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PROXIMATE ANALYSIS AND SPATIOTEMPORAL DISTRIBUTION OF BLACK SOOT IN PARTS OF RIVERS STATE, NIGERIA

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Abstract

This study undertaken as a result public outcry over the appearances of strange black dusty deposit noticeably seen on cars, clothes on lines and rooftops after hours of smog in Port Harcourt and environs raising veil anxieties about the resulting health impacts, involved the proximate analyses of black soot samples collected in parts of Rivers State (Bolo Town in Ogu/Bolo LGA, Onne in Eleme LGA and Rumuolumeni in Obio/Akpor LGA). The study examined the composition/characteristics of the soot and their spatial variations in the three Local Government Areas of Rivers State where the soot samples were collected. The Samples were analyzed in the laboratory using acid digestion followed by an Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES Varian 725-ES). Results indicated that the soot are a product of incomplete combustion and are composed in elevated concentration (compared to WHO/EPA Allowable limits) of the following heavy metals: lead (Pb) 164.924mg/kg, Cadmium (Cd) 2.30mg/kg, Nickle (Ni) 0.147mg/kg, Copper (Cu) 0.67mg/kg, Zinc (Zn) 0.05mg/kg, Mercury (Hg) 0.05mg/kg, cobalt (Co) 0.47mg/kg . They are also composed of Polycyclic Aromatic Hydrocarbon (PAHs) and Total Petroleum Hydrocarbon (TPH). For Bolo in Ogu/Bolo LGA PAH ranged between 88-189ng/m3, TPH ranged between 18.8 – 94.2mg/kg; Onne in Eleme LGA PAH ranged 50-190ng/m3 and TPH 16.0 – 88mg/kg, Rumuolumeni in Obio/Akpor LGA PAH ranged between 44 – 190ng/m3, TPH 16.2 – 96.0mg/kg. The soot is between $PM_{2.5}$ and PM_{10} in size. Meteorological parameters of the area showed that temperature oscillate between 24˚C and 27˚C. Relative humidity of the area is between 92% and 100% and wind speed is 3.6km/hr in Bolo, 10.7km/hr in Onne and 7.6km/hr in Rumuoluemeni. The prevailing wind direction is southeast and air quality index is between 157AQI and 190AQI. The prevailing wind direction and the size of the soot of $PM_{2.5}$ and PM_{10} account for the variation in the distribution of the soot across the LGAs. The study further showed that temperature, rainfall, wind speed and direction accounts for the dispersion and persistence of the particulate matter. The air quality Index visual app report shows that concentration of soot is between 4:00am and 11:00am. Having identified activities of artisanal refining as the major cause of the presence of black soot, it is hereby recommended that all forms of illegal and artisanal refinery should be stopped forthwith.

Keywords: *Black Soot, Proximate Analysis, Air Pollution, Spatiotemporal Distribution, Rivers State.*

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Introduction

Air, a non-visible form of matter is one of the most important of earth's resources without which life cannot exist on the planet. It is however, a sink into which gaseous and particulate matter from anthropogenic and other natural sources are released. Air pollution occurs when excessive/harmful substances are introduced in the atmosphere which lowers the quality of air and affects the quality of life (Ukaegbu *et al*., 2020). Air becomes polluted when it carries gaseous and particulate matter at levels that are objectionable; i.e. capable of causing discomfort or harm to man or his amenities. According to Yakubu, (2017), air pollution constitutes the largest among all of the environmental risks: 3 million annual deaths are associated with outdoor air pollution exposure. In 2012 alone, 11.6 percent of global deaths equivalent to 6.5 million deaths were outdoor air pollution-related. 94% of the approximately 90% of air pollution-related deaths occurring in low- and middle-income countries are as a result of non-communicable diseases, including cardiovascular diseases (CVDs), chronic obstructive pulmonary disease (COPD), and lung cancer (Yakubu, 2017).

Air pollution significantly influences the climate, living environment, and human health (Ofremu *et al*., 2024). Air pollutants can directly harm sensitive plants and trees through toxic exposure, while when deposited in rain, they can acidify ecosystems and contribute to nutrient overload in water bodies like rivers and lakes, impacting the health of aquatic life and surrounding habitats (Bolan *et al*., 2024)

There was public outcry and anxiety over the state of the air quality in Rivers State in late 2016. The continuous deterioration of air quality in Port Harcourt metropolis and its environs where it is regularly observed intense carbonised aerosols generally referred to as 'black soot', resulting from a myriad of sources descend on the city as dry deposition. This dry deposition phenomenon of black soot over Port Harcourt and surrounding towns was most evident during the dry season of December 2016. 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. According to WHO, (2017), Soot can have adverse health consequences on population health, however, babies and children (particularly due to their premature respiratory organs, the elderly, and people with preexisting health conditions, including heart or lung diseases (such as asthma) are more vulnerable (Joshi, 2024). Like other particle pollution, soot is associated with difficulty in breathing; eye, lung, and throat irritation; birth related problems, such as low birth weight; and, heart disease due to its fine particulate matter than can deeply penetrate the respiratory system when inhaled, causing inflammation and systemic health issues (Shetty *et al*., 2023)

From about 3:00am in the morning to about 11:00am in the morning the clouds become darker, with particulate matters dropping on car tops, roof tops, and resident cannot spread clothes on the lining as the droplets will stain the clothes. When it rains, it washes the atmosphere of this soot and the entire surface runoff is black, drainage systems turn black, receiving water bodies such as streams and creeks receiving the "black" runoff with its attendant danger. Monuments, grave stones, house railings are all stained by this menace. Many fish farmers have shut down their fish farms and those who could afford have taken the extra measure of roofing their ponds. The black soot contaminates the ponds and snuff out life in the fish. Residents in parts of Rivers State, especially Port Harcourt, Bolo, Okrika etc, are getting apprehensive about the air they breathe. In the morning when residents wake up their nostrils are blocked with black particulates matters, their sputum is thick and black, residents cannot open their windows at night and early in the morning because of the soot, air

conditioner filters are constantly black and clogged. To put it brusquely, many residents are terrified to breathe.

Up until now, deductions made based on the cause, of the "soot" has been mainly logical based on the intense oil activities of the area. However, this research is carried out to ascertain specific issues and come to a scientific conclusion and solution.

Materials and Methods

The Study Area

Rivers State was created out of the old Eastern Region of Nigeria on May 27, 1967, before Bayelsa State was later carved out of it in 1996. Rivers State, named after the many rivers that border its territory, was part of the Oil Rivers Protectorate from 1885 until 1893 when it became part of the Niger Coast Protectorate. In 1900 the region was merged with the chartered territories of the Royal Niger Company to form the colony of Southern Nigeria".

Covering a total of 11,077km land area, Rivers State is bounded in the south by the Atlantic Ocean, in the north by, Imo and Abia States, in the east by Akwa Ibom State and in the west by Bayelsa and Delta States. Rivers State "is currently made up of 23 local government areas. These are Ogba/Egbema, Ndoni, Ahoada, Ikwerre, Etche, Andoni/Opobo, Bonny, Okrika, Iyigbo, Khana, Gokana Tai/Eleme, Obio/Akpor, Emohua, Degema, Asari Toru, Akuku, Abua/Odual, Omumma, Opobo/Nkoro, Ogu/ Bolo, Ahaoda West, Ahoada East and Eleme" (Ngex, 2013).

The capital of Rivers State is Port Harcourt. It is situated 52 kilometres (32 mi) southeast of Ahoada and about 40 kilometres (25 mi) northwest of Bori. It is bounded to the south by Okrika, to the east by Eleme, to the north by Obio-Akpor and to the west by Degema. It has a total size of 109 square kilometers (42 sq mi)".

