



HEALTH RISK ASSESSMENT OF HEAVY METALS IN AMBIENT AIR AROUND CALABAR METROPOLIS, NIGERIA

Ewona, Igwe Otaba¹ and Ibor, Iwara Edet.

¹Department of Physics, Cross River University of Technology, Nigeria

²Department of Chemistry, Cross River University of Technology, Nigeria

Corresponding Author: Ewona Igwe Otaba, +2348035802720, igweewona@gmail.com

Abstract

Airborne heavy metals are highly toxic and contribute, significantly, to various respiratory and cardiovascular disorders, we find today. Tiny particles of most trace metals which are often mined or used in manufacturing processes find their way into the air we breathe. They can be released into the air in the form of metallic fumes or suspended particulates by fuel combustion, or smelting and disposal of wastes. They are carried by aerosol particles of particulate matter such as PM_{2.5} and PM₁₀. Most of these particles find their way into vital organs of the body where they are deposited. These metals are toxic to the body and some of them possess carcinogenic properties resulting in various. The current study is focused on the characterization of particulate matter in Calabar. The suspended particulate matter, SPM in Calabar was investigated with data collected between August 2020 and February, 2021 to cover the heights of the two seasons namely: rainy and dry seasons, experienced in the area. Gravity settling method was used to collect dust samples from Calabar ambient air in 10 locations evenly distributed within the metropolis. The study found that there was heavy presence of dust especially during the dry season of the year. The air at this time appears to be hazy and foggy reducing visibility to a few meters at the height of the dry season in December and January. This is attributable to the North East Trade Winds which blow in dust particles from the Sahara Desert. The wet season also experiences some thick dust collections on open surfaces. Authors found that this could be due to the heavy quarrying activities and the location of two large cement factories located at the outskirts of the city. Metals such as Lead (Pb), Nickel (Ni), Manganese (Mn), Zinc (Zn), Copper (Cu), Iron (Fe), Chromium (Cr) and Cadmium (Cd) were identified in significant quantity in pretreated dust samples after being subjected to spectrophotometric analyses. It can be observed that though Nigeria has no regulatory measures for ambient trace metal concentration, the values of trace metals in the sample that were identified all exceeded WHO regulatory threshold values. The SPM average concentrations varied between 9.98 $\mu\text{g}/\text{m}^3$ and 19.71 $\mu\text{g}/\text{m}^3$ with a mean value of 15.379 $\mu\text{g}/\text{m}^3$ in the wet season and between 16.06 $\mu\text{g}/\text{m}^3$ and 24.69 $\mu\text{g}/\text{m}^3$ with a mean value of 19.465 $\mu\text{g}/\text{m}^3$ in the dry season. Both the dust and concentrations of trace metals in SPM demonstrate seasonal-dependence and a strong tendency to trigger cancer and non-cancer health risks in Calabar.

Keywords: Trace metals. Health analyses, Suspended particulate matter, seasonal variations

1. Introduction

Particulate matter refers to any substance except pure water that exists as liquid or solid in the atmosphere in microscopic or sub microscopic

size but larger than molecular dimensions under normal atmospheric conditions. They are often classified by their sizes, which are invariably

related to the kind of effects they create in the environment.

Particulate matter which are, generally, considered as non-gaseous represent an index of diverse classes of substances also referred to as aerosols. Most Nigerian urban cities are confronted with the challenge of especially atmospheric pollution arising from suspended particulate matter. Concerns about air pollution in urban regions are growing and is receiving increasing attention, worldwide, especially pollution by trace metals and particulate matter (Udo et al, 2018, Udo et al, 2020 and kabamba et al., 2016). On a global scale, particulate matter (PM) also influence directly or indirectly the earth's radiation energy balance and can subsequently impact on global climate change (IPCC, 2001).

A number of studies have been undertaken focusing on the characteristics of aerosols in megacities of the world including Beijing, Colombo, Oxford, Amsterdam, Athena, Jeddah, Nigeria etc. PM₁₀ particles (the fraction of particulates in air of very small size (<10 µm) are of major current concern, as they are small enough to penetrate deep into the lungs and so potentially pose significant health risk. (Guttikunda et al, 2014, Ewona, et al, 2013).

