Molecular Examination of Polycyclic Aromatic and Total Petroleum Hydrocarbons in Soot in Port Harcourt Metropolis Using Advanced Analytical Instruments

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ABSTRACT

A short-term study was carried out to comparatively evaluate the polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPHs) in soot evading Port Harcourt and its environs. Samples were collected from three (3) different locations namely; Eleme Petrochemicals, Rumuodomaya Town, and University of Port Harcourt (Uniport) to determine the level of residual polycyclic aromatic hydrocarbons and total petroleum hydrocarbons in soot as dispersed from source to the troposphere. The evaluation was carried out using Gas Chromatography Flame Ionization Detector (GC-FID) and Gas Chromatography-Mass Spectrometer (GC-MS). Soot particles collected from the various locations were trapped in a tenax Gas Chromatography adsorbent tube for Gas chromatography analysis. The total petroleum hydrocarbons were analyzed according to ASTMD 3911. The result of polycyclic aromatic hydrocarbons obtained from Eleme Petrochemicals (0.04 mg/m^3), Rumuodomaya Town (0.02 mg/m^3), and University of Port Harcourt (0.01 mg/m^3) were below the permissible limit of World Health Organization (W.H.O.) standard for work place of 0.2 mg/m^3. This indicates that areas under study were free from polycyclic aromatic hydrocarbons pollution. However, the values of total petroleum hydrocarbons which has no regulatory limit for soot showed high values of 21.44 mg/m^3(Eleme Petrochemicals), 18.91 mg/m^3(Rumuodomaya Town), and 12.68 mg/m^3(University of Port Harcourt). This suggests that the weight of total petroleum hydrocarbons inhaled by humans and deposited on the body were unsafe. This study recommends safety measures to be taken to reduce emissions of this menace and steps to be taken by the residents to stay healthy in Port Harcourt and its environs.

KEYWORDS: *Soot, pollution, polycyclic aromatic hydrocarbons, total petroleum hydrocarbons, Gas Chromatography-Mass Spectrophotometer*

1.0 INTRODUCTION

Soot is a mass of impure carbon particles resulting from incomplete combustion of hydrocarbons (John *et al.*, 2001). Hence, it is described as a deep black powdery or flaky substance consisting largely of amorphous carbon, produced by the incomplete burning of organic matter; fossil fuels, bio fuels and biomass (Cain *et al.*, 2010). It contains a lot of acid as well as chemicals, metals, soils and dust such as sulphates, nitrates, ammonia, sodium chloride, mineral, dust, and water. These particles leave an ugly sight and foul smell. The chemical compoundsin soot hurts the fragile ecosystem considerably and most importantly poses health risk when inhaled (Zouaoui and Madona, 2014; Ogele, 2020).It is an environmental contaminant and it is referred to as a climate enforcer (Nnaemeka *et al.*, 2018).Soot is a gas phase combustion process but usually extended to include the residual pyrolyzed fuel particles such as coal, cenospheres, charred wood and petroleum coke that may be airborne during pyrolysis (John*et al.*, 2001;Nadia, 2018). It can be divided into an organic fraction that is made up of a number of organic compounds and an elemental carbon fraction that has graphite-like structure with many structural defects. These defects give elemental carbon the characteristics of absorbing light, reducing visibility and serves as threshold catalyst for certain atmospheric chemical reactions (George, 1985).

As an airborne contaminant, it has different sources all of which are products of pyrolysis. Other sources of soot include internal combustion engines, power plant boilers; hog fuel boilers, ship boilers, central steam heat boilers, waste incinerators, local field burning, house fire, forest fires, fire places,furnaces, etc (Seonah*et al.*, 2019).The composition is dependent on the source of burning but it is mixture of tiny particles and liquid droplets formed in the air from metals, acids and chemicals like sulphur and nitrogen oxides (Niessner,2014). However, to achieve incomplete combustion, the fuel must burn at lower temperatures with a slightly reduced supply of oxygen (Maduawuchi, 2021). Black carbon, a major component of soot absorbs lighter than any other form of particulate matter (PM) up to one million times more energy than same mass of carbon dioxide (Xiang*et al.*, 2017).