Initially, "agriculture was the main occupation of the people of Rivers State and the agricultural policy of the state government is anchored on food production. This offers employment for young school leavers and university graduates. These agricultural activities are grouped under Community Block Farming Scheme, Community Fishing Scheme, Livestock Scheme and Rabbitry" (Ngex, 2013). But now, it is the production of oil and gas that Rivers State is most famous for, with vast reserves of crude oil and natural gas, Rivers State" account for more than 40% of Nigeria crude oil production" (Ngex, 2013). Apart from this, there are many petrochemical related industries in the state, which also harbor the first petroleum refinery in Nigeria, and the gigantic liquefied natural gas project is located in Bonny in the State as well. Some of the oil production and petrochemical related companies in Rivers State include but are not restricted to;

i. Shell Petroleum Development Company of Nigeria Limited
ii. Lewis Oil and Gas
iii. Omega Maritime Services
iv. Polmaz Limited
v. Chevron Texaco Nigeria Limited.

The main activities of these companies are in three stages, upstream, midstream and downstream activities. Now the area which is directly related to the study is the upstream activities. Upstream activities "involve exploring for crude oil deposits and the production of

crude oil". Examples of firms that would belong in the upstream segment of the industry include companies that own rights to drill for oil such as ExxonMobil, Shell Petroleum, and Chevron Texaco etc., which all have their presence in Rivers State.

Over the years, the activities of these companies have gone on with mediocre monitoring from the government. Thus, leading to poor and cheaper work practices on the part of these companies, with less time spent on R & D for best pollution reduction practices and more time spent on profitability. This has slowly but surely taken its toll on the environment leading to the manifestation of all sorts of environmental degradation.

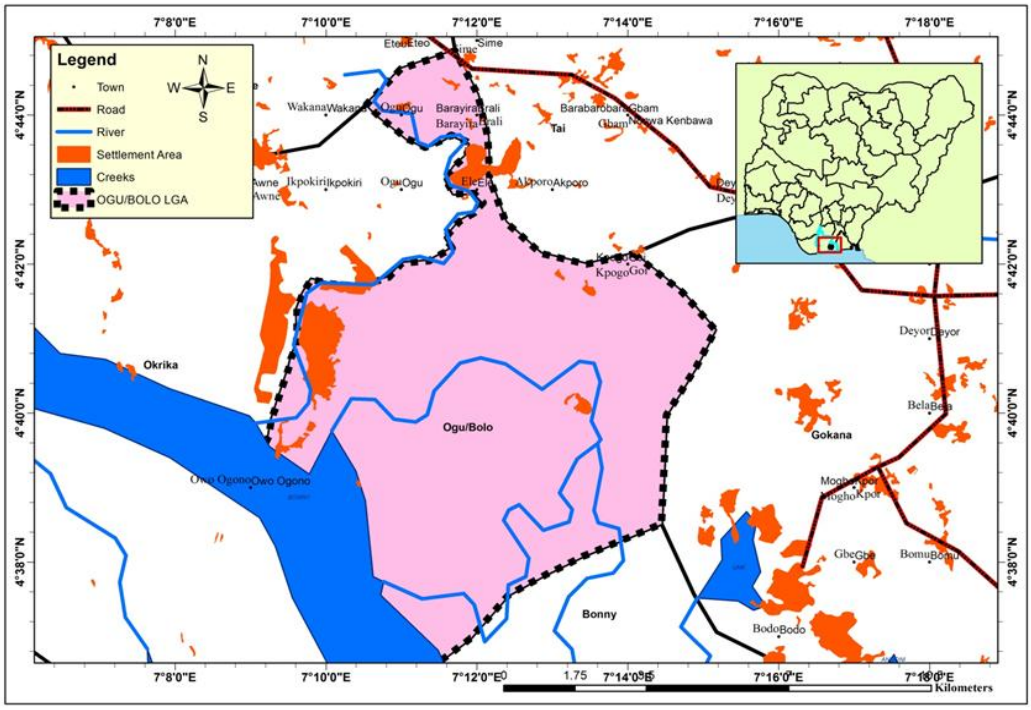
Some of the active labour force engaged in one form of agricultural activity or another, with yam, cassava, plantain, maize, cocoyam and vegetables as the predominant food crops in the area are having very reduced yields, owing to the hydrographic conditions of the State only a fraction of the land size is cultivated with crops.

Ojimba, (2012) States that "oil pollution arising from oil spillages and gas flaring regularly occur, therefore, destroying the environment, while the rivers and farmland which the inhabitants rely on for their fishing and farming activities have been rendered unwholesome. This environmental destruction had increased the poverty level of the inhabitants"

According to the National population Census board, the last known population of Rivers State was 2,343,300 people as at the year 2015. This was 1.29% of the total Nigerian population. If the population growth rate remains the same as it was in the period between 2006-2015, which was estimated at 9.28% per annum, Port-Harcourt recent population as at the year 2018 will be estimated to be 3,058,484 people.

The focus of this study is three communities: Bolo in Ogu/Bolo LGA, Onne in Eleme LGA and Rumuolumeni in Obio/Akpor LGA.

Bolo is geo referenced on Lat 4°34´ S to Lat 4°45´ S and Long 7°10´E to Long 7°15´E is in the South-Eastern part of Ogu/Bolo Local Government Area, sharing boundaries with Tai, Gokana, and Bonny Local Government Areas of Rivers State, in the Niger Delta of Nigeria. Bolo is an Island settlement with several archipelago types of villages and fishing ports straddled along its numerous and dense network of creeks. A maze of rivers and winding creeks intersect it, and within it are, stretches of marshy land having mangrove trees with thickets of tangled roots as the vegetation. Bolo is host to two oilfields: Bodo West and parts of Bomu II oilfields with the associated product pipelines including the Trans Niger Pipeline. These pipelines have not been maintained and are vandalized by illegal oil bunkers to locally refine petroleum products.



Map of Ogu/Bolo LGA

Figure 1 *Ogu/Bolo Local Government Area*

Onne is a relatively major port in the region and has several quays with facilities for cargo ships up to 60,000. It is also the main base for the offshore activity in the region, and a large number of supply-vessels call at Onne every week. This section of the port is called Onne Oil and Gas Free Zone (OOGFZ) and contains several quays to cater to off shore supply vessels and a shipyard (WAS - West Atlantic Shipyard). The Onne oil and gas free zone also contains Shell Nigeria Exploration & Production Company (SNEPC), one of the largest bases of Shell offshore in Africa including berths leased out to Exxon Mobil, Total S.A. and other oil companies. Onne is in Eleme Local Government Area that makes up the present Rivers State of Nigeria. Eleme is located between longitude 70 and 70 15′ (seven degrees and seven degrees fifteen minutes) East of the Meridian and latitudes 40 60′and 40 35′ (four degrees sixty minutes and four degrees and thirty-five minutes) North of the Equator. The total area of Eleme is about 138 square kilometers (km^2). It is bordered on the north by Obio/Akpor and Oyigbo Local Government Areas, on the east by Tai Local Government Area, on the south by Ogu/Bolo and Okrika Local Government Areas as shown in Figure 2.

