



Particulate Geochemistry of air in some areas of Port Harcourt Metropolis

*S. Abrakasa^{1,2}

¹Geology Department, University of Port Harcourt, Nigeria

²Centre for Petroleum Geosciences, University of Port Harcourt, Nigeria

*sabrakasa@hotmail.com

Abstract A preliminary study of the particulate geochemistry of air in some parts of Port Harcourt was undertaken. PM_{2.5} were sampled and samples were analyzed for PAHs, trace metals and water soluble ions using GC-MS, and Atomic Absorption Spectrophotometer. The results indicated the present of high amount Benzo(a)pyrene amongst benzo[b]-fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP). Ni was in high amounts relative to Pb and Fe and sodium and chloride were also in high amounts relative to calcium and potassium. The total PM_{2.5} concentrations was 62 µg/m³ at Odili Way and 124 µg/m³ at Abuloma compared to WHO threshold of 10 µg/m³ for annual mean and 25 µg/m³ for 24-hour mean, it implies pervasive pollution, the Benzo(a)pyrene which a marker for air quality standard ranges between 190ng/m³ to 170ng/m³ for both sample stations relative 1ng/m³ ascribed by WHO. It also indicates pervasive pollution, while the present of Ni indicates combustion activities related to Oil refineries, petrochemicals, and artisan refineries, the presence of sodium and chloride indicates activities that are carried out in riverine or coastal environment.

Keywords particulate matter, geochemistry, air quality, PM_{2.5}

Introduction

Particulate geochemistry is an emerging science, it is an aspect of medical geology or medial geochemistry, it entails the study of air borne particulate matter in the atmosphere, their origin (natural or anthropogenic) nature (solid or liquid), compositional distribution and their health implication as part of the air inhale by humans.

Air borne particulate matter (PM) is a complex mixture of solid and liquid particles, it is composed of a wide range of organic and inorganic components. Particulate matter is variable in size and composition and are function of events such as forest fires, dust storms, traffic and present and operation of various industries. Other sources of particulate matter are

- i) Dusts generated by the natural weathering of rocks, and dusts generated by anthropogenic activities such as mining, industrial processes i.e. cement manufacturing, flour milling, and stone crushing construction i.e. dusts released by building collapse or demolition [1].
- ii) Volcanic ash and gases.
- iii) Soils and dusts containing heavy metals, organic contaminants, or pathogens.
- iv) Solid, gaseous, and aqueous wastes or byproducts of mining, mineral processing, smelting, and energy production i.e. flyash [1].
- v) Result of combustion processes, including the burning of fossil fuels for steam generation, heating, household cooking, agricultural field burning, diesel fueled engine combustion, and various industrial processes. Emissions from these anthropogenic sources tend to be in fine fractions [2].

Classically, particulate matter is defined according to its size, e.g. PM₁₀, PM_{2.5}, which refers to particulate matter of 10µm or 2.5 µm diameter, this is due to the fact that air quality policy and emission regulations are typically



based upon mass of different size fractions. Also the diameter of the PMs determines their residence time in the atmosphere, migration distance and health implications.

The particulate matter of 10 μ m are inhalable and may reach the upper part of the airways and lungs however, those of 2.5 μ m deeply penetrate the lungs and perhaps reach the alveoli, those of 0.1 μ m diameter can pass from the lungs directly into the blood streams.

Historical Perspective

Earlier concerns for air quality was foremost expressed by the inhabitants of Athens and Rome at about 150BCE – 4BCE, because they observed that emissions from smelting furnaces, potteries and other preindustrial workshops darkened the skies [3]. In the mid of the 18th century, there were observations of Sahara dust falls in Western Europe. Following the “dust bowl years” of the 1930s, awareness of soil-derived atmospheric dusts increased considerably in the United States, particularly after 1945 [2]. At about 1945, the pollution threats that were salient became very obvious such as photochemical smog, ozone depletion and certain indicator of globalization such as climate change. In the mid 1950s, the industrial revolution that swept across Europe, brought about the age of smoke, because of the widespread use of coal fired electrical plants especially in London for domestic as well as industrially energy use, manufacturing cities such as Birmingham, Leeds, Manchester, Chicago, Pittsburgh and Germany’s Ruhrgebiet were highly and negatively impacted, this marked the spread of coal-fired industrialization [3]. The concept of ‘social-cost balancing’ allowed a pragmatic trade-off of polluted air in return for economies success, employment and consumer good. This was weighing cost of imposing sanctions on the polluter against the benefits of abating pollution. The London’s Great Smog of December of 1952 resulted in the death of 12,000 persons and lead to the introduction of stringent legislation to control air pollution in Britain. The Clean Air Act of 1956 was established to regulate domestic and industrial smoke emission [3]. Various news items had been read on air pollution including that of BBC on 4th of March, 2017 which was captioned

