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Assessment of total petroleum hydrocarbon (TPH) and some heavy metal contents in soot from Port Harcourt city local government area

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Abstract
Recently, the occurrence of soot in the city of Port Harcourt has been very alarming attracting the attention of the inhabitants as to its dangerous effect. Therefore, this study was carefully designed to investigate the concentrations of some heavy metals and total petroleum hydrocarbons (TPH) in soot from Port Harcourt city local government area. The Mini Vol air sampler was used to collect the soot samples. Two samples each were collected from four different communities (Borokiri, Amadiama, Abuloma and Old GRA) making a total of eight locations from the study area. The collected soot samples were digested and atomic absorption spectrophotometer was used to analyse the concentrations of the heavy metals (Pb, Ni, Cr, Cu, Cd and Zn) in the soot. The concentrations of the heavy metals obtained were found to be within the following range Pb (0.984-1396µg/m^3), Ni (0.513 -0.717 µg/m^3), Cr (3.384-5.280 µg/m^3), Cu (0.0740.216 µg/m^3),) Cd (0.001-0.0036 µg/m^3)) and Zn (0.057 -0.077 µg/m^3). The concentrations of Pb, Ni, Cr, and Cu were above the permissible limit set by WHO while that of Zn and Cd were within the WHO limit. Gas chromatography detection was used to analyse for total petroleum hydrocarbons and the concentration across the eight sample locations ranged from 8.712-17.2746mg/kg with a mean concentration of 13.376 ±2.695 mg/kg. The TPH concentrations across all the sampling locations were above the WHO limit. It is our utmost view from the results of the study to state that the Port Harcourt city local government area is polluted with some heavy metals and total petroleum hydrocarbons and we recommend that the companies operating around the study area should treat their waste before discharging them. Also, the government of rivers state should see it as a matter of necessity that the activities of illegal artisanal refineries are curtails to ensure a safe environment for the indigene.

Keywords: soot, Port Harcourt, heavy metals, TPH, locations, gas chromatography, concentration, spectrophotometer, absorption etc

Introduction
Residents of Port Harcourt City Local Government Area and its environs have since the last quarter of 2016 been experiencing adverse environmental impacts of soot pollution. The soot consists of aerosols, which are tiny particulate matter whose granulometric dimensions range from sub-micron diameters to about 10 microns and greater in size. They are suspended in the lower troposphere, inhibiting cloud formation and capable of causing long term environmental and health hazards to residents in Port Harcourt and environs. The presence of the soot in every area of the city constitutes hazards of air pollution and thus have appreciable effects on air quality, visibility and ultimately exacerbates the changing climate impacts in the Port Harcourt metropolis and the surrounding communities in the region. Soot is a mass of impure carbon particles resulting from the incomplete combustion of hydrocarbons. The quality of air in the Port Harcourt metropolis and surrounding towns, as well as other parts of the Niger Delta have been studied by various scholars, who rank the region's air quality amongst the top 10 most polluted regions in the world [6, 10].

Heavy metals are particulate inorganic pollutants released in the atmosphere through natural and man-made processes. Heavy metals are relatively dense and toxic at low concentration [12], they can be transported from one place to another air through wind blow dust [11]. Several pollutants may be directly emitted by human activities whereas the others may be formed in the air with the effect of sunlight, as in photochemical smog. The particles may range from carbonaceous sooty to heavy metal complex organic compound as well as nuclear fallout. They may have a periodicity which is especially manifested in the biological pollutants, including the airborne spores [9]. The composition of inhalable particulate matter is complex and differs depending on the source and location. The occurrence of toxic metals such as Pb, Zn, Cu, and Ni in inhalable particulates may contribute to substantial health effects [8]. Some of these heavy metals in particulates are strong triggers of carcinogenesis, teratogenesis and mutagenesis [3].