Some studies on the health problems associated with exposure to PM containing heavy or trace metals with an aerodynamic diameter of 10µM or less (PM₁₀) have been linked to both long-term and short-term effects, such as declining lung function, increased respiratory problems, chronic pulmonary diseases, heart diseases, lung cancer, damage to other organs and premature death along with a rise in mortality (Miller et al, 2007, Sharma, 2005, Wel, 2014).

Among the inorganic compounds found in the air, the most important are trace metals, which are emitted by various natural and anthropogenic sources such as crustal materials, coal and oil combustion, road dust, construction activities, motor vehicles emissions, incineration, forest fire, and industrial metallurgical process.

Industrial metallurgical process is regarded as one of the most important anthropogenic trace metal emission sources and produce the largest emissions of trace metals such as Arsenic(As), Manganese (Mn), Cobalt(Co), Cadmium (Cd), Copper (Cu), Nickel (Ni), Iron (Fe), and Zinc (Zn). Magas et al, (2007) and Mavriodis and Chalowlakou, (2010) have suggested that airborne particulate matter with elevated metal concentration may have a serious impact on human health which mostly includes respiratory disease and damage to other organs.

A variety of trace metals in particulate matter are responsible for its toxicity to the ecosystem. Though trace metals constitute less than 1% concentration in a given ecosystem, their effects are very hazardous. The European programme for monitoring and evaluation of the long-range transmission of air pollutants, (EMEP) and other research groups around the world have reported that PM₁₀ carrying heavy metals are highly toxic species of particulate matter which are very hazardous to the biosphere and the ecosystem in general. These observations are influencing the environmental legislative authorities all over the world to update and modify their air quality standards, (WHO, 2006; European commission, 2004, USEPA, 2008, Vousta et al, 1996).

Metallic trace elements released from both natural and anthropogenic sources enter the environment and follow normal biogeochemical cycles to the detriment of their host. In a given ecosystem, there are inter- relationships between trace metals in air, soil and plants.

Most trace metals in the air occur as part of the dust particles prevalent in urban atmospheric environment. This is primarily due to the large scale variety of anthropogenic activities that release huge amounts of terrestrial materials and their primary and secondary products into the air. Their origin may generally have diverse sources such as volcanic eruption, dust storm, mining activities land clearing and bush burning. Others are industrial processes which involve refining of petroleum and coal, chemical plants, smoke stacks, construction industries and automobile exhaust emission, etc.

Particulate air pollutants are a major problem to health status in developing countries due to poor maintenance culture and excessive use of fossil fuels, especially petroleum, coal, wood for energy and flaring of gas. (Abidde, 2009). For example, Lead is a metabolic poison and a neurotoxin that binds to essential enzymes and cellular components and inactivates them. Worldwide atmospheric lead emissions amount to about two million metric tons per year or two-third ($\frac{2}{3}$) of all metallic air pollution. Most of this lead is from leaded gasoline. Particulate matter of less than $2.5 \mu\text{m}$ (PM_{2.5}) is a recognized carcinogen and a priority air pollutant owing to its respirable and toxic chemical components (Morakinyo et al., 2021).

Trace metals in the air can be washed down by rain and through natural sedimentation amongst other result in water pollution. Water contaminated with trace metals could be unsuitable for human and livestock drinking, irrigation, aquatic ecosystems protection, recreation, and aquaculture.

Ten years (2010-2020), literature-based data from ambient air and surface dust were compiled and analyzed to understand contamination level of nine heavy metals (HMs), in Saudi Arabia. The results showed that the average concentrations of Cd and As in PM_{2.5} and PM₁₀ exceeded the standard limits of National Ambient Air Quality Standards (NAAQS) of Saudi Arabia, the World Health Organization (WHO), and the Europe Union (EU). Abdulaziz, et al (2022).

Street dust is an important pathway in the exposure of people to toxic elements. The ingestion of dust particulates with high concentration of potentially toxic metals, possess a potential threat to human health.