“Nigeria’s Port Harcourt covered in mystery cloud of soot” this could be considered as an immediate cause for this study. The driver of this study is the quest from the Government and concerned individuals for studies to unravel the source for the cloud of soot the pestered the citizenry of the state.

Aim and Objectives of the Study

The aim of the study is to delineate the particles observed, quantify them and based on the empirical data generated provide information on potential health risk and make suggestions on risk management

The objectives include (i) quantify potential trace metals in the soot, (ii) determine the water soluble inorganic ions, (iii) carry out analysis on particulate PAHs in the soot.

Hypothesis of the Study

Particulate matter is classified into suspended particulate matter (SPMs) and Respirable suspended particulate matter (RSPMs). The RSPMs consist of the PM₁₀ and PM_{2.5} both are inhalable, however the PM₁₀ reaches the exterior airways and the lungs, while the PM_{2.5} which are the thoracic particles reaches the lower lungs, the alveoli and can pass from the lungs into the blood stream directly, it has been observed that the decreasing human life span has been stated to bear some relationship with increasing environmental dangers [4].

Sample and Sampling Method

Samples employed in this study are basically soot the PM_{2.5}, soot in this context is not limited to carbon sourced from incomplete combustion, but entails all particles that consist air at the time and place of sampling. Samples were obtained with the aid of a MiniVol portable air sampler manufactured by Airmetrics. Basically, a programmable air-pump attached to a timer is used, air is suctioned into a vacuum which is filtered via Whatman high quality quartz micro fibre filters (47mm diameter) to constraint particulates of the size of interest, particulate matter is collected on filter paper and stored in a desiccator. Global positioning system (GPSmap 76) Garmin receiver instrument was used to obtain sample coordinates. Sampling stations were in Abuloma and environs.



Sample Treatment

Samples for trace metals analysis and other water soluble ions were treated by ultrasonication in 20mL of distilled and deionized water at room temperature (25°C) for 30mins. The extract was made up to 100mL and aspirated into the AAS (Atomic Absorption Spectrophotometer) for the determination of Ni, Pb and Fe.

Samples for PAH analysis were treated with 10mL dichloromethane (DCM) and agitated for 1Hr. The extract was concentrated to 1mL for injection into the GC-MS for analysis of some PAHs. The PAHs of interest are naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]-fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3,cd]pyrene (Ind).

GC-MS Analysis

GC-MS analysis of the PAHs was performed for monitoring fragment ions of some biomarker compounds on a Hewlett-Packard 5890 II GC with a split/splitless injector (280 °C linked to a Hewlett-Packard 5972MSD with electron voltage of 70eV, filament current of 220µA, source temperature of 160°C a multiplier voltage 1600V and interface temperature 300 °C. the acquisition was controlled by HP Vectra 48 PC chemstation computer both in full scan mode and selected ion mode (30ions, 0.7cps 35ms dwell) for greater sensitivity. Separation was performed on a fused silica capillary column (30m X 0.25 mm.i.d.) coated with 0.25µm, 5% phenyl methyl silicone (HP-5), which is supplied by HP which is currently known is Agilent, UK. Calibrated UV visible spectrometer was used for used for analysis of anions.

