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Review Article

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The total petroleum hydrocarbon contents of the ambient air within Port Harcourt and environs

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Abstract The Total Petroleum Hydrocarbons (TPH) of three locations: Aba Road, Woji and Iwofe within and around Port Harcourt metropolis were studied. Soot particles in the ambient air were trapped on a tenax GC Adsorbent tube, for GC analysis. Sampling was done on weekly basis for four weeks respectively. TPH was analyzed according to ASTM D3921 (EPA, 2015). From the results obtained, Aba Road, Woji and Iwofe recorded mean values of 36.99mg/m^3, 22.71mg/m^3 and 22.18mg/m^3 respectively. Subjecting the obtained values to ANOVA showed that there was no significant difference between the three locations. However, comparing the results with World Health Organization (WHO, 1978) reference guidelines (diesel: 0.09mg/m^3/30 minutes; 0.009mg/m^3/annum; gasoline: 14.8mg/m^3/30 minutes; 9.00mg/m^3/8hrs; 2.16mg/m^3/24hrs; 0.013mg/m3/annum), showed that TPH in the ambient air in the three locations of Port Harcourt, exceeded permissive limits. This study recommends measures to be taken to reduce emission of soot and steps to be taken by the general populace to stay healthy in Port Harcourt and environs.

Keywords ambient air, TPH, hydrocarbon, Harcourt and environs

Introduction

Total Petroleum Hydrocarbons (TPH), is a general term used for a mixture of different hydrocarbons found in crude oil and other petroleum products. Several hundreds of these compounds occur and are the most common contaminants of the environment. Their presences in the environment pose a risk to human health and cause damage to the ecosystem in general.

TPHs do not occur in any one sample. The make-up of TPH in an environment at a particular point ant time depends on the composition of the crude oil and the petrochemical product spilled or emitted into the environment. Their carbon chain ranges from C6through C35of hundreds and thousands TPH. Therefore, evaluating these compounds individually is impracticable. Hence evaluations for overall TPH are common and generally accepted. TPH can be grouped into three categories for easy evaluation namely; Gasoline range (GRO) >C6 – C10; Diesel range (DRO) >C11 – C28 and lube oil range >C28 – C35. In the past, TPH was reported as single overall number. However, analyses are now generally reported as TPH in the various ranges which they occur [1].

Some TPH compounds are implicated with nervous disorders thereby causing headaches, dizziness and nausea in affected persons. TPHs have also been implicated with blood, immune system, lungs, skin and eye dysfunction. Some members of the TPH family, for instance benzene, benzo (a) pyrene, gasoline, etc. have been shown to be

carcinogenic [2-3]. Compounds such as jet fuels, benzene, hexane, xylene, toluene, naphthalene, mineral oils as well as other petroleum products are good sources of TPH. TPH may be found in one or a mixture of these compounds and they are all hydrocarbon compounds.

Nigeria's Niger Delta region is an oil rich region that is susceptible to real and imagined shocks. This oil – rich marshland houses a beehive of oil and gas activities majorly international oil companies (IOCs). Port Harcourt, capital of Rivers State is the hub of the oil and gas industry in Nigeria. Port Harcourt lies within the oil – rich Niger Delta region of Nigeria. The Eleme Petrochemical Company and the Port Harcourt Refinery are both situated within reach to the city of Port Harcourt.

For over two years the city of Port Harcourt has been experiencing heavy black soot deposition. The persistent black soot being noticed in the city of Port Harcourt and its environs since the last quarter of 2016 have become environmental issue to the residents of the city as they have always complained about waking up in the morning to see their houses and cars covered by soot. Owoade *et al*. [4], investigated the coarse and fine particulate matter fractions in an industrial area in Lagos State during the wet and dry seasons. The study showed that six metals (Cr, Mn, Fe, Cu, Zn, and Pb) measured in both fractions of the particulates recorded higher concentration during the dry season indicative of serious health effects on humans and animals. Khan *et al*. [5] worked on PM2.5 in a health risk assessment in Southeast Asia. The results obtained from the study far exceeded WHO guideline [6] and USEPA [7] national air quality standards (NAAQS) by 48% and 19% respectively. Soot is regarded as an environmental hazard as the size of the soot particle enables it to penetrate deep into the respiratory tract [8]. Soot is made up carbon of varying sizes with metals and VOCs absorbed to the carbon components. The very fine particles of soot (usually ≤ 2.5μ) interact with gas-phase species as well as other soot particles to create larger soot particles.

Several researches are ongoing to evaluate the health implications of the deposition of black soot in Port Harcourt City and its environs. In order to provide useful scientific data, this research was conducted to evaluate the concentration of the Total Petroleum Hydrocarbons present in the ambient air within Port Harcourt metropolis and environ.