People living along highways, high traffic congested areas, production industries, and automobile workshops are usually at high risk of heavy/trace metals poisoning. Hence, this study aims at the characterization of trace metals Calabar ambient air, with a view to providing

information that will assist in environmental remediation measures in the area.

The work of Udo, et al (2020) which was carried out with the current author, on the characterization of air quality parameters in Calabar, focused more on the gaseous and particulate matter. The aim of the current study is to characterize particulate matter in the ambient air of Calabar. Specifically, the study intends to:

1. collect dust particulate and other forms of air sediments in selected locations in Calabar Metropolis.
2. determine the level of trace metals in dust particulate.
3. undertake spectral analyses of the sediments to determine its basic characteristics.

2. Methodology

The purpose of this this research work is to analyse treated ambient air sediments (samples) by using Ultra Violet Visible Spectrophotometer, which applies Beer's, Lambert's Law. The law states that the intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically.

The air samples (sediments) were collected by gravity settling method (Warner 1976), by using high density polyethylene (HDPE) containers with 10cm diameter funnel. This method involves sedimentation through the downward movement of particles resulting from gravitational attraction. Ten stations were selected for the study marked S₁ to S₁₀. Experimental details and analyses can be found in Ewona, et al. (2021).

As reported, the method used in this research work was the UV Visible Spectrophotometer. This was chosen because the instrument applies Beer-Lambert's Law. The spectrometer allows for the examination of different wavelengths (λ) present in electromagnetic radiation. In spectrophotometric analysis, a source of radiation is used that extends into the ultraviolet region of the spectrum. From this, definite wave

lengths of radiation are chosen processing a bandwidth of less than 1nm which provides for measurements at spectral range. The introduction of the Photometer in the spectrophotometer, introduces a signal that corresponds to the difference between the transmitted radiations of a reference material and the transmitted radiation of a sample at selected wave lengths.

In spectrophotometry and colorimetry, when light falls upon a homogeneous medium, a portion of the incident light is reflected, a portion is absorbed within the medium, and the rest is transmitted. The light intensities are

expressed as follows, $I_O = I_a + I_t + I_r$. where I_O is for the incident light, I_a is for the absorbed light, I_t for the transmitted light and I_r for the reflected light.

3. Results

The results of this work are presented in the form of tables and charts as shown in figure 1. Figure 1 shows a plot of the concentration of various elements present in the durst samples against each station for the wet season. It can be observed that the entire atmosphere is covered with dust as much as $20 \mu\text{g} / \text{m}^3$.