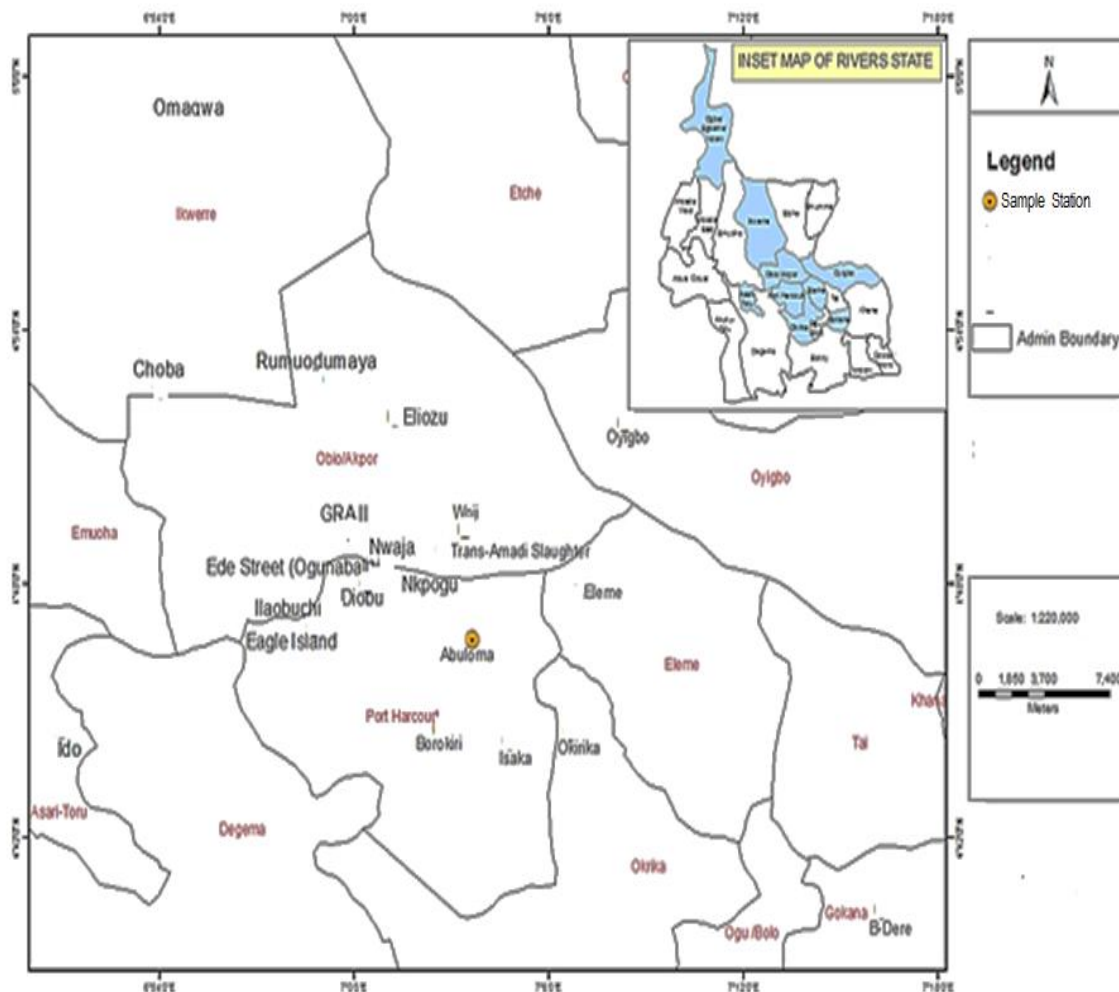


Figure 1: Sampling location with the Port Harcourt Metropolis



Results

Table 1: Result of Analysis of PM_{2.5} Samples

FIELD ID	Odili Way (ng/m ³)	Abuloma (ng/m ³)
Anions		
Sulphate	0.036	0.012
Nitrate	0.015	0.010
Chloride	0.879	2.139
Cations	0	0
Sodium	0.358	0.854
Calcium	0.196	0.213
Potassium	0.000	0.001
Magnesium	0.018	0.053
PAH, mg/kg	0	0
Naphthalene	1.843	ND
Acenaphthylene	ND	ND
Acenaphthene	1.743	1.843
Fluorene	2.678	2.468
Anthracene	2.040	1.641
Phenanthrene	1.957	1.574
Fluoranthene	ND	3.312
Pyrene	1.444	3.355
Benzo (a) anthracene	ND	ND
Chrysene	ND	ND
Benzo (b) fluoranthene	115.26	183.77
Benzo (k) fluoranthene	101.80	106.18
Benzo (a) pyrene	195.30	165.79
Dibenz(a,h)anthracene	ND	ND
Indeno(1,2,3-cd)pyrene	ND	39.16
Benzo (g,h,i) perylene	ND	ND
Total	424.08	509.14
HEAVY METALS, mg/kg	0	0
Iron	0.0001	0.0001
Chromium	0.0001	0.0001
Cobalt	0.0001	0.0001
Copper	0.0001	0.0001
Lead	0.0001	0.0002
Nickel	0.0005	0.0010