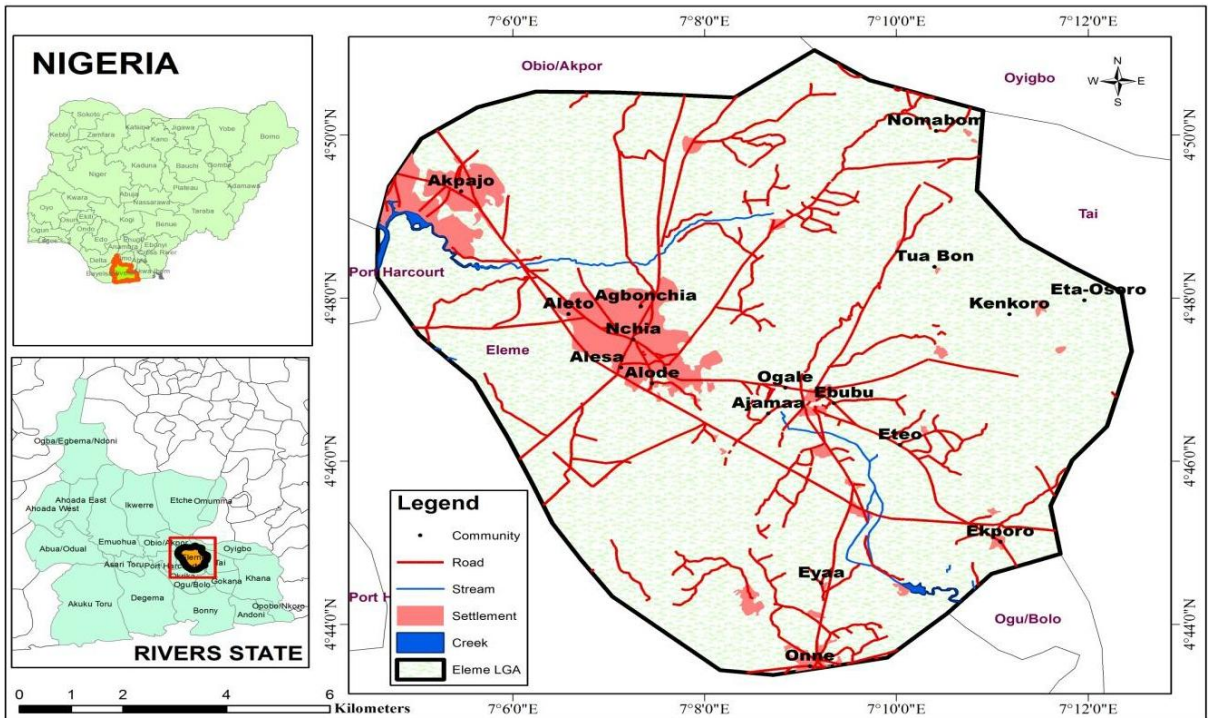


Figure 2. *Eleme Local Government Area*

With the discovery of oil in the Niger Delta in the 1958, the Eleme LGA became home to both Oil Refineries and Fertilizer industries, increasing the role of a more industrial economy. About 100 wells are thought to be in use throughout the Eleme territory. Oil from operations in Eleme was included in the first shipment of 22,000 barrels of crude oil exported from Nigeria to Europe in 1958.

Rumuolumeni Community in Obio/Akpor LGA (Fig 3) is situated between latitude 4˚49ˈN and longitude 6˚ 58ˈE, this latitudinal location implies that the study area lies within the tropical region with all its climatic and topographic characteristics. Rumuolumeni is bounded by Mgbuoba on the North, Rumueme on the east, and on the South by other parts of Port Harcourt. The area has an estimated total land mass of 15km and has a total population of 32,000 (NPC, 2006), which forms part of the entire population of Obio/Akpor Local Government Area in Rivers State. It also houses the Rivers State Government owned Ignatius Ajuru University of Education. The area possesses substantial natural resources prominent among which are major oil and gas deposits, a variety of solid minerals, good agricultural land and water resources, a large labour force and a vibrant private sector.

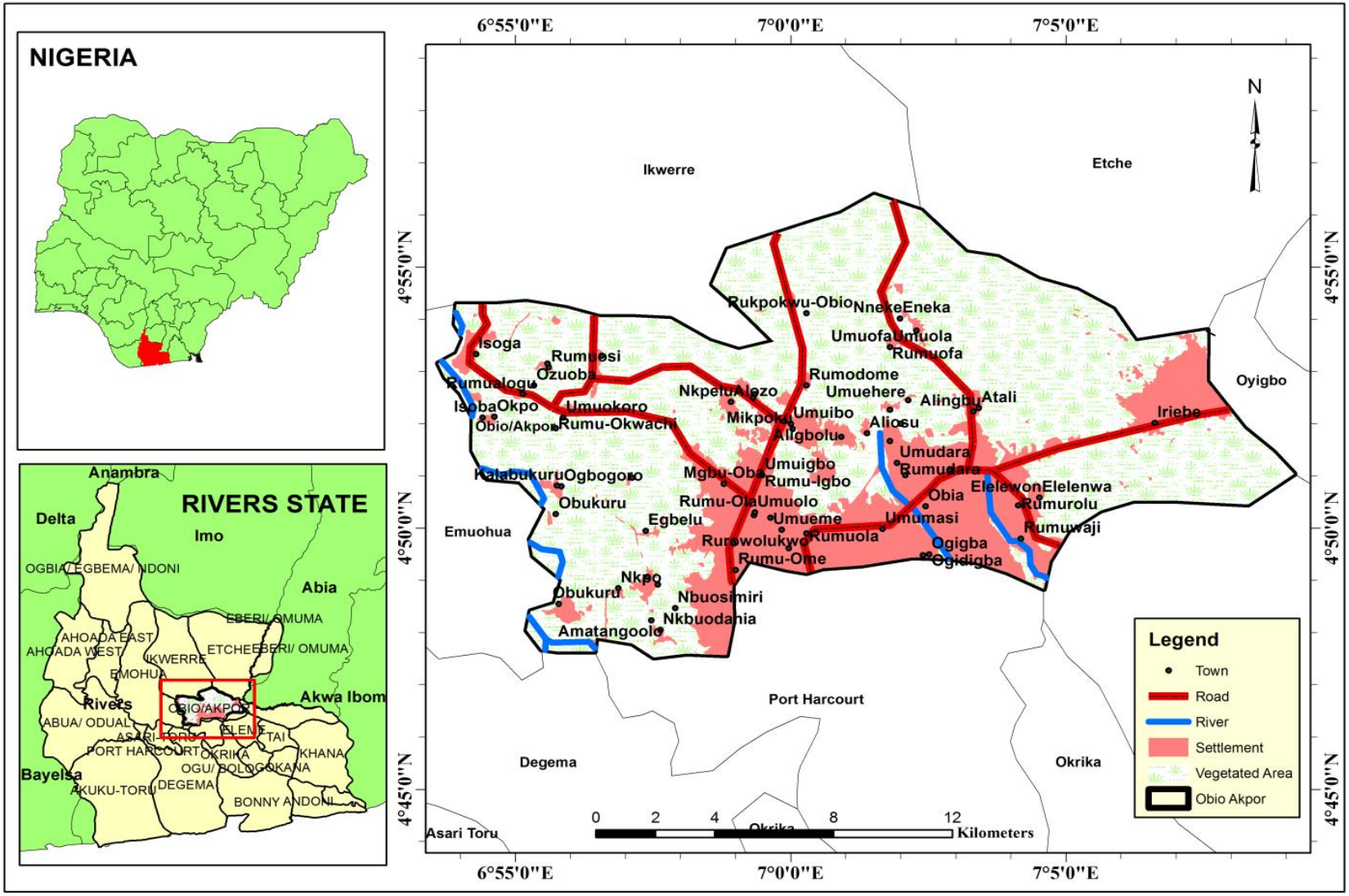


Figure 3: *The Study Area (Obio/Akpor Local Government Area Study Area)*

Climate/Meteorology of the Area

The study area is within the humid tropical belt of the Niger-Delta. The climate of the area is profoundly influenced by its proximity to the Atlantic Ocean. Rainfall is experienced throughout the year with peaks in June and September and lower amounts of rainfall from November to February (Fig 4). The mean annual rainfall is, above 2200 mm. The southwest trade winds bring moisture into the area from the coastal area. Two seasons namely, wet and dry, characterized the area. The wet season spread from April to October while the dry season was from late November/early December to March.