Materials and methods

Methods: ASTM D3921 (EPA 2015)

Summary of analysis

The compounds (TPHs) were extracted from the sample with a solvent and the extract was introduced into a vial for GC analysis.

Health, safety and environment

Equipment

Weighing balance with accuracy to ± 0.0001g, Water Bath, Desiccators, Micro-Syringes, Vials, GC/FID.

Glass ware

Volumetric flasks, pipettes, burettes, conical flasks, glass separator funnels of suitable capacity for the sample volume fitted with glass stopper, and taps, measuring cylinders.

Reagents and chemicals

All reagents used in this research were of analytical grade. Dichloromethane, activated silica gel 60 (70-230 mesh size) dried overnight at 1200 C and stored in a desiccator containing a drying agent, anhydrous sodium sulphate also treated as above and stored in the desiccator till required for use.

Procedure

Sampling

TPH adsorbed on to particulate matter in the air were trapped on TenaxGC Adsorption tube exposed to the air for 28 days. Weekly samples were harvested, labeled, and stored under cold storage in air-tight black sampling inert

containers. Three locations were chosen for sample collection namely; Woji, Aba Road within Port Harcourt, and Iwofe. These points covered Port Harcourt metropolis and environs.

Period of sampling

Sampling covered the second half of December 2016 through first half of January, 2017.

Extraction Procedure

10g of sample was weighed into a 100ml conical flask followed by 30ml of extraction solvent (dichloromethane). The flask was covered properly with aluminum foil paper and agitated or swirled for 1-2 minutes while releasing the cover to control pressure build up. Thereafter, the extract was allowed to settle in a space of 10-15 minutes. The extracted mixture was passed through a filter paper containing 1-3g of sodium sulphate and 2-4g of activated silica gel for removal of moisture content. The volume of extract obtained was recorded for further calculation. The extract was transferred into vials ready for GC analysis.

GC/FID Analysis

1µL of sample extract in a vial was injected through the injection port of the GC connected to the fluid ionization detector (FID). Various peaks of hydrocarbons were identified with the aid of peaks obtained from known concentrations of serial dilution of TPH standard solutions. (C6 – C38). Injection port temperature was at 320 ºC to keep extracted components in a vaporized state. The flow rate of the carrier gas (Helium) was 0.65cc/min. Prior to sample analysis, a blank of extracting reagent was run through the column to knock off any interference in the developing reagent. The carrier gas line, GC and FID were checked and were found to be working in optimal condition.

Calculation

$$\frac{\text{Instrument Reading x Total Volume of Extract x Dilution Factor}}{\text{Weight of Sample}}$$

Results and Discussion

Table 1: Total Hydrocarbon Levels of the Ambient Air in Port Harcourt and Environs WOJI

Carbon Length	Amount (mg/l)			
	Week 1	Week 2	Week 3	Week 4
C8	1.943	3.182		
C9				
C10	1.259	2.001	4.049	2.349
C11		1.568		
C12	2.224	3.563	7.247	4.084
C13	9.329	1.112	2.754	1.559
C14	1.477	2.850	5.822	2.357
C15			1.430	
C16	6.966	1.203	2.631	1.498
C17	2.928	5.811	2.231	7.828
C18			4.762	
C19				
C20	1.503	2.195	5.614	3.259
C21				
C22	1.671		4.971	4.699
C23	2.806		5.368	7.188
C24	4.521		9.998	1.077
C25	6.651		1.624	1.537
C26	1.260		2.630	2.292
C27	1.783		4.114	2.951
C28			4.295	3.188

TOTAL	12.257	14.871	40.616	23.070

Table 2: Iwofe

Carbon Length	Amount (mg/l)			
	Week 1	**Week 2**	**Week 3**	**Week 4**
C8				
C9				
C10	3.728	4.859	2.493	1.733
C11				
C12	6.502	8.468	4.810	3.159
C13	2.966	3.259	1.957	1.443
C14	4.817	6.157	3.751	2.515
C15				
C16	1.857	2.494	1.825	1.085
C17	7.810	1.129	8.949	4.986
C18				
C19				
C20	3.857	6.320	4.564	
C21				
C22				
C23				
C24				
C25				
C26				
C27				
C28				
C29	6.160			
TOTAL	27.200	26.999	16.188	10.437

Table 3: Aba Road

Carbon Length	Amount (mg/l)			
	Week 1	**Week 2**	**Week 3**	**Week 4**
C8				
C9				
C10	3.496	9.284	10.399	2.847
C11		2.827		
C12	6.367	16.518	17.985	5.110
C13	2.605	6.674	6.722	2.158
C14	5.398	12.305	12.914	4.014
C15				
C16	2.278	4.983	5.241	1.647
C17	1.166	2.431	2.084	7.319
C18				
C19				
C20	6.156	8.596	8.639	
TOTAL	21.930	53.340	56.212	16.510