Soot is produced through incomplete combustion processes as shown below;

$CH_4 + 2O_2 \rightarrow CO + 2H_2O$ + soot

Sootalso called particle pollution is one of the deadliest forms of air pollution. It is a type of particle pollution called $PM_{2.5}$ or even smaller. It is smaller than dust or mold particles or approximately $^{1}/_{30}$ of the size of a human hair (Johansson*et al.*, 2018).

Soot emission is gaining global recognition due to its adverse effect on climate and human health. It is a monstrous phenomenon because its formation is a complex process (Mathieu*et al.*, 2019). Soot production cannot be predicted by numerical simulation due to the fact that most devices involve turbulent flames. Environmental soot (black carbon) and carbon black are causative agents to many ailments to humans, animals, and even aquatic habitants. The term soot is used interchangeably with carbon black but they are physically and chemically distinct (Niranjan and Ashani, 2017). Both are formed by the incomplete combustion of hydrocarbons but different carbon contents and constituents. There are three (3) main types of diseases due to soot and carbon black exposure namely; cancer, respiratory diseases (bronchitis, asthma), and cardiovascular dysfunctions (strokes) (Niranjan and Ashani, 2017). Soot and carbon black-induced cancer mechanismare involvement of oxidative stress, Deoxyribonucleic Acid (DNA) methylation, formation of DNA adducts and aryl hydrocarbon receptor activation (Niranjan and Ashwani, 2017). Silicon iron, manganese and cobalt in soot also affect the oxygen reactive species (ROS)-medicated DNA damage. ROS-induced DNA damage is also activated by

eosinophils and neutrophils through halide (Cl^- and Br^-) dependent DNA adduct formation (Niranjan and Ashwani,2017). The T helper type 2 cells and most cells are essential mediators in the pathology of soot or Carbon Black (CB) induced respiratory diseases. In soot and CB cardiovascular dysfunctions, telomerase transcriptase plays a vital role. The elemental carbon amount in soot is relatively less than 60% of the total mass of the particle (Watson and Valberg, 2001). The impact of soot on the ecosystem depends on the distribution and its distance from the source of origin. Soot or carbon black is emitted both in anthropogenic and natural occurring fuels. It causes human morbidity and premature mortality. It also affects visibility and causes haze (Zouaoui and Madonna, 2014). The inhalation of particulate matter composed of black carbon, sulphates, nitrates, ammonia, sodium chloride, mineral dust and water poses high health risks. These compounds react with moisture in the atmosphere and cause acid rain also the incomplete combustion resulting in soot formation forms dioxins and other toxic compounds (Donev *et al.*, 2019).It is an established fact that soot incorporated into existing cloud droplets will lead to a decrease in cloud albedo by radiation adsorption while soot activated as cloud condensation nuclei can lead to increase in cloud albedo and decrease precipitation (Zuberi*et al.*, 2005).

Polycyclic aromatic hydrocarbons (PAHs) are mutagenic, toxic and carcinogenic compounds. They are rapidly distributed due to their property of lipid-solubility (lipophilic). They belong to the class of chemicals known as Persistent Organic Pollutants (POPs). POPs are artificial chemicals which are either intentionally or unintentionally produced and are toxic with long range of transport leading to global pollution (Abiodun *et al.*, 2017). They are environmentally persistent and have various structures and toxicity. Apart from being both mutagenic and carcinogenic, they are also immune-suppressant (Hussein and Mona, 2016).

Total petroleum hydrocarbons (TPH) are the summation of volatile petroleum hydrocarbons (VPH) and extractible petroleum hydrocarbon (EPH) (Edwin-Wosu and Albert, 2010). Volatile petroleum hydrocarbons (VPH) are also known as petrol (gasoline range organics) and include hydrocarbons from C_6-C_{10}. Diesel range organics (DRO) include hydrocarbons from C_{10}-C_{28} (Edwin and Albert, 2010). They are less soluble in water but are absorbed readily on particulate matter. TPHs consist of three (3) groups of compounds namely alkanes, alkenes and aromatics (Abiodun*et al.*, 2017). Alkanes are found in refined products-gasoline, diesel, fuel, kerosene, jet fuel and heating oils and are subdivided into several classes which include linear alkanes (n-alkanes), branched alkanes, isoprenoids, cycloalkanes such as steranes and triterpanes and unresolved complex mixtures (UCM) (Abiodun*et al.*, 2017). TPH can be determined by the sum of concentration of alkanes and unresolved complex mixtures (UCM) (Harji *et al.*, 2008).