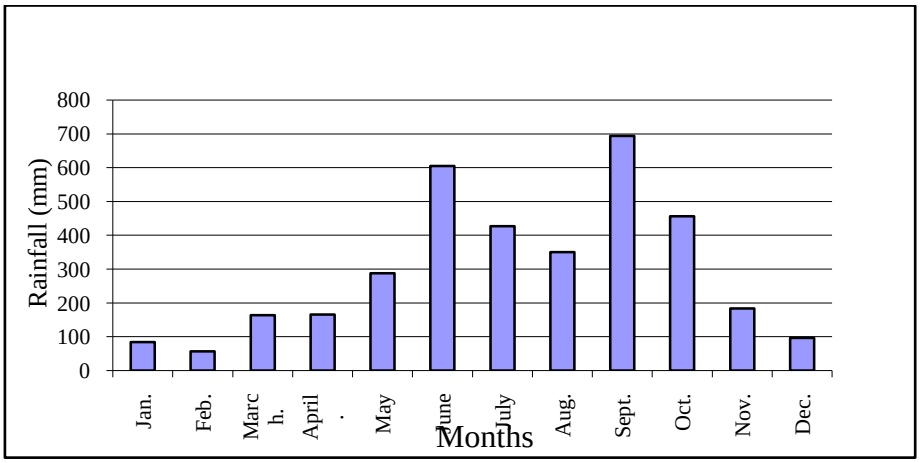


Figure 4 *monthly rainfall patterns in Rivers State.*

The pattern of relative humidity correlated with that of the rainfall described above. High values (over 95%) occurred in the node in the rainy season. In the dry season, the high daily relative humidity values ranged from 86.5 to 92.0% and occurred between 2100hrs and 2400hrs and later from 0100 to 0800 hours. The lower relative humidity values of 45.5 – 66.0% were obtained between 1300 and 1600h (Fig 5).

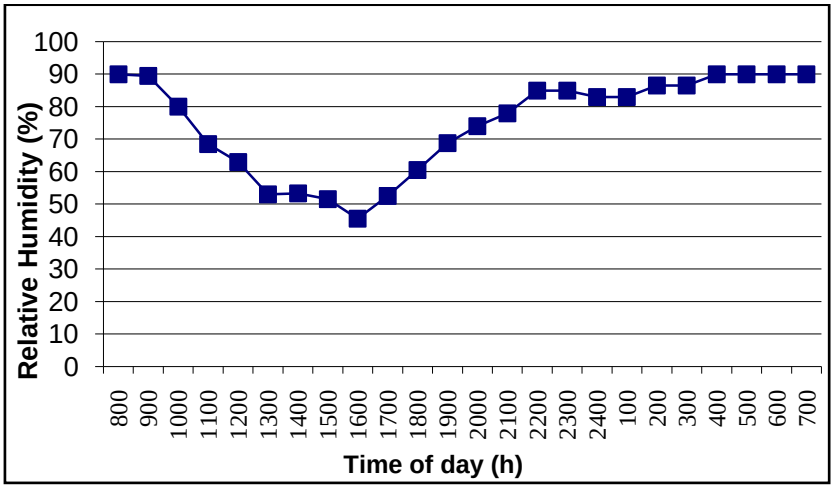


Figure 5 *Relative humidity (%)*

The highest temperature (^{o}C) values ranged from 34.0 – 36.3 and they occurred between 1300 and 1800hours while the lowest temperature values ranged from 25.3 – 26.0 between 0400 and 0800h in the dry season. Temperatures ranged between 24.5 and 29.0 ^{o}C in the early hours (0400 – 0600 h) in the rainy season. Higher temperatures (from 29 – 32 ^{o}C) occurred between 0900 and 1800 h (Fig 6).

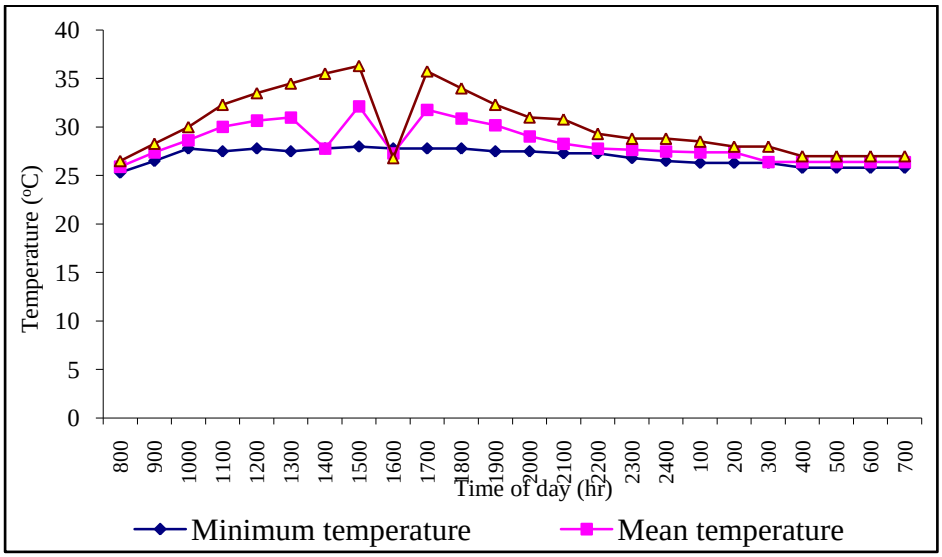


Figure 6: *Average daily temperature distributions for the Study area*

The mean daily sunshine is between three and six hours in dry season and it often falls to less than two hours in the wet season. The mean annual solar radiation varies from 1.5 – 1.9 J/cm^2/day. The longest monthly sunshine hours occur in December/January in the dry season while due constant cloudiness from rain clouds, July usually experience the lowest values of sunshine hours. Sunshine hours are directly proportional to the net radiation. Net radiation and air temperature are highest during the dry season except when relatively cold harmattan winds occur. All these parameters are very important as they influence the composition of the waste, the formation of leachate and migration in the subsurface

Southwesterly winds were prevalent in the rainy season in the node. The predominant wind speeds ranged from 7.5 – 20.5 m/s in Port Harcourt. The wind directions in the area were Westerly (W), South Westerly (SW), North Westerly (NW) and Southerly (S). In the dry season, the predominant wind speeds in the area ranged from 0.9-2.5 m/s, followed by winds with speed of 3.4-5.4 m/s. The average percentage of calm was 20.8 %. The implication is that atmospheric pollutants would be dispersed to the cardinal directions.

Method of data collection

For the purpose of this research, the focus was on gathering experimental data and generalizing it across the study area as it relates to this particular phenomenon. The goal of conducting a quantitative research study is to determine the relationship between the independent variable and dependent or outcome variable within the study area. This is a quantitative experimental research design because it aims to establish causality.

Approaches used to collect data for this study are;

I. Experiments
II. Observation and recording of the event.
III. Obtaining relevant data from government bodies, institutions, and organizations around the study area.

Both primary and secondary data are used. The primary data were collected via experiments. The secondary data were collected mainly from electronically stored information and also diverse sources of physically documented data archived over the years. The primary and secondary data were collected to cover every aspect of the study. The primary data are related to the composition of pollutants present in the atmosphere for characterization. The secondary data shows similar studies done in the line and past degradation on the environment as it pertains to the occurrence of the black soot.

Sample and sampling techniques

Sampling is a means of gathering valuable information about a population. It involves using a lesser part of the population in an effort to make conclusions about the whole population. In this study, samples of black soot were collected from three locations in three towns in three local government areas namely Obio/Akpor, Eleme, and Ogu/Bolo.

Sample Locations

Three sampling location points were randomly established in each of the randomly selected communities in the three Local Government Area selected for this study.

At Bolo Town, the primary school field, the bridge head and the community landing jetty were selected. At Onne, the location selected to collect the soot samples are Trailer park junction, the Community centre and by the Naval College while at Rumuolumeni, the three points selected were Aker base, Iwofe Jetty and Nkpolu Junction. These places were selected because sampling equipment will not be tampered at the time of sample collection.