Table 4: Mean Total Petroleum Hydrocarbons of Ambient Air within Port Harcourt and Environs

Woji		Iwofe		Aba road	
Location	**Conc. {mg/kg}**	**Location**	**Conc. {mg/kg}**	**Location**	**Conc. {mg/kg}**
1	12.28	1	27.20	1	21.93
2	14.87	2	26.99	2	53.34
3	40.62	3	16.19	3	56.21

4	23.07	4	10.34	4	16.51
Total: 90.84; x = 22.71		Total: 80.72; x = 20.18		Total: 147.99; x = 36.997	

Table 5: Analysis of Variance for TPH in Three Major Locations within Port Harcourt Metropolis and Environ.

Independent Variables	N	Mean	SD	SE	Source of Sig. Variance	Sum of Square	df	Mean Sq.	F
Woji	4	22.71	12.80	6.40	Between	657.82	2	328.91	1.49
Iwofe	4	20.18	8.33	4.17	0.28 Within	1982.52	9	220.28	
Aba Road	4	37.00	20.68	10.34					
Total	12	26.63	15.49	4.47	Total	2640.33	11		

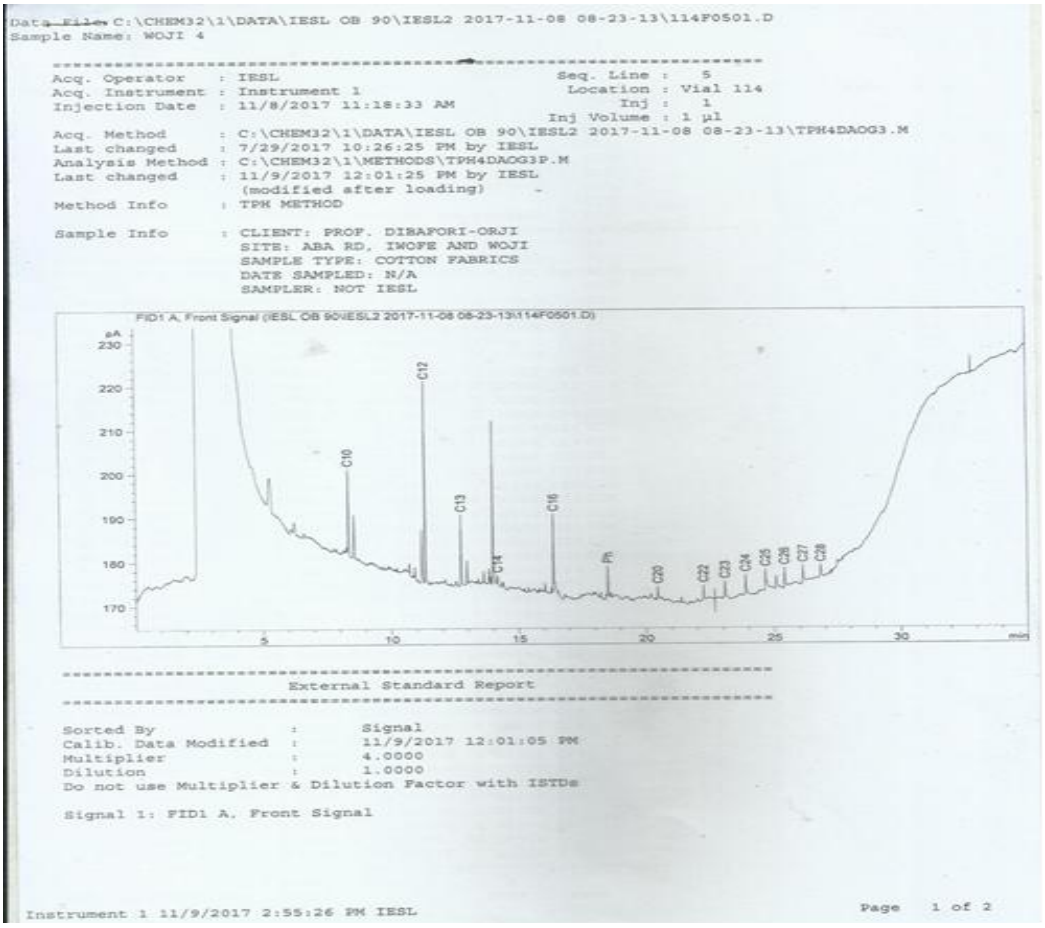

Figure 1: Typical Chromatogram showing individual components of TPH contained in the Ambient Air Sample