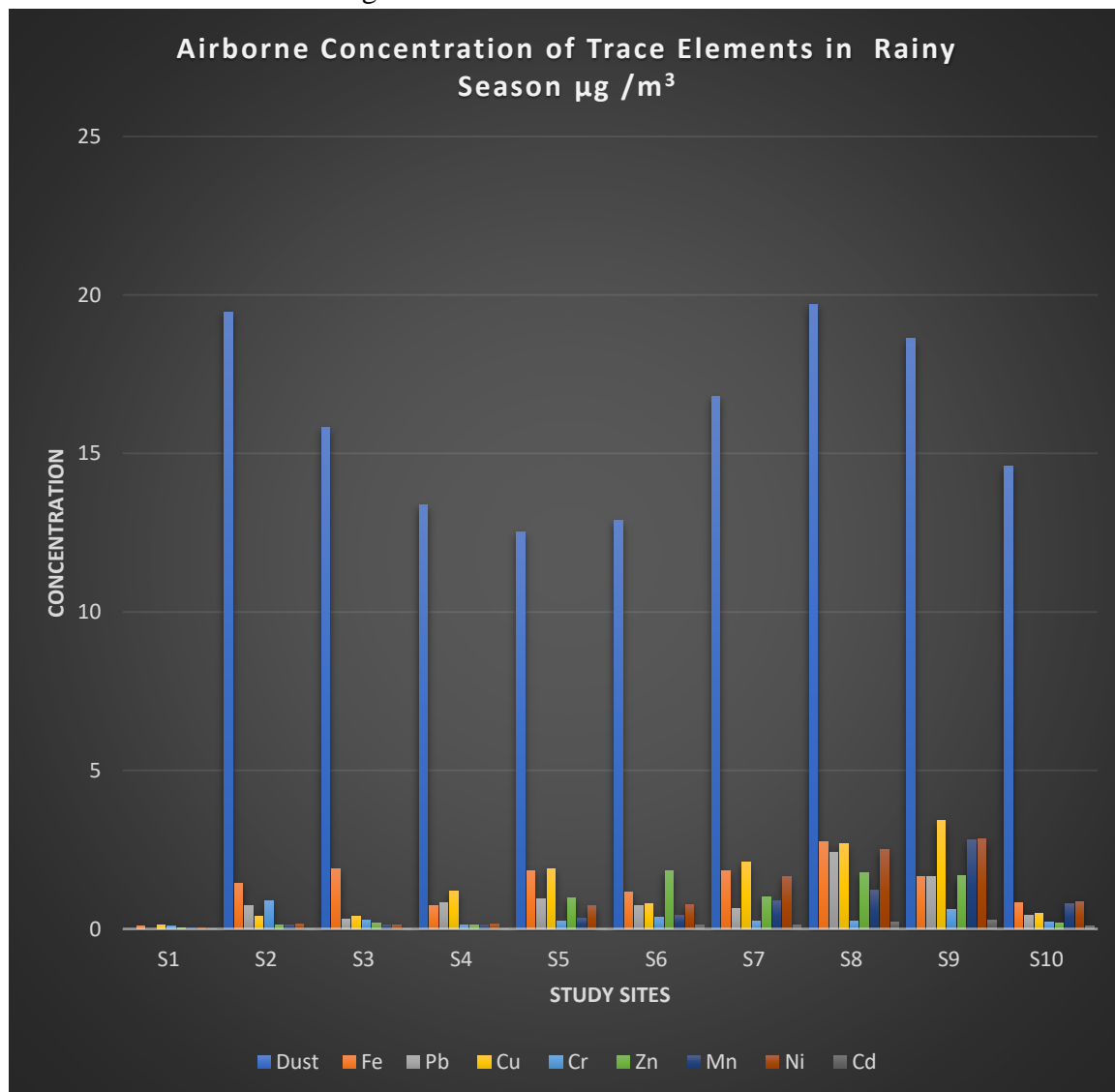


Fig. 1: Concentration of dust and trace metals in Wet Season

The figure 1. above shows concentrations are highest in site 7, 8 and 9. Sites 7,8 and 9 indicate a heavily polluted atmosphere. The authors observed that except in site 1 and 10 Iron had

concentrations above $1 \mu\text{g} / \text{m}^3$. The concentration of dust particles in the dry season is shown in figure 2.