Field methodology (Collection of Soot samples by Filtration and impaction)

The complexity and diversity of particulate composition, size, mass, and concentrations in the atmosphere dictate the need for accurate and representative sampling. The major purpose of ambient particulate sampling is to obtain mass concentration and chemical composition data, preferably as a function of particle diameter. This information is valuable for a variety of problems: effects on human health, identification of particulate matter sources, understanding of atmospheric haze, and particle removal processes. To this end the filtration and impaction method was adopted for the collection of the black soot samples. Fibre filter meshes were acquired and were placed strategically in open fields and on top of vehicles in the location identified. The Fibre Filter Mesh were placed between the hours of 5:30am and removed by 10:00am. Each Fibre Filter mesh is dusted and collected sample placed into an individual Ziploc bag, labelled and shipped to Kenoly Nigeria Ltd Laboratory, Old Refinery Road, Elelenwo Port Harcourt, a DPR accredited lab along with a filled request form.

The reasons as to why samples for the study were collected in this manner are;

- It is less expensive to obtain samples in this manner as compared to a sample collection of the whole area.

- Sample collection in this manner will provide data required more quickly, thus saves time.
- Also, with resources concentrated on fewer sampling sites, the study and the sampling analysis can be broadened in depth and scope to allow for more specific analytical results.

In this study, a ***probability sampling - cluster sampling*** was adopted which, according to (Hajimia, 2014) "is the process of randomly selecting integral groups, within the defined population sharing similar characteristic". This sampling method was chosen because; it is very advantageous when populations are large and spread over a large geographic area like in our study area. In addition, it is very convenient and expedient.

Laboratory Analysis

The Soot samples were analyzed in the laboratory using acid digestion and then extracted into a water based solution and the solution is further analyzed for soot concentration using an Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES Varian 725-ES).

Analyses of the metals were carried out with atomic absorption spectrophotometer UNICAM 969 and operated as per the manufacturer's manual. The reagents used for this study were all of analytical grades and standard solutions were prepared from 1000 µg g-1 stock solution of Cd, Cr, Pb and Ni. Also, the glass wares used were thoroughly washed with (1:4) HNO_3 and then rinsed with distilled water.

Results and Discussions

This study is aimed at examining the characteristics/composition the substances commonly called "black soot" in the study area which has been collected from the selected local government areas. Soil samples were also collected for analysis to determine its heavy metal concentrations, conductivity and pH levels in comparison with permissible limits. This will lead to a better understanding of the effect on the chemical composition on the soil.

Table 1 below shows the composition (characteristics) of the black soot sample collected within the study period while table 2 shows the meteorological parameters.

Table 1 ***Heavy Metals/ Polycyclic Aromatic Hydrocarbons PAHs) and Total Petroleum Hydrocarbon (TPH) Concentration***

Heavy Metals/Others	**Bolo N 04° 39' E 007° 13 (Ogu/Bolo LGA)**	**Onne N 05° 01' E 006° 52' (Eleme LGA)**	**Rumuolumeni N 04° 43' E 006° 57 (Port Harcourt LGA)**	**Mean Concentration**	**Allowable Limits (WHO/EPA)**
Lead (Pb)	188.300mg/kg	189.472mg/kg	117 mg/kg	164.924mg/kg	**0.5** ($\mu g/m^3$)
Nickel (Ni)	0.15mg/kg	0.18mg/kg	0.11 mg/kg	0.147mg/kg	**0.5** ($\mu g/m^3$)
Cobalt (Co)	0.18mg/kg	1.17mg/kg	0.07 mg/kg	0.47mg/kg	**0.5** ($\mu g/m^3$)
Mercury (Hg)	0.0122mg/kg	0.0132mg/kg	0.130mg/kg	0.05mg/kg	**0.5** ($\mu g/m^3$)
Cadmium (Cd)	0.100mg/kg	4.7163mg/kg	2.1096mg/kg	2.30mg/kg	**0.5** ($\mu g/m^3$)
Aluminium (Al)	**	**	**	**	**0.5** ($\mu g/m^3$)
Zinc (zn)	0.05mg/kg	0.04mg/kg	0.0mg/kg	0.05mg/kg	**0.5** ($\mu g/m^3$)
Copper (Cu)	1.01mg/kg	1.00mg/kg	0.01mg/kg	0.67mg/kg	**0.5** ($\mu g/m^3$)
PAHs	88 – 189 ng/m^3	50 – 190ng/m^3	44 – 190 ng/m^3		**1** (ng/m^3)
TPH	18.8 – 94.2 mg/kg	16.0 – 88mg/kg	16.2 – 96.0mg/kg		

Table 2 *Meteorological Parameters*

Heavy Metals/Others	**Bolo (Ogu/Bolo LGA)**	**Onne Wharf (Eleme LGA)**	**Rumuolumeni (Obio/Akpor LGA)**	Allowable Limits (WHO/EPA)
PM 2.5	16.6 – 360 µg/m^3	62-270 µg/m^3	0.035 – 396.8 µg/m^3	**10 µg/m^3(annual means) 25 µg/m^3 (24hrs means)**
PM 10	1053.97 µg/m3	1154.45 µg/m3	1926.3 µg/m3	
US Air Quality Index	190AQI	168AQI	157AQI	
Temperature	24°C	27°C	26°C	Nil
Relative Humidity	98%	94%	92%	
Prevailing Wind Direction	South – East	South-East	South-West	Nil
Wind Speed	3.6km/hr	10.7km/hr	7.6km/hr	Nil
Time				

Table 3 ***pH of soil samples***

Code	**Locations**	**pH**
0029	ELEME (ONNE) 1	6.2
0030	ELEME (ONNE) 2	6.4
0031	ELEME (ONNE) 3	6.5
0032	ELEME (ONNE) 4	6.6
0033	OGU/BOLO (BOLO) 1	6.8
0034	OGU/BOLO (BOLO) 2	6.7
0035	OGU/BOLO (BOLO) 3	6.5
0036	OGU/BOLO (BOLO) 4	5.2
0037	OBIO/AKPOR(RUMUOLUMENI)	5.5
0041	OBIO/AKPOR(RUMUOLUMENI)	6.9
0042	OBIO/AKPOR(RUMUOLUMENI)	6.8

Discussion of Results

The Composition (characteristic) of the Soot

Results (from laboratory and textural analysis) show the composition of the black soot. The primary combustion products of crude oil are CO_2 and water. In addition, dense black smoke, primarily composed of elemental carbon (soot) is produced. The soot is often absorbed

(coated) by condensed organic compounds, sulphates and pre-existing particles, such as soil dust and/or sea salts. Other gaseous pollutants resulting from the combustion are CO, NO_X, SO_2, PAHs, VOCs found in the vapour phase of the smoke. Chemical reactions within the smoke plume and atmosphere produce secondary ground level ozone (O_3). Combustion of PAHs produces more toxic higher molecular weight organic compounds. From Table 1, the black soot sampled primarily contained the following heavy metals - Lead (Pb), Cadmium (cd), and Nickle (Ni) in elevated concentrations indicating that the source to be petroleum product. Being products of incomplete combustion, Polycyclic Aromatic Hydrocarbon (PAHs) and Total Petroleum Hydrocarbon (TPH) – (a *term used to describe a large family of several hundred chemical compounds that originally come from crude oil)* were very pronounced

The Possible Sources of the black Soot

The causes and mechanisms of air pollution are quite variable; however, the distribution of pollution sources, air temperature, pressure, wind speed and direction, relative humidity and the boundary layer structure determine the intensity of air pollution within a geographic location. From samples collected, the occurrence/prevalence of black soot is heavily concentrated with 200m of the prevailing upwind direction of artisanal refinery sites (Fig. 7 and Table 2). Air pollutants are emitted at low (ground) levels or High levels. Low level emitting sources include the hundreds of artisanal refineries sited in many coastal communities in Rivers State (Fig.8: B, C and Fig. 9). Figure 7 shows that Ogu/Bolo LGA is a major centre of artisanal refineries. The smokes/soot from these area travels from the coastal area into the inland of Onne, Port Harcourt and Obio/Akpor carried by the prevailing up winds. According to Giadom, (2018), there are about 217 artisanal refineries within coastal communities South of Port Harcourt whose distillation of crude oil produces a lot of smoke and particulate matter into the atmosphere (Fig 8B). Other sources may include, the destruction by security forces of the artisanal refinery sites (Fig 10), vehicular emissions, and all other combustion sources such as asphalt plants, tyre burning operations, abattoir combustion of animal hides and skin, etc. which situate at or close to ground level (0-10m). While High level emitters include numerous gas flare stacks from International Oil Companies (IOCs). The observation drawn from this research on the sources of black soot agrees with the works of Ede and Edokpa, (2017).