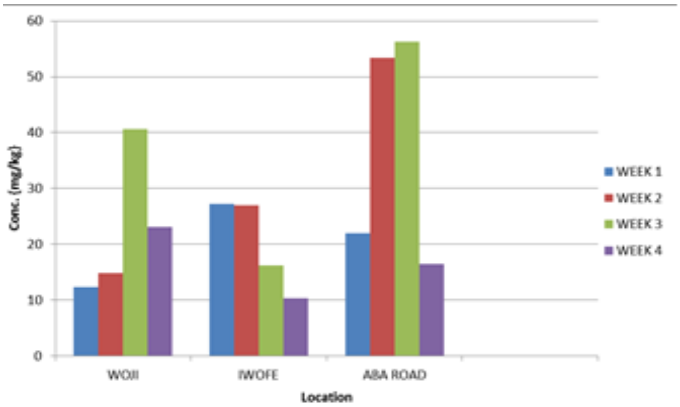

Figure 2: Weekly Mean Concentration of TPH

Table 1 gives the components of TPH values of the ambient air within Port Harcourt and environ. Table 2 gives the weekly TPH values of the sampled area. Table 3 shows the ANOVA of PAHs values from Table 2. The results in table 3 revealed that there is no significant difference in the concentration of TPH among the three locations Woji, Iwofe and Aba Road: F {2,9} = 1.49, P = 0.28 > 0.05 level of significance.

Identified components were in the gasoline (>C6-C10) and diesel (C11-C28) ranges. No Naphtha was identified. C12 –C14, C16, C17 and C20 appear to be the most abundant of the TPH family in all samples. This means that the source of the TPH is basically the same. In Aba road, the total weekly mean TPH emission was 36.99mg/l. This was followed by Woji (22. 71mg/l) and lastly Iwofe (22.18mg/l). This is expected because Aba road is the busiest point of the three sampling locations. In addition to the soot emissions, added loads fromtheir vehicular emissions and human activities are expected. Figure 1 shows components of the TPH family present in the studied ambient air. Figure 2 gives the bar charts of the mean concentrations of TPH in Woji, Iwofe and Aba Road.

WHO [6] in conjunction with USA National and State regulations and guidelines with respect to TPH in water, air and other media came up with the following guidelines: for Diesel fuel emissions, 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/m3. 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 as guidelines for gasoline fuel emissions. Finally, for Naphtha, the average acceptable ambient air concentration ranges from 4.00mg/m^3/ 30mins, 2.7mg/m^3/8hrs, to 0.40mg/m^3 24hrs or per annum.

The figures obtained in this research far exceeded WHO guidelines. Emitted soot when breathed into the lungs can trigger some deleterious health conditions. Soot is of immense health and environmental concern. Soot particles are ≤ 2 microns. This makes it easier for them to pass through the alveolar membrane of the lungs into the blood carrying with them other primary pollutants like heavy metals, PAHs and VOCs.

These hydrocarbons and metallic carcinogens when present in the body will end up causing nervous disorders, cancers of various degrees and even death [9]. According to Stephen [10], some hydrocarbon mixtures contain priority pollutants including volatile organic compounds (VOCs) and semi volatile compounds, and metals each of which have their own specific toxicity information.

Gas Chromatography used in this research has been used to quantify TPH in ambient air. It's been reported that compounds in the boiling range 800-2000 C in ambient air may be captured on a Tenax GC adsorbent tube which is thermally desorbed for GC analysis [11]. This is also applicable for gasoline (Faniel, 2015). In this method, over 90 percent recovery was reported. The method used in this research [7] is in conformity with EPA, 1988.

Conclusion/ Recommendation

Particles were collected from Air samples within Port Harcourt and Environ. GC analyses showed presence of some members of the TPH family in all three locations. Statistics showed that there was no significance difference in the three locations. However, the figures obtained exceeded WHO [6] guidelines for diesel and gasoline emissions respectively.

Residents of Port Harcourt have been under the siege of soot emitted from unknown sources for the past two to three years. If this is allowed to continue for upwards of five to ten years, Port Harcourt city may not be fit to live in. Apart from oil and gas industries that are operating in Port Harcourt and environs, the increased presence of soot in the environment has been suspected to come from illegal refineries that exist within the creeks around Port Harcourt city.

It is therefore recommended that close monitoring of the environment be conducted by the State's Environmental Agency. Also, the general public should be addressed on the need to properly cover foods especially food vendors.

need to properly cover foods especially food vendors. Inhabitants of the city of Port Harcourt should maintain indoor life. Finally, the Federal Government of Nigeria should encourage indigenous refining of petroleum products to cut down the incidence of illegal bunkery. Any culprit caught after this measure, should be severely penalized.

Appreciation

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