International Agency for Research (IARC) on cancer has postulated that one (1) TPH compound (benzene) is cancer causative agent to humans and also other TPH compounds benzo{a}pyrene and gasoline are most likely and possibly carcinogenic to humans. Others are not classified by IARC. Direct exposures to TPH include breathing contaminated air (volatile fractions (vf), which are emitted as gases) and skin direct contact while passing through contaminated areas. Most of the health disorders include but not limited to skin and eye irritation, breathing and neurological disorders and stress (Saranya *et al.*, 2020).

Clean air is sacrosanct to life on earth as well as clean water. The atmosphere which inhabits the air and the ecosystem which integrally connects the overall wellbeing of man and other lives needs to be free from all contaminants most especially the danger posed by soot to the environment.

Nigeria and most importantly Port Harcourt is exposed to immeasurable and unavailable levels of the pollution in the form of soot which is detrimental to the ecosystem. The expanding levels of oil exploration and production activities is not in reality the root cause of black soot but the activities of illegal oil refinery operators who run from the creek to the hinterlands of some communities around the Port Harcourt metropolis and the action of security agencies who burn the bunkered petroleum products (Mina *et al.*, 2020).

Soot has a great impact on the global/regional climate by altering the atmospheric radioactive properties and serves as Cloud Condensation Nuclei (CCN) and distorts the cloud albedo (Kirsten *et al.*, 2009). It converts solar radiation to heat and affects rain fall patterns especially in Port Harcourt.

Hence, the need to evaluate the level of polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPHs) in soot obtained from three (3) different locations namely; Eleme Petrochemicals, Rumuodomaya Town, and University of Port Harcourt (Uniport) metropolis in Rivers State.

2.0 MATERIALS AND METHOD

2.1 Sample Collection

Samples were collected from three different locations namely; Eleme Petrochemicals, Rumuodomaya Town, and University of Port Harcourt (Uniport) by spreading plexi-glass materials. These samples were taken to the laboratory for analysis.

2.2 Procedure for PAHs Analysis

2.2.1 Preparation of the Column

Column was prepared by inserting a glass wool plug into the base of the column and 10 g of silica gel was pre-conditioned (baked) at 105^{o}C overnight and the column was tapped to pack the gel properly. The column was well eluted with n-hexane and was not allowed to dry well during this time.

2.2.2 Fractionation of Sample Extract

The sample extract 1 ml as added to the top of the column was eluted with 60 ml of n-hexane to get the aliphatic hydrocarbon. Then, elute was collected in a conical flask. While the hexane was drying off but not completely, 40 ml of dichloromethane (DCM) was added to elute for PAHs. Elute was collected in a conical flask. Both fractions were concentrated each to 2 ml using the rotary evaporator at 60^{o}C. For the PAH concentrate, n-hexane was re-exchanged and finally, re concentrated. The concentrates were transferred into sample vials. The final volumes of the extracts were noted. Then samples were ready for GC analysis (GC Agilent Technologies7890A equipped with 5975 MSD).

2.3Total Petroleum Hydrocarbons (TPHs) Analysis

2.3.1 Procedure for TPHs Analysis

A solvent mixture of acetone and dichloromethane (50:50) was prepared then, 10g of the well mixed sample was weighed into solvent rinsed beaker. The weight was recorded in the extraction log book. 100 ml of the solvent mixture was added to the sample and 1 ml of the surrogate spike standard was also added and the beaker was covered with aluminum foil. The sample was left over night and was filtered through Whatman No. 41 filter paper packed with 10 g Na_2SO_4 into a round bottom flask. The sample was concentrated mechanically by shaking gently in a fume hood, and then the extract was solvent exchanged with n-hexane. The extract was re-concentrated to 1 to 2 ml and then transferred using pipette into the sample vial. The same was

done for the solvent blank by taking the extracting solvent through the same procedure as the sample and final concentration analyzed using GC (Agilent Technologies 7890A) with FID as the detector.

3.0 RESULTS AND DISCUSSIONS

The results of PAHs and TPH analysis in soot as presented in Tables 1 and 2 revealed varied concentrations of their components.