Model of the dispersion of air pollutants in Port Harcourt Metropolis (Comprising Port Harcourt, Obio/Akpor, Ikwerre, Okrika and Eleme) reveal the sources of the emissions to be located in localities south of Bodo, Bolo, Bakana, Isaka and Buguma; with a trajectory oriented South West- North East over the city of Port Harcourt (Ede & Edokpa, 2017). The authors further argue that the spatial extent of the black soot envelop was between 200-230 Km^2; thus every receptor within the Port Harcourt metropolis was at high risk. From this work by Ede and Edokpa, the artisanal refineries from Bodo West and Bolo are responsible for the back soot prevalence in Bolo, Onne and Okrika while that of Rumuelumeni is contributed by the artisanal refineries in Isaka, Bakana and Buguma. The pollutant load observed in the city is higher during the night (post-midnight) than the day time hours. This is due to radiation inversion created by night time radiation of heat energy from the earth's surface; air closest to the surface cools faster than overlying layers, effectively trapping this cold parcel of air and also the pollutant load. Furthermore, most artisanal refining activities happen at night, sea breezes transport the aerosols from their coastal locations into the Port Harcourt city.

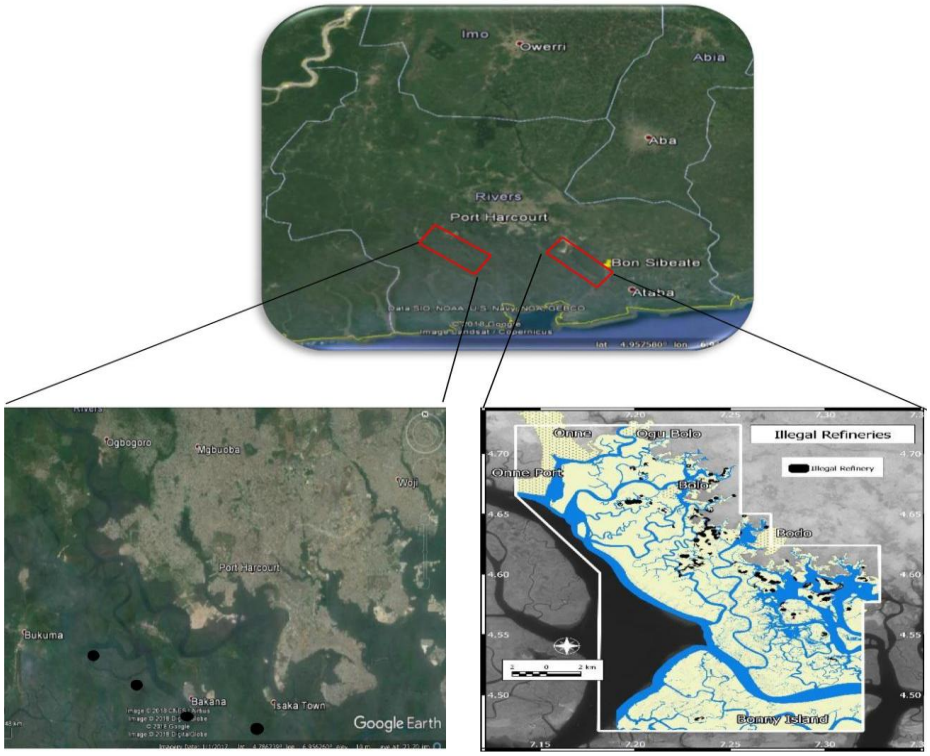


Figure 7 *Imagery shows artisanal refinery corridors (black dots) south of Port Harcourt, North of the Bonny River. Source: (NOSDRA, & UNEP Ogoni Report)*

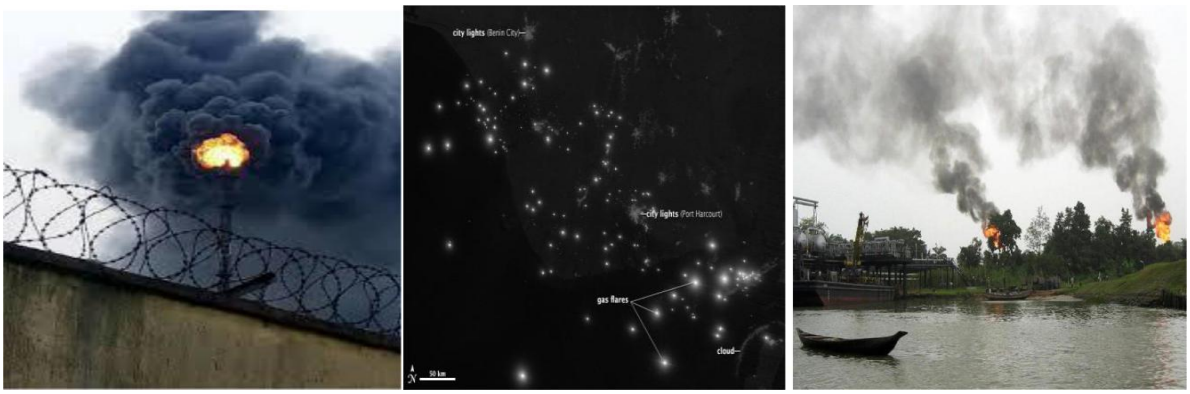


Figure 8 (a, b & c) *Show Gas flare in the Niger Delta and NASA Satellite Imagery of the Delta at night showing gas flares. Source: Curse of the Black Gold: 50 Years of Oil in the Niger Delta*



Fig 9 Artisanal *Refinery (Source: Stakeholder Democracy Network, SD*



Figure 10 *Combustion Sources (Artisanal Refineries) of Black Soot*



Figure 11 *Artisanal Refinery Boat set ablaze by the Nigerian Military fighting illegal bunkering add to the black soot concentration in the Atmosphere*

Spatio-Temporal Distribution of the black Soot

The particulate matter concentration of black soot over the study area shows that Suspended Particle Matters (SPM) ranges from 16.6 – 360ug/m^3, 62-270ug/m^3 and 0.035 – 180ug/m^3 exceeding the national limits of 40 -60ug/m3 and WHO limits of 10 -25ug/m^3. And the SPM from laboratory analyses reveal them to be of petroleum combustion origin.

Air Visuals is a famous app used to detect the state of the air at any location in the world. When used to detect that of Port Harcourt city, it returned a rather negative result stating that the city has an Air Quality Index of 190 (AQI), is unsafe and contaminated with $PM_{2.5}$, a deadly pollutant capable of causing cancer, respiratory illnesses and can lead to premature death. The air in a city is rated safe when it has an Air Quality Index between 0 to 50, rated moderate when it has an AQI between 51 to 100, rated unhealthy for sensitive groups when it has an AQI of between 101 to 150, rated unhealthy when its AQI stands between 151 to 200, very unhealthy when it stands between 201 to 300 and declared hazardous when it is above 300. Port Harcourt has an AQI of 190 (Table 2) meaning it is unhealthy to live in.

Air Quality Index (AQI) (Air Visual App) report (Table 2) shows that Concentration of soot is 4:00am to 11am in the morning. From observation during the study, artisanal Refining starts about 12:00am, you will know by the thick flames that go up at the areas known for the refining. It was also observed that soot begin to collect from 2:00am and float onshore as from 4:00am up until about 11am. This is due to radiation inversion created by night time radiation of heat energy from the earth's surface; air closest to the surface cools faster than overlying layers, effectively trapping this cold parcel of air and also the pollutant load and the sea breeze transports the aerosols from their coastal locations into the Port Harcourt City and environs.

