample (37mgg^{-1}) and least (25.5mgg^{-1}) in the NG5 soil sample which is the Abraka motor way sample. The 4-6 ring PAHs on the other hand, were highest (40mgg^{-1}) in the Abraka motor way soil sample and least in the Erhiemu soil sample (NG2). As reported by Chadwick *et al.* (1987) and Homann *et al.* (1994); molecular structure of PAH dictates their level of carcinogenicity, mutagenicity and toxicity. Low molecular weight PAH ($\leq$ 3 rings), often display acute toxicity and low carcinogenicity, while high molecular weight PAH ($>$ 3 rings), show low toxicity, but outstanding carcinogenicity and or mutagenicity.

Sources of PAHs

In order to find out the effect of PAHs to the environment, it is necessary to look into their probable sources. Some PAH isomer ratios have been demonstrated by previous studies to be useful in the identification of PAH sources [4, 8, 16] i.e. whether they are of petroleum sources or pyrogenic sources (combustion). One of the frequently used isomer ratios is the Ant/ (Ant + Phe) ratio. According to this isomer ratio, the ratio $<$ 0.1 indicates petroleum input and the ratio $>$ 0.1 indicates pyrogenic input [2]. However, there are limitations to the use of this isomer ratio as demonstrated by Fraser *et al.* (1998). They demonstrated that Anthracene undergoes more rapid photochemical reaction in the atmosphere than Phenanthrene. The implication is that during atmospheric transport, the original composition information will not be preserved.

Therefore, in order to carry out an accurate PAH source apportionment in soils, isomer ratios where the isomer pairs degrade photolytically at comparable rates have to be adopted. From CCME (2008), the isomer ratio Flu/ (Flu + Py) is a more accurate ratio as it meets with the condition. The Flu and Py isomer pair degrades photolytically at comparable rates. The ratio $<$ 0.4 indicates petroleum input; ratio between 0.4-0.5 indicates liquid fossil fuel (vehicle and crude oil) combustion input and ratio $>$ 0.5 indicates grass, wood or coal combustion input [14]. In this study, the ratios of Flu/ (Flu + Py) ranged from 0.38-0.46 (Table 2). This shows a predominance of input from liquid fossil fuel combustion. This could be as a result of vehicular traffic as is the case in NG5 and also as a result of the oil spillage from the oil prospecting industry in the areas. There is also contribution from petroleum sources as can be seen from the PAH pool.

CONCLUSION

The study showed that the PAH concentrations of the study areas, ranged from 1-17mgg^{-1}. The Low Molecular Weight PAHs were prominent in the Egbo-Uwherhie soil sample implying high toxicity of the soil in the said area and the High Molecular Weight PAHs were prominent in the Abraka motor way soil sample, implying the risk of high carcinogenicity of the soil in that area. The study also showed that all the soil samples from the study areas showed more exogenous input than endogenous input. The PAH diagnostic ratio of all the samples showed

predominant input from liquid fossil fuel combustion especially as a result of crude oil spillage and vehicular emission.

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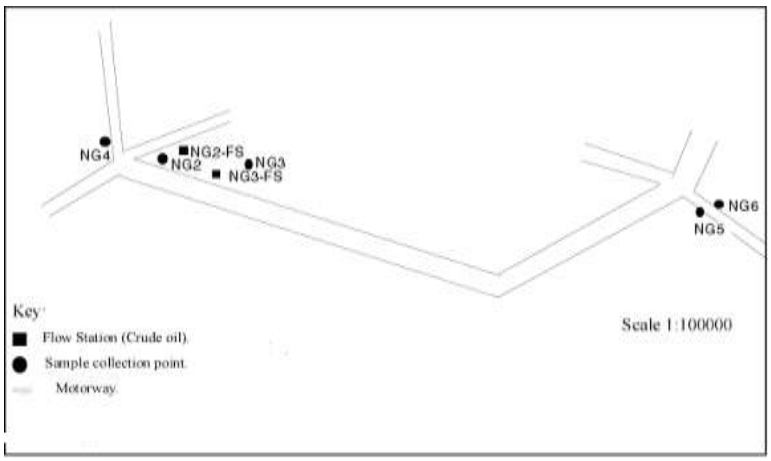
Tables and Figure



Key: NG2=Erhiemu NG3=Egbo-Uwherhie NG4=Afioseri NG5=Abraka Motor Way Ng6=Abraka Farm Field

Figure 1: Schematic Diagram Showing Study Areas

Table 1: Individual PAH Concentrations (mgg^{-1})

Ind PAHs	NG2	NG3	NG4	NG5	NG6
Naphthalene	2	3	3	4	4
Trimethylnaphthalene	4	5	3.5	3	4
Fluorene	4	5	4	2.5	3
Methylfluorene	5	7	5	2	3
Phen/Anthr	15	17	13	14	15
Fluoranthene	4	5	4	6	5
Pyrene	5	6	6	7	8
Methylpyrene	3	4	5	8	7
Benz (a) anthr/chrysene	3.5	4.5	4	7	6
Benz (b)/(k) fluoranthene	9	10	8	6	6
Benzo (a) pyrene	3.5	4	3	3	2
Dibenz (a,h)anthr/Inden(1,2,3-cd)Py	2	3	2	2	1.5
Benzo (ghi) Perylene	1.5	2	1.5	1	1

Key: Concentrations were Determined using Internal Standard Injection

Table 2: PAH Diagnostic Ratio (Flu/ Flu + Py)

Study Area	NG2	NG3	NG4	NG5	NG6
Ratio	0.44	0.45	0.40	0.46	0.38

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BIOGRAPHY

Dr. Wisdom Ivwurie is a senior lecturer at the department of chemistry, Federal University of Petroleum Resources, Effurun. He is involved both in teaching and research. He is a member of various research groups in the university, amongst are Small Scale Refinery Research team, Power plant research team. He is also the current Ag. Head of Department of Chemistry of the Federal University of Petroleum Resources, Effurun.

Prof. Colin Snape (RSE) is the Director of Engineering Doctorate Centre in efficient fossil energy technologies and faculty of engineering, University of Nottingham. He is also the director of midlands energy graduate school. He is a fellow of the Royal Society of Edinburgh. He has been involved in fuel science and related disciplines for over 30 years and has contributed to the chemical engineering course at Nottingham by developing and delivering basic chemistry and thermodynamic modules.

Dr. Cheng-Gong Sun is an assistant professor of clean fossil energy technologies, faculty of engineering, University of Nottingham. He has worked in the general field of clean fuel and energy technologies for nearly 20 years, with comprehensive research expertise on clean fossil and biomass fuel technologies, fluidized beds, catalysis and adsorption materials.

Miss Emelife Stella Chinelo is a first class graduate of applied chemistry from Usmanu Danfodiyo University Sokoto. She is a much focused young girl who has a deep flair for research and acquiring knowledge. She won the vice chancellor's award for the overall best graduating student of Usmanu Danfodiyo University Sokoto 2012/2013 academic session. She is planning on resuming her MSc programme sometime this year (2016) abroad.