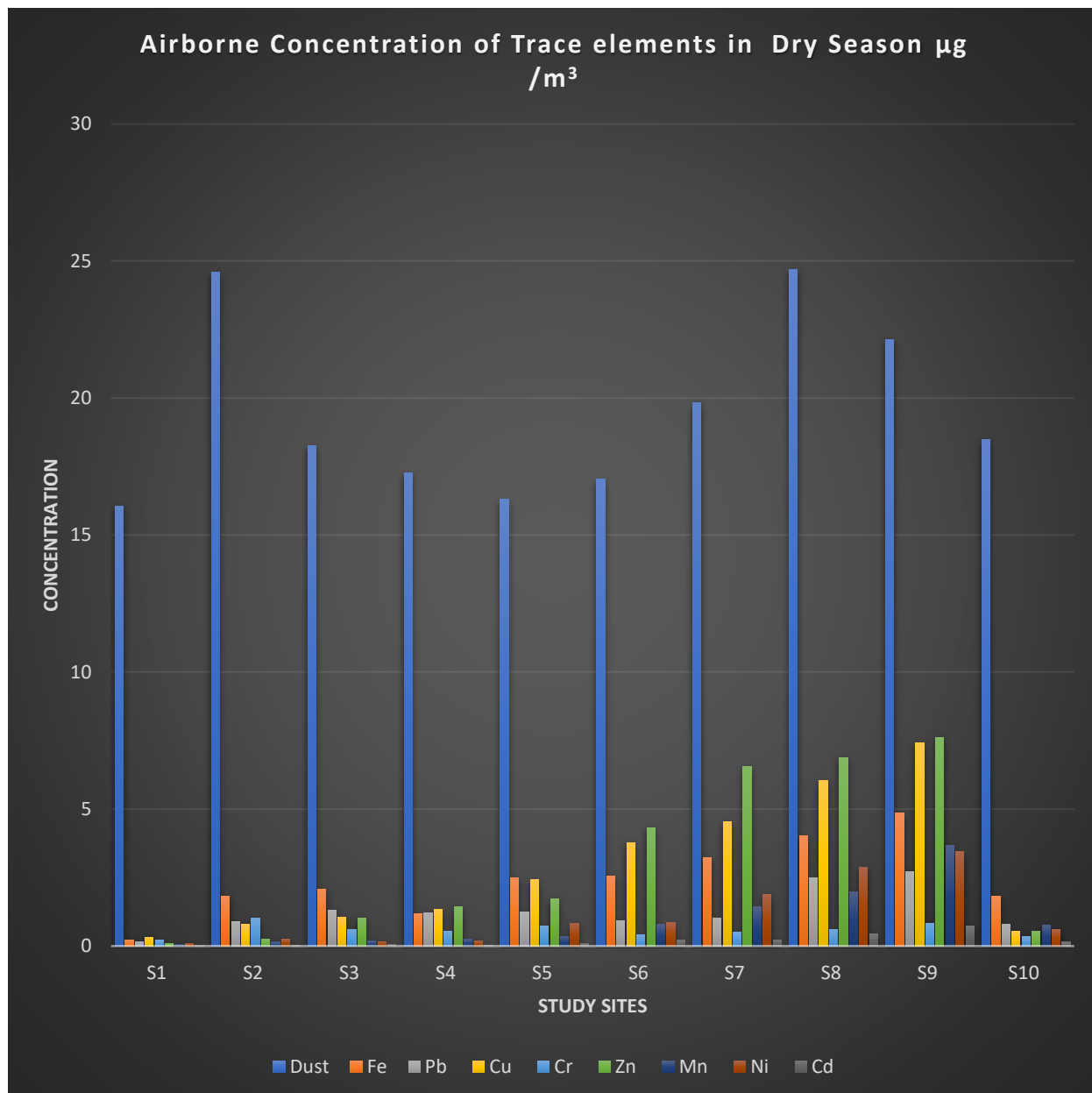


Fig. 2: Concentration of dust and trace metals in Dry Season.

Concentrations are generally higher in dry season again with values highest in sight 7, 8 and 9. Sites 7 and 8 represents the two major market sites in Calabar while site 9 represents Port Complex located near the Nigeria Export processing zone where a lot of metal works and manufacturing is going on.

Table 1 compares concentration values with WHO regulatory standard to see the health implication of the ambient air in Calabar metropolis, in terms of trace metals.

Table 1: Shows Threshold limit values (TLVs) for heavy metals in the air.

Table 1: Trace metal concentration (µg/m³) against WHO regulatory standard

METALS	WET	DRY	MEAN	WHO	NIS(mg/l)
Fe	1.419	2.432	1.925	1.00	2.00
Pb	0.877	1.274	1.075	0.05	0.01
Cu	1.349	2.824	2.087	1.00	1.00

Cr	0.330	0.585	0.457	0.05	0.05
Zn	0.792	3.045	1.919	1.00	5.00
Mn	0.690	0.962	0.826	0.05	0.05
Ni	0.979	1.115	1.047	0.02	0.02
Cd	0.090	0.195	0.142	0.10	0.01

WHO AQGS (2005)

It is clear from table 1 that the ambient air in Calabar poses serious health hazard to inhabitants of the city as average values of all trace metals exceed WHO regulatory limits in all the sites selected for the study. Figures 3, 4 and 5 show minimum concentration of trace metals in all 10 stations. Apart from dust

particles, all trace elements are within both Permissible Exposure Limits, PEL and Recommended Exposure Limits REL at minimum trace metal concentration. However, this is not the case at maximum mean concentration levels as shown in figure 4 and 5 respectively.