Burning fossil fuels release gases and chemicals into the air in an especially destructive feedback loop. Air pollution not only contributes to climate change but is also exacerbated by it. The introduction of carbon dioxide and other greenhouse gases which are by-products of combustion raises the earth's temperature or rather increases heat. This increasing warmer weather facilitates smog formation due to atmospheric chain reactions in the presence of more ultraviolet radiation. The soot hung around the city of Port Harcourt because of temperature inversion and meteorological factors that either brought from offshore to onshore or hindered their dispersal. Temperature inversion prevents the ascent of hot, polluted air and the descent of fresh, clean air. As were noted in the Great London of 1952 and Los Angeles smog. It therefore seems to have been caused by the standstill, created by the clash between the South-east trade wind, from the Atlantic Ocean that bring the rainy season, and The north -west trade wind from the Sahara desert that brings dry season

Meteorology and Dispersion of Air Pollutants

Meteorological factors such as temperature, humidity, rainfall, wind speed, solar radiation, turbulence and stability are critical in the dispersion and persistence of particulate matter and other gaseous air pollutants. Stability conditions in the atmosphere determine the rate of dispersion of air pollutants. When there are temperature inversions, aerosols form a ceiling as vertical mixing within the boundary layer is limited; wind speeds are reduced and the concentration of particulate matter steadily accumulates. Under these conditions photochemical reactions lead to the formation haze. The occurrence of Haze indicates widespread, long duration, severe and rapid accumulation of high concentration pollutants in the atmosphere (Li *et al*., 2022). Haze pollution has been essentially attributed to pollutants in

the lower atmosphere and the favourable meteorological condition at the time of the emissions (Gorai, *et al*., 2015).

Haze is an atmospheric phenomenon in which dust, smoke and other dry particulates obscure the clarity of the sky. Ground level ozone and particulate load in the atmosphere undergoes complex photochemical reactions in the presence of volatile organic compounds (VOC), sulphur dioxide (SO2) and oxides of nitrogen (NO_X) to form the horizontal obscuration of smog and haze. It is relatively common during temperature inversions when there is rising temperature with height, and wind is calm. The ground level ozone present during these episodes of air pollution inhibits plant growth and poses respiratory hazards to man and animals. This was an everyday experience during the 2016/2017/2018 dry season soot pollution in Port Harcourt.



Figure 12 *Ground level haze and smog within Port Harcourt Metropolis during the soot invasion*

Winds are the most important factor in the dispersion of air pollutants. However, Urban Heat Islands created in the city due to radiation from concrete bricks, buildings, pavements and other anthropogenic sources sets up self-contained circulatory patterns; forming a haze-hood from which pollutants cannot escape. This results in the pall of aerosols that covered the skies of Port Harcourt metropolis

The Atmospheric Boundary Layer (ABL) expands to about 1000m during the day and contracts to about 400m during the night over land. This explains the higher concentration of pollutants over the Port Harcourt metropolis during the night (Ede & Edokpa, 2017). As the day breaks and the heat flux created by solar radiation builds, convective energies generate the required turbulence that disperses the accumulated pollutants by afternoon to early evenings. Furthermore, the maritime air masses that are prevalent over the city engender a moist atmosphere for most parts of the year. Water vapour within the atmosphere provides the envelope that houses air pollutants. It is within this parcel, that other atmospheric reactions taking place give rise to secondary pollutants such as the formation of ground level ozone and other acid wet and dry deposition compounds of sulphur and nitrogen.

The occurrence of black soot during the dry season was observed to be determined by dynamics of wind flow within the troposphere. The convergence of the continental and maritime air masses over the region in December/March induces a ‘doldrum-like’

phenomenon, which does not enhance mixing and dispersion of particulates emanating from various combustion sources within the region (Fig 4.5).

Rainfall and other forms of precipitation scavenge particulate matter and other forms of air pollutants from the atmosphere. However, observed meteorological data shown in figs 3.4 and fig 4.6 above reveal the lowest amount of rainfall and the lowest number of rain days in 2016 (the lowest since 2010), which began from the start of the dry season in November, 2015. This explains the over accumulation of particulate matter in the atmosphere leading to the very high concentrations of the black soot in December 2016 to April 2017. The rainy season in 2017 had relatively more rain days and amount compared to 2016. This explains the lesser amount of 'black soot' experienced during the dry season of 2017-2018.

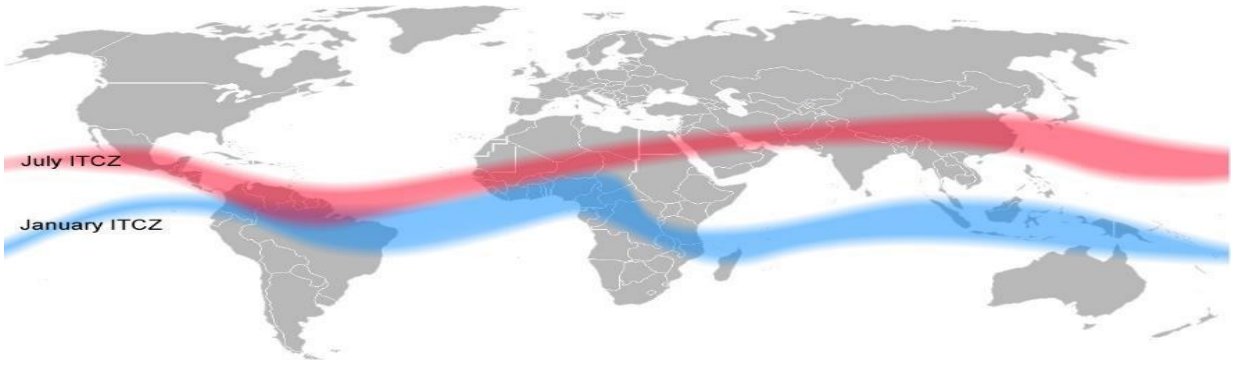


Figure 13 *Inter-Tropical Convergence Zone and the control of air masses/aerosol movement.*

Black Soot Impact on Soil and Environment

The pH of the soil is a significant parameter that directly impacts mineral mobility. The soil pH of the sampling sites varied on the average from 5.2 to 7.2 (Table 10). Soils are measured acidic if the pH measured in water is less than 7 and strongly acid if the pH is less than 5, both measured in water. Based on the test results the pH of the soil ranges from slightly acidic to a little over neutral.

In the soil samples collected the ranges of the heavy metals tested as follows; Fe 0.003-4.40; Zn 0.008-5.03; Cr 0.006-2.470;Cu 0.064 – 5.0; Cd 0.84 – 4.83; Ni 0.008 – 6.64; Pb 1.11-8.31; Mn – 18.50. Gas flares and other combustion sources release greenhouse gases of carbon dioxide (CO_2) methane (NH_4) and nitrous oxide (N_2O) which contribute significantly to global warming. Furthermore, the high concentration of volatile oxides of carbon, nitrogen and sulphur released into the air mix with rain water to form acid rain and ultimately increases the acidity of the soils which is deleterious to crops.

Heavy metals contaminated soils are generally nutrient deficient and are likely to become unproductive in future. The soil chemistry distinguishes heavy metals as a distinct group of elements because of their toxic effect exercised on plants upon their high concentrations. However, there is no shared opinion on the risk of any particular heavy metal in soils.

The Implications of Black Soot on health

Air pollution has both acute and chronic effects on human health, affecting a number of different systems and organs. The health hazards range from minor upper respiratory irritation to chronic respiratory and heart disease, lung cancer, acute respiratory infections in children and chronic bronchitis in adults, aggravating pre-existing heart and lung disease, or asthmatic attacks. Short and long term exposures have been linked with premature mortality and reduced life expectancy. Air pollutants have been identified as causes of increasing mortality or serious illness. They pose a present and/or potential hazard to human health; based on clinical, epidemiological, and/or animal studies which demonstrate that exposures to these pollutants are associated with health effects (Kampa and Castanas, 2008).