Study Location
The study was conducted in Port Harcourt City Local Government Area (PHALGA) of Rivers State, Nigeria. It is situated approximately on latitude 4^0 40`N – 50`N and between longitude 70.00`E – $7^0$ 10`E. It has a land area of about 70.31Km^2. Two samples each were collected from four different locations of the Local Government Area, namely Abuloma, Amadi-Ama, Borokiri and Old GRA.

Sampling procedure
Two sample each were collected from four different sample locations (Abuloma, Amadi-Ama,

Borokiri and Old GRA) making a total of 8 samples. The samples were collected using MiniVol Air Sampler which was exposed to the air for a period of 6 hours on each sampling day. Quartz filter papers of diameter 47mm were used to trap the particles. The quartz filter paper on which the particles were trapped were stabilized in a desiccator for 24 hours before and after sampling in order to get rid of any moisture in them.

Total Petroleum Hydrocarbons Determination:

1g of soot sample was weighed into a 100ml conical flask. 30ml of dichloromethane (extraction solution) was added. The flask was covered properly and agitated for two minutes. The extraction was allowed to settle for a period of 20 minutes. The extracted mixture was passed through a filter paper containing sodium sulphate and silica gel for removal of moisture content. The extract was transferred into a vial for GC analysis.

Finally, 1µL of sample extract in a vial was injected through the injection port of the GC where the different component was determined.

Determination of Heavy Metals

The soot loaded filters were extracted in an acid mixture to extract heavy metals. This acid mixture was made of hydrochloric acid and nitric acid in a ratio of 3:1. Each filter paper was carefully placed in Teflon tubes and 10 ml of the acid mixture was slowly added to cover the samples. The Teflon tubes were closed and placed in stainless steel bombs which were in turn placed on a hot plate and heated at 150°C for 6 hours. The digested samples were allowed to cool to room temperature, filtered and transferred into polypropylene graduated tubes. The Teflon tubes were rinsed three times with distilled water, filtered and the content added to the digested sample in the polypropylene tubes. The resulting solution was diluted with deionized water to a 30ml mark. The metal extract was then analysed using atomic absorption spectrophotometer (AAS). An unexposed filter paper was prepared as a blank using the same method described for the exposed filter paper

Results and Discussion

The results of the levels of the heavy metals from the eight sample locations are shown in table 1 below

Table 1: Heavy metal concentrations (µg/m^3) of soot samples from Port Harcourt City Local Government Area

		Heavy Metal (µg/m^3)				
Sample Location	**Lead (Pb)**	**Nickel (Ni)**	**Chromium (Cr)**	**Copper (Cu)**	**Cadmium (Cd)**	**Zinc (Zn)**
Borokiri (A)	1.017	0.698	4.011	0.129	0.0036	0.064
Borokiri (B)	0.984	0.606	3.384	0.095	0.0029	0.057
Amadi –ama (A)	1.068	0.717	5..280	0.0158	0.0031	0.077
Amadi-ama (B)	1.013	0.674	4.871	0.0131	0.0028	0.072
Old GRA (A)	1.138	0.587	4.471	0.094	0.0015	0.069
Old GRA (B)	1.058	0.513	3.930	0.074	0.0010	0.063
Abuloma (A)	1.396	0.636	4.981	0.181	0.0028	0.071
Abuloma (B)	1.251	0.607	5.131	0.216	0.0018	0.068
Mean ±SD	1.116±0.142	0.629±0.067	4.507±0.675	0.135±0.048	0.0024±0.009	0.068±0.0006
WHO Guideline value (µg/m^3)	0.500	0.500	5.00	0.037	0.005	0.1- 0.5

The results of the levels of total petroleum hydrocarbons (TPH) from the eight sample locations are shown in table 2 below

Table 2: Total Petroleum Hydrocarbon Concentrations (mg/kg) of soot samples from Port Harcourt City Local Government Area