Table 1: PAHs concentrations obtained in mg/m^3

COMPONENTS	EP	RUMU	UNIPORT	STANDARD
Benzene, 1,2,3- trimethyl	0.02	0.06	0.35	0.20
Naphthalene	0.01	0.01	0.70	0.20
2-methylnaphthalene	0.09	0.07	0.19	0.20
Acenaphthylene	0.01	0.05	0.41	0.20
Acenaphthene	0.19	0.02	0.02	0.20
Fluorene	0.14	0.03	0.01	0.20
Anthracene	0.04	ND	0.84	0.20
Phenanthrene	0.07	ND	ND	0.20
Fluoranthene	0.05	ND	ND	0.20
Pyrene	0.50	ND	ND	0.20
Benz(a)anthracene	0.30	ND	ND	0.20
Chrysene	0.01	ND	ND	0.20
Benzo(b)fluoranthene	0.06	ND	ND	0.20
Benzo(k)fluoranthene	0.08	ND	ND	0.20
Benzo(a)pyrene	0.10	ND	ND	0.20
Diben(a,h)anthracene	0.01	ND	0.11	0.20
Indeno(1,2,3-cd)pyrene	0.35	0.02	0.60	0.20
Benzo(g,h,i)perylene	0.06	0.01	0.04	0.20
Total	**0.04**	**0.02**	**< 0.01**	**0.20**

Table 2: TPHs concentrations obtained in mg/m^3

COMPONENTS	EP	RUMU	UNIPORT	STANDARD
C_8	0.36	0.03	0.10	N/A
C_9	0.24	0.15	0.49	N/A
C_{10}	0.13	0.92	0.10	N/A
C_{11}	0.73	0.17	0.23	N/A
C_{12}	0.97	0.86	0.60	N/A
C_{13}	1.20	0.21	1.01	N/A
C_{14}	1.73	0.17	0.73	N/A
C_{15}	0.87	1.20	0.10	N/A
C_{16}	0.33	1.17	1.12	N/A
C_{17}	1.48	0.52	0.23	N/A
Pristane	0.19	0.14	0.17	N/A
C_{18}	0.83	1.14	1.39	N/A

Phytane	0.10	0.83	0.10	N/A
C_{19}	1.41	0.23	0.25	N/A
C_{20}	0.30	0.84	0.09	N/A
C_{21}	0.11	0.52	0.05	N/A
C_{22}	0.27	0.70	0.02	N/A
C_{23}	1.11	0.04	0.53	N/A
C_{24}	0.87	1.23	1.08	N/A
C_{25}	0.13	0.71	0.22	N/A
C_{26}	0.51	0.12	0.70	N/A
C_{27}	0.36	0.25	0.29	N/A
C_{28}	0.24	0.44	0.11	N/A
C_{29}	1.47	0.15	0.23	N/A
C_{30}	0.38	0.23	0.51	N/A
C_{31}	0.49	0.52	0.29	N/A
C_{32}	1.22	1.34	0.30	N/A
C_{33}	0.19	0.03	0.03	N/A
C_{34}	0.51	0.65	0.10	N/A
C_{35}	0.24	0.12	0.51	N/A
C_{36}	0.41	0.25	0.17	N/A
C_{37}	0.03	0.90	0.05	N/A
C_{38}	0.52	0.44	0.13	N/A
C_{39}	0.09	0.37	0.10	N/A
C_{40}	1.39	1.30	0.27	N/A
Total	**21.44**	**18.91**	**12.68**	

*Where, EP = Eleme Petrochemicals; RUMU = Rumuodomaya; UNIPORT = University of Port Harcourt; ND = Not detected; N/A = Not applicable

The result obtained based on five (5) grouping of PAHs (Prabhukumar and Pagilla, 2010) revealed that sample 1 from Eleme Petrochemicals contained 0.1 mg/kg of benzo{a}pyrene (the most carcinogenic PAHs). However, benzo{c}pyrene was not detected in samples 2 and 3 from Rumuodomaya Town, and Uniport respectively. Dibenzo{a,h}anthracene which belongs to group 2A of PAHs was detected in Eleme at 0.01 mg/m^3 and 0.11 mg/m^3 in Uniport respectively. It was not detected in sample 2 from Rumuodomaya Town. These detected levels were lower than the permissible emission limits of 0.2 mg/$m^3$for PAHs.