Particulate Matter is a general term used to describe solid particles and liquid droplets found in air. The composition and size of these airborne particles and droplets vary. Some particles are large enough to be seen as dust or dirt, while others can only be seen using powerful microscopes. Two size ranges (PM_{10} and $PM_{2.5}$) are widely monitored; and behave differently in the atmosphere. $PM_{2.5}$ and submicron particles remain airborne for long periods and can travel hundreds of kilometers, while the PM_{10} and coarser particles have shorter residence times within the atmosphere, they are not readily transported for long distances; and so are deposited close to their sources.

Particulate matter load ($PM_{2.5}$ and PM_{10}) - The ultra-fine and submicron particulates (<1μm) are particularly more toxic than the coarse grade particles (>10 μm). They are capable of penetrating the alveoli and enter into circulatory system where they may be deposited in the heart and other organs and systems of the body; while the coarser particulates are deposited in the upper respiratory tract. The submicron particulates often exist in association with heavy metal colloids, PAHs and other organic components due to their very large surface area. Once they enter into the circulatory system, they form endotoxins which express particulate matter toxicity. Air pollutants are of varying composition; the dose and duration of exposure to these toxins lead to diverse impacts on human health.

Submicron and ultra-fine particulates can also find their way into the human system through ingestion. They are invisible to the human eye, and thus get deposited on exposed food materials and are ingested with food and water. Sporadic air pollution events, like the soot phenomenon contributes to increased mortality and clinical visits and admissions. Epidemiological and animal studies indicate that besides the primarily affected cardiovascular and respiratory systems; acute and chronic exposures to these cocktails of air pollutants can indicate as nausea, difficulty in breathing, skin irritation, birth defects, serious developmental delays in children, reduced activity of the immune system, leading to a number of other diseases (Cohen *et al*., 2005; Huang and Ghio, 2006; Sharma and Agrawal, 2005). The concern with the respirable submicron particulate matter is that they have longer residence times in the atmosphere, can penetrate tiny spaces and are carried to longer distances, several tens to hundreds of kilometres. These are the real dangers, and no one is spared.

Health concerns arise due to the potentially high concentrations of inhalable and respirable particles and toxic gases from the combustion of petroleum hydrocarbons. PAHs are carcinogenic. Another potentially deleterious effect of the combustion of petroleum hydrocarbons is the reduction in atmospheric visibility. Poisonous chemicals associated with combustion of petroleum hydrocarbon include nitrogen dioxide (NO_2), sulphur dioxide (SO_2),

volatile organic compounds (VOC) like benzene, toluene, xylene and hydrogen sulphide. Others are carcinogens like benzo (a) pyrene. These chemicals intensify asthma, cause chronic bronchitis and pain. Benzene is well known as a cause of leukaemia and other diseases of the blood system.

There have been reported cases of cardiovascular related illnesses in the three local government areas where this study was conducted. This is apart from the many cases of physical burns and scars suffered as a result of explosion at the refinery sites.

Summary

This study was undertaken as a result public outcry over the appearances of strange black dusty deposit noticeably seen on cars, clothes on lines and rooftops after hours of smog in Port Harcourt and environs raising veil anxieties about the resulting health impacts. It involved the proximate analyses of black soot samples collected in parts of Rivers State namely (Bolo Town in Ogu/Bolo LGA, Onne in Eleme LGA and Rumuolumeni in Obio/Akpor LGA). The aim of the study was to examine the impact of soot on selected communities in Rivers State. The objectives included the determination of the composition/characteristics of the soot and their spatial variations in the three Local Government Areas of Rivers State where the soot samples were collected. The soot samples were analyzed in the laboratory using acid digestion followed by an Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES Varian 725-ES). Meteorological parameters were also examined to know which has strong influence in the spatio-temporal distribution of the soot across the State.

Results indicated that the soot are a product of incomplete combustion and are composed in elevated concentration (compared to WHO/EPA Allowable limits) of the following heavy metals lead (Pb) 164.924mg/kg, Cadmium (Cd) 2.30mg/kg, Nickle (Ni) 0.147mg/kg, Copper (Cu) 0.67mg/kg, Zinc (Zn) 0.05mg/kg, Mercury (Hg) 0.05mg/kg, cobalt (Co) 0.47mg/kg . They are also composed of Polycyclic Aromatic Hydrocarbon (PAHs) and Total Petroleum Hydrocarbon (TPH). For Bolo in Ogu/Bolo LGA PAH ranged between 88-189ng/m3, TPH ranged between 18.8 – 94.2mg/kg; Onne in Eleme LGA PAH ranged 50-190ng/m3 and TPH 16.0 – 88mg/kg, Rumuolumeni in Obio/Akpor LGA PAH ranged between 44 – 190ng/m3, TPH 16.2 – 96.0mg/kg. The soot is between $PM_{2.5}$ and PM_{10} in size.

Meteorological factors such as temperature, humidity, rainfall, wind speed, solar radiation, turbulence and stability are critical in the dispersion and persistence of particulate matter and other gaseous air pollutants. Stability conditions in the atmosphere determine the rate of dispersion of air pollutants. When there is temperature inversions, aerosols form a ceiling as vertical mixing within the boundary layer is limited; wind speeds are reduced and the concentration of particulate matter steadily accumulates. Under these conditions, photochemical reactions lead to the formation of haze. The occurrence of Haze indicates widespread, long duration, severe and rapid accumulation of high concentration pollutants in the atmosphere. Haze pollution has been essentially attributed to pollutants in the lower atmosphere and the favorable meteorological condition at the time of the emissions.

Winds are the most important factor in the dispersion of air pollutants. However, Urban Heat Islands created in the city due to radiation from concrete bricks, buildings, pavements and other anthropogenic sources sets up self-contained circulatory patterns; forming a haze-hood

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Conclusion

The study in conclusion observed the possible environmental and health challenges associated with the soot which includes:

i. Ecological damage to plants (crops) through deposition of oxides of carbon, nitrogen, sulphur and volatile organic compounds in the aerosols on plant leaves, acidification of soils and water bodies. This will ultimately lead to poor crop/fruit yields, fish catches, dwindling agricultural productivity and livelihoods.
ii. Increased Health Hazards expressed as heightened respiratory diseases especially in children and the elderly, and the risk of developing mutations, carcinogenesis in the long term and teratogenic possibilities in developing foetuses, as a result of constant inhalation of these carbonised aerosols
iii. Rapid deterioration of amenities such as car chassis, roofing sheets and other metallic and non-metallic materials
iv. Increased cost of house care as constant cleaning and washing of household ware is required and
v. Reduction in the Aesthetic value of our surroundings, due to the deposition of the black soot on all surfaces.

Recommendations

Having identified activities of artisanal refining as the major cause of the presence of black soot, it is hereby recommended that all forms of illegal and artisanal refinery should be stopped forthwith. It is further recommended that:

i. Windows should be closed as early 7pm and remain shut until about 11:30am.
ii. Members of the public are further advised that they should regularly clean their air conditioner vents, dust their window nets regularly and while doing so should wear face masks
iii. People should avoid spreading their clothes on the lines before 11:00am and should ensure that their clothes are removed (whether wet or dry) once it is getting towards evening and when it is raining
iv. The State and Federal Government in conjunction with the community where these artisanal refineries are sited work in synergy to stop effectively stop this illegal oil bunkering and artisanal refining.

v. Government can establish modular refineries where the Communities and State Government will be joint ventures. The boys should be employed and trained and put to run and manage these modular refineries and

vi. Finally, Military personnel deployed to stop the artisanal refining activities should instead of burning boats and other equipment used devised other means of effectively carrying out their assignments. For example, they could seize the products and transport same to the Government refineries for proper refining and sell them off

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