Sample Location	Total Petroleum hydrocarbon (mg/kg)
Borokiri (A)	17.27463
Borokiri (B)	16.12648
Amadiama (A)	8.71292
Amadiama (B)	11.32236
Old GRA (A)	12.30834
Old GRA (B)	14.27990
Abuloma (A)	13.78230
Abuloma (B)	13.20657
Mean ±SD	13.3764±2.6959

Lead

The concentrations of the studied heavy metals are presented in table 1 which reveals that Lead recorded the highest concentrations at Abuloma (1.396µg/m^3 and 1.251 µg/m^3) followed by Old GRA (1.138µg/m^3 and 1.058 µg/m^3), Amadi-ama (1.068 µg/m^3 and 1.013µg/m^3), and Borokiri (1.017µg/m^3 and 0.984µg/m^3). The mean concentration from the eight locations was 1.116 ± 0.142µg/m^3. The values obtained showed that all the locations and their mean exceeded the World Health Organization allowable limits of 0.5µg/m^3 for Lead in the atmosphere. The high concentration of lead across the eight locations may be due to industrial and automobile emissions owing to the proximity of the locations to these sources. This work is consistent with the one reported by Ede and Edokpa [4] on soot from Port Harcourt. This study was far below the studies by Okorie *et al*. [5] on soot from the exhaust of heavy duty trucks and power generating plants in Kogi state. Lead is not useful to human body and its toxicity affects almost the central nervous system and peripheral, renal functions, blood cells, it is associated with reproductive toxicity, hypertension and neurological disorder some which may be irreversible [14].

Nickel

From table 1, the concentration of nickel ranged from 0.513 to 0.717ug/m^3. The highest concentration of 0.717ug/m^3 was observed at Amadi-ama while the lowest concentration of 0.513µg/m^3 was found at Old GRA. The mean concentration from the eight locations was 0.629 ± 0.067µg/m^3. The concentration of all the locations and their mean values were high compared to the World Health Organization limit of 0.5µg/m^3. The result obtained in this study was higher than the study carried out by Ede and Edokpa [4] in soot from Port Harcourt. Nickel is

an essential trace element, ordinarily Nickel is not known to be toxic to the body, however,
Nickel can combine with carbon monoxide (CO) to form a complex Nickel tetracarbonyl (Ni $(CO)_4$), which is very poisonous even more than CO, which is one of its precursor [14].

Chromium
Table 1 also showed results of the levels of chromium in soot samples. The mean concentration was 4.507 ± 0.645µg/m^3. The highest concentration of 5.280µg/m^3 was obtained at Amadiama while the lowest concentration of 3.384ug/m^3 was obtained at Borokiri. Chromium values recorded at the various sampling locations were within the WHO guideline of 5ug/m^3 except for Amadi-ama and Abuloma that recorded a slightly higher concentration than the WHO limit which may be due to population densities and their closeness to Tans-amadi where high level of industrial activities occur. The levels of chromium obtained in this work were far higher than the levels reported by Okorie *et al*. [5] in soot from the exhaust of heavy duty trucks and power generating plants in Kogi State. Exposure to high level of chromium can result to lung cancer, nose bleeds holes and ulcers in the nasal septum, also the presence of chromium can change the composition of an ecosystem thereby altering species diversity [12].

Copper
As shown in table 1, the lowest concentration of copper (0.074µg/m^3) was obtained at Old GRA while the Abuloma had the highest concentration of 0.216ug/m^3. The mean concentration of copper from the eight sample locations was 0.135 ± 0.048µg/m^3. The level of copper across the eight locations and their mean were above the WHO permissible limit of 0.037ug/m^3 for copper in ambient air. The relatively high concentration of copper recorded across the eight sampling sites could be attributed to traffic emissions and the proximity of the sampling sites to the Trans-Amadi industrial layout. Okorie *et al*. [5] reported a range of 70 to 990mg/kg of copper in soot sample which is far below the range recorded in this study. Copper is essential for health, but high level of exposure can be harmful to human and animals [1].