The group 3 which include acenaphthylene, flourene, phenaphthrene, anthracene, fluoranthene, pyrene, and benzo{g,h,I,}perylene fell under non-carcinogenic to humans were all detected in the three (3) samples from Eleme Petrochemicals, Rumuodomaya and Uniport respectively. However, fluoranthene and pyrene (0.05 and 0.5 mg/m^3) were only seen in sample 1 from Eleme Petrochemicals. Benzo{g,h,i}perylene were detected in the three (3) samples (0.06, 0.04 and 0.01 mg/m^3). From the result obtained, it could be inferred that sample 1 from Eleme Petrochemicals was the most contaminated and tagged carcinogenic. The results further revealed that as the soot samples dispersed and travel further away from the source, the level of toxicity decreased. This result further revealed that the inhabitants of Eleme were more vulnerable to these pollutants.

Comparing the total value from the control subtraction of PAHs, 0.04 mg/m^3 for Eleme Petrochemicals and 0.02 mg/m^3 for Rumuodomaya Town, and < 0.01 mg/m^3 for Uniport, it can be deduced that as the soot travels in the atmosphere and moves away from the source, the adverse effect lowers though still below the Permissible Emission Limit (PEL).The Occupational Safety and Health Administration (OSHA) has also set a limit of 0.2 mg/m^3 of PAHs in air; the National Institute for Occupational safety and Health (NIOSH) recommends that the average workplace air levels for coal tar products not exceed 0.1mg/m^3. The TPH values of Eleme Petrochemicals, Rumuodomaya Town, and Uniport recorded mean values of 21.44 mg/m^3, 18.91 mg/m^3 and 12.68 mg/m^3 respectively which exceeded the permissible emission limit. However, for total petroleum hydrocarbons (TPHs), there was no regulatory limit for soot but these high levels above suggest the weight of these hydrocarbons inhaled by humans and deposited on the skin and eyes. These could be the causative agents for skin and eye irritations in inhabitants of Port Harcourt. A certain amount of these hydrocarbons in human body can lead to so many ailments. According to Dibofori-Orji *et al.*(2019), the TPH values of Aba road, Woji, and Iwofe, all in Port Harcourt recorded mean values of 36.99 mg/m^3, 22.71 mg/m^3 and 22.18 mg/m^3 respectively which corresponds with our findings that farther away from the source of pollution, the concentration of these pollutants decreased. The pollution level of TPH in Port Harcourt and its environs was high.

4.0 CONCLUSION

The result showed that the PAHs levels were within the tolerable limit but the TPH in the three (3) samples were above the WHO, 1978 reference guideline. This study asserts that if the government cannot curtail or curb the activities of these illegal refineries and indiscriminate combustion of seized products, crops will continue to die, marine and aquatic lives will be greatly and grossly affected and incidence of cancer, stroke and respiratory disorder will be on the increase and ultimately lead to state of emergency. This study further encourages that State Environmental Agency should intensify efforts and organize orientation programs to enlighten the inhabitants on the need to reduce outdoor activities and wear mask if they must. Health of the citizens is in jeopardy if there is no check. This is a clarion call to clean air while supporting the economic growth of the region and improve agriculture. This is achievable because the life span of soot is about two weeks and the stratosphere can be mopped up by stopping these activities of illegal refineries.

4.1 RECOMMENDATIONS

Air pollution in Port Harcourt and its environs is preventable with sufficient action from relevant authorities. The following recommendations were outlined:

- Government should cease the burning of confiscated bunkered products; these products should be tested to ascertain their quality and standard
- Government should also enact policies to issue licenses for modular refineries. Depending on their capacity, a modular refinery can refine a truck of crude oil a day and this, will ameliorate poverty, provide jobs and reduce crime rate in the southern region of the country and beyond
- Science research centers and laboratories in institution of higher learning should collect samples of this soot or further analyze findings from this work to ascertain the lethal compositions of the constituents and alert the relevant authorities on the dangers of this

menace. The $PM_{2.5}$ of soot is small hence it can be inhaled via the lungs through the blood stream causing various health challenges.

COMPETING INTERESTS

The Authors declare no conflicts of interest exist and have no relevant financial or non-financial interests to disclose.

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