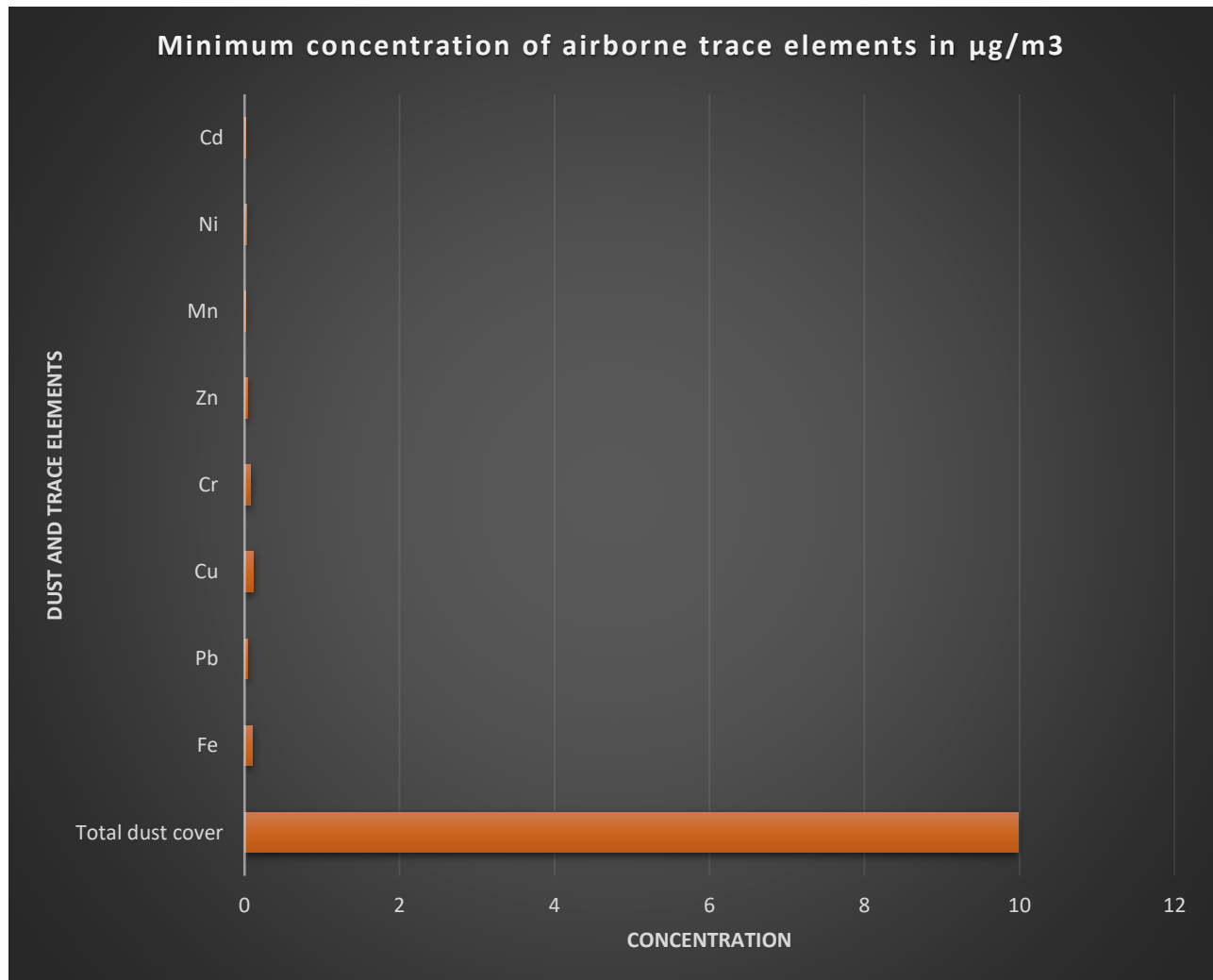


Fig. 3: Showing a bar chart of the minimum of all the parameters measured for both wet and dry season