Cadmium
Table 1 shows that the concentration of cadmium in soot sample from the eight locations ranged from 0.0010 to 0.0036µg/m^3. Borokiri had the highest concentration while the lowest concentration was found at Old GRA. The mean concentration was 0.135 ± 0.048µg/m^3. All the concentrations across the eight locations and their mean were within WHO allowable limit of 0.005ug/m^3. The relatively high concentration obtained at Borokiri may probably be due to the emission from sea going vessels at Kidney Island which is close to the sampling points. Possible sources of cadmium include vehicular exhaust emissions, plastics containing cadmium pigments and burning of municipal wastes containing Ni-Cd batteries [3]. People that lives in areas polluted with cadmium often suffer from diseases like osteoporosis and increase risk of fractures [2], however the concentrations from the studied locations do not indicate that these locations are not polluted by cadmium.

Zinc

The concentration of zinc ranged from 0.057 to 0.077µg/m^3. Amadi-ama had the highest concentration while Borokiri had the lowest concentration of zinc. The mean from the eight samples locations was 0.068 ± 0.006µg/m^3. The concentration across the eight locations and their mean was far below the WHO allowable limit of 0.1 – 0.5µg/m^3 for zinc in ambient air. However, the presence of Zinc across the sampling locations could be attributed to windblown soil and resuspended road dust. These concentrations correlate with work by Rashidatu [7] who reported a range of 0.058 to 0.078µg/m^3 on soot samples in Accra Ghana. Though zinc at high concentration is harmful but the values found in these work shows no cause for concern.

Total Petroleum Hydrocarbons
From table 2, the concentrations of total petroleum hydrocarbon for the eight samples studied ranged from 8.7129 to 17.2746mg/kg with a mean concentration of 13.3767 ± 2.6959mg/kg. Borokiri had the highest concentration of 17.2746 while Amadi-ama had the lowest concentration of 8.7129. The level of TPH obtained in this study was far below the level obtained by Ede and Edokpa [4] who reported a range from 16.2 to 96.0mg/kg in soot sample from Port Harcourt and its environs. WHO [13] in conjunction with USA National and State Regulations and Guidelines, gave the following guidelines for TPH in water, air and other media: for Diesel fuel emission, the average acceptable ambient air concentration for a period of 30 minutes is 0.09mg/m^3 and an annual air concentration of 0.009mg/m^3. For naphtha, the average acceptable ambient air concentration ranges from 4.00mg/m^3/30minutes, 2.7mg/m^3/8hrs to 0.40mg/m^3/24hrs or per annum. For gasoline fuel emissions a range starting from 14.8mg/m^3/30mins, 9.00mg/m^3/8hrs, 2.16mg/m^3/24hrs and annual concentration of 0.0013mg/m^3 were set. The values of TPH in this study far exceeded the WHO guidelines which indicate that the soot samples across the eight locations were contaminated with TPH. The compounds in different TPH fractions affect the body in different ways. Some of the TPH compounds, particularly the smaller compounds such as benzene, toluene, and xylene (which are present in gasoline), can affect the human central nervous system. If exposures are high enough, death can occur. Breathing toluene at concentrations greater than 100 parts per million (100ppm) for more than several hours can cause fatigue, headache, nausea, and drowsiness.

Conclusion
This study examined the concentrations of some heavy metals and total petroleum hydrocarbon in soot samples from eight locations in Port Harcourt. The results revealed that some of the heavy metals were higher than WHO permissible limit for heavy metals in ambient air while some were within the permissible limit. The level of total petroleum hydrocarbon in all the samples exceeded the WHO permissible limit. The high level of some heavy metals and total petroleum hydrocarbon may be attributed to anthropogenic and industrial activities taking place in and around the study area. Therefore, it is necessary that the industries operating within the study area are monitored by relevant regulatory agencies to forestall further emitting of these substances into the atmosphere.

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