Discussion of Results

Particulate concentrations are the bases for preliminary assessment of air quality. The particulate size that impacts most on human health is the PM_{2.5} and are mostly collectively referred as soot [9]. The sampling procedure was sustained for 2Hrs at each station at the rate of 6.7 liters of air per hour, as a preliminary study. Particulate concentration was at 62 µg/m³ at Odili Way and 124 µg/m³ at Abuloma.

The concentrations of the metal and non-metallic ions such as Na which has the highest concentration ranging 0.36 ng/m³ to 0.85ng/m³, while Ca ranges from 0.20 ng/m³ to 0.23 ng/m³. Chloride has the highest concentration for the non-metallic ions and ranges from 0.9 ng/m³ to 2.2 ng/m³ while sulphate and nitrate are both one order of magnitude less relative to chloride.

The PAHs present in the soot as analyzed by GC-MS, are benzo(k)fluorantene, benzo(b)fluorantene benzo(a)pyrene, Indeno pyrene are most pronounced, and benzo(a)pyrene bears highest concentration. The lighter molecular weight PAH i.e. acenaphthylene, acenaphthene, Fluorene and Phenanthrene are much less in concentration.



Discussion of Findings

The concentration of PM_{2.5} at the sample stations were 62 µg/m³ and 124 µg/m³ at Odili Way and Aboluma respectively, though the sample were collected for less than 24 hours, considering WHO standard of PM_{2.5} at 10 µg/m³ for annual mean and 25 µg/m³ for 24-hour mean [10]. The result indicates extensive contamination, the mass concentrations of PM_{2.5} in this preliminary study are about one order of magnitude greater than the threshold values as recommended by WHO considering the two sample stations, this infers high risk to human health for long term exposure for dwellers in the environs of the sample stations. The explanation is that these particles have very high penetrative potential to lower lungs and passes directly from the lungs to the blood stream, assuming the inhalation rate of an average adult man is 15m³/day, the risk is very discernible.

The air borne potential of the PMs varies with their size (diameter), PMs of lesser diameter have the highest residence time in the atmosphere, they could be airborne for weeks, this also determine their potential for long distance travel and transport. PMs sourced from Urban and Suburban areas may precipitate and form part of the Urban and Suburban run offs for larger particulate sizes, however smaller particles may be transported to other sites.

The water soluble ion analysis indicates high concentration of Sodium, Potassium and Chloride. High chloride concentration indicate potential contribution of PMs from coastal or near coastal environments. The explanation is that turbulence of the sea and river surfaces originates droplets of sea water which vaporizes into the atmosphere and eventually adsorbs into the PMs and are transported into nearby coastal towns. The high content of chloride and sodium corresponds to sea salt sourced from sea spray.

The high concentration of nickel in the PMs infers PMs that are generated in relation to combustion or burning activities in relation to oil exploration and oil refineries [5-6], Pb is the next higher in concentration, its contribution is mostly due to vehicular emissions from exhaust fumes and car tyre abrasions.

The concentration of the PAHs in the PMs was fairly significant for Benzo (b) fluoranthene, Benzo(k) fluoranthene, and Benzo (a) pyrene. These compounds are among the group of Borneff compounds [7]. The Borneff compounds usual characterize combustion and exist as solids in the atmosphere. However, the lighter weight PAHs which are Acenaphthylene, Acenaphthene, Fluorene, Anthracene normally constitute vehicular emission and exist as gases. In recent times air quality assessment is based on Benzo(a)pyrene, which has been establish as a maker for PAHs in the atmosphere, due to its persistent contribution to carcinogenic activity. The EU (European Union) places a target value of 1ng/m³ of benzo (a) pyrene [8]. The study showed that benzo (a) pyrene concentration varies from the 190ng/m³ to 170ng/m³ for both sample stations. This result shows that the samples have benzo (a) pyrene concentrations that are two orders of magnitude higher than the accepted limit. Average inhalation rate are 15.2m³/day and 11.3m³/day for men and women respectively.

Conclusion (Implication of Findings)

The high concentration of sodium and chlorine indicates PMs that originates from riverine/coastal environment due to potential sea spray. Activities that could potentially generate PMs in coastal environment are artisan crude oil refineries and the process of preventing this practice by the JTF (Joint Task Force). Another potential activity could be the artisan asphalt industries located in coastal environment.

The high concentration of Ni compared to other trace elements indicates combustion emissions from activities that are within riverine environment such as Oil refineries, petrochemicals, artisan refineries etc. The high benzo(a) pyrene content serves as a pointer to local asphalt industries and the burning of tyres during festive periods.

Recommendations

- It is recommended that a wider scope of the study be undertaken
- A revisit on EIA and EA (Environmental Auditing) of industries activities
- Placement and implementation tougher penalties for defaulting local artisan industries
- Providing limiting designs for modular refineries to check artisan refineries
- Education of local farmers on alternative to biomass burning



References

- [1]. Wiseman, C L.S, and F Zereini. 2010. "Airborne Particulate matter: Sources composition and concentration." In *Urban Particulate Matter: Origin, Chemistry, Fate and Health Impacts*, by F Zereini and C L.S Wiseman, 1-2. Heidelberg: Springer.
- [2]. Derbyshire, E. 2005. "Natural Aerosolic Mineral Dusts and Human Health." In *Essentials of Medical Geology: Impacts of the Natural Environment on Public Health*, by O Selinus, B J Alloway, J A Centeno, R B Finkelman, R Fuge, U Lindh and P Smedley, 459-480. London: Elsevier Academic Press.
- [3]. Mosley, S. 2014. "Environmental History of Air Pollution and Protection." In *The Basic Environmental History*, by M Agnoletti and S Neri Serneri, 143-166. London: Springer International Publishing.
- [4]. Abrakasa, S, and M. C. Onojake. 2012. "Petroleum Related Environmental Pollution in Nigeria: Potential Ways for Constraints." *International Journal of Environment and Bioenergy* 53-61.
- [5]. Celo, V, and Dabek–Zlotorzynska. 2010. "Concentration of and Source origin of trace metals in PM2.5 collected at selected Canadian site within the Canadian Air Pollution Surveillance program." In *Urban Particulate Matter: Origin, Chemistry, Fate and Health Impacts*, by F Zereini and C L Wiseman. Heidelberg. : Springer.
- [6]. Tompkins, J, S Beccaceci, S L Goddard, D Hussain, I Hessey, R J Brown, P Quincey, K Whiteside, P Hughey, and S Brennan. 2015. *Annual Report for 2014 on the UK PAH Monitoring and Analysis Network. Report to the Department of Environment, Food and Rural Affairs; the Department of Environment. Northern Ireland: The Welsh Government and the Scottish Government.*
- [7]. Holland, M R, H H Jones, J Berdowski, A Bleeker, and A J Visschedijk. 2001. *Economic Evaluation of Air Quality Targets for PAHs. European Commission DG Environment., Economic Evaluation of Air Quality Targets for PAHs. European Commission DG Environment.*
- [8]. Kalaiarasan, M, R Balasubramanian, K W Cheong, and K M Tham. 2010. "Vertical Distribution of Airborne Particulate Matter in a Tropical Urban Environment: Changes in Physical and Chemical Characteristics." In *Urban Particulate Matter: Origin, Chemistry, Fate and Health Impacts.*, by F Zereini and C. L Wiseman. Heidelberg.: Springer.
- [9]. Weidman , J , and S Marshall . 2012. *Soot pollution 101; what you need to know and how you can help prevent it. . District of Columbia: Center for American Progress.*
- [10]. WHO. 2016. *WHO’s Urban Ambient Air Pollution Database–Update Public Health.*, Geneva.: Social and Environmental Determinant of Health Department.