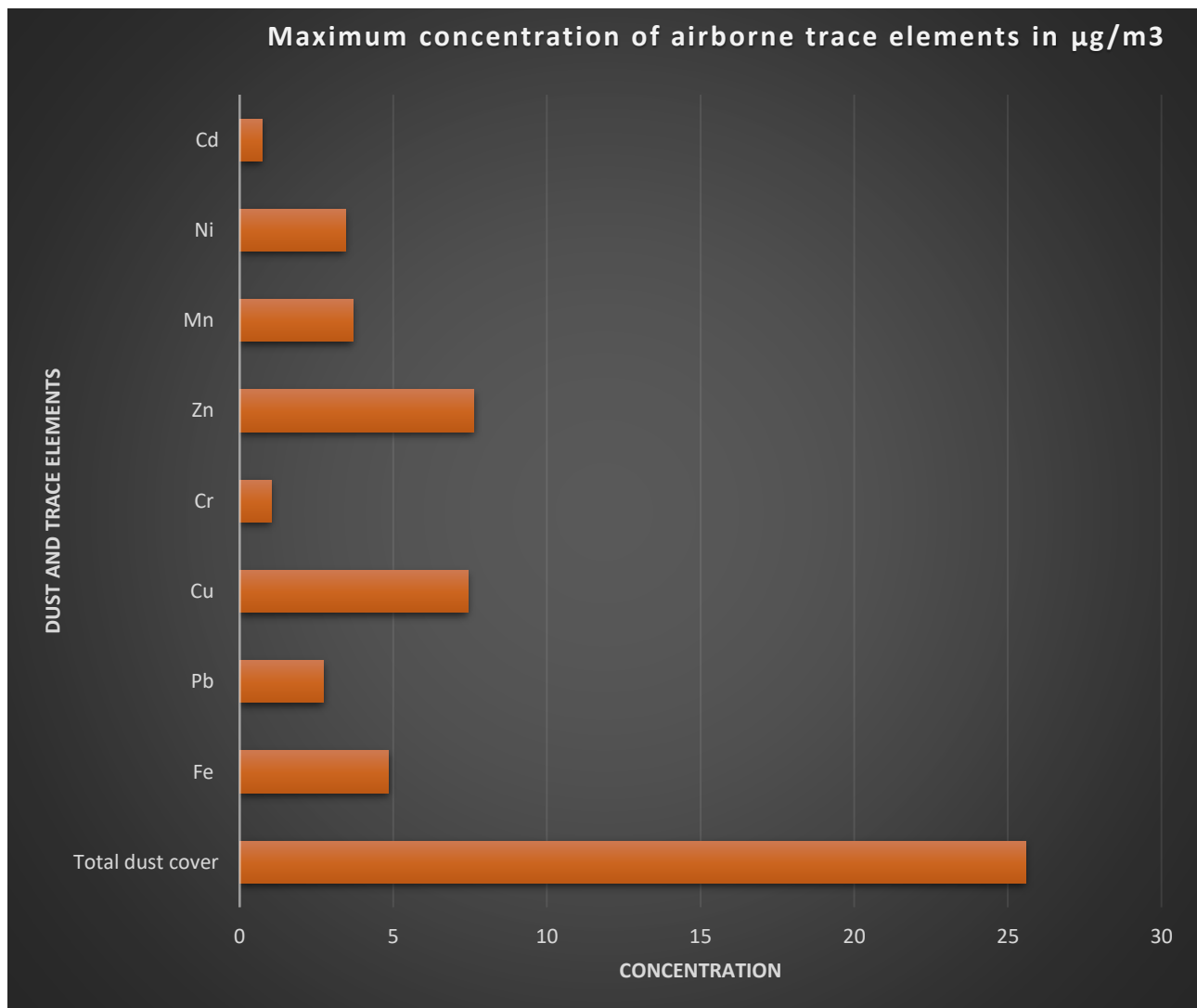


Fig. 4: Showing a bar chart of the maximum of all the parameters measured for both wet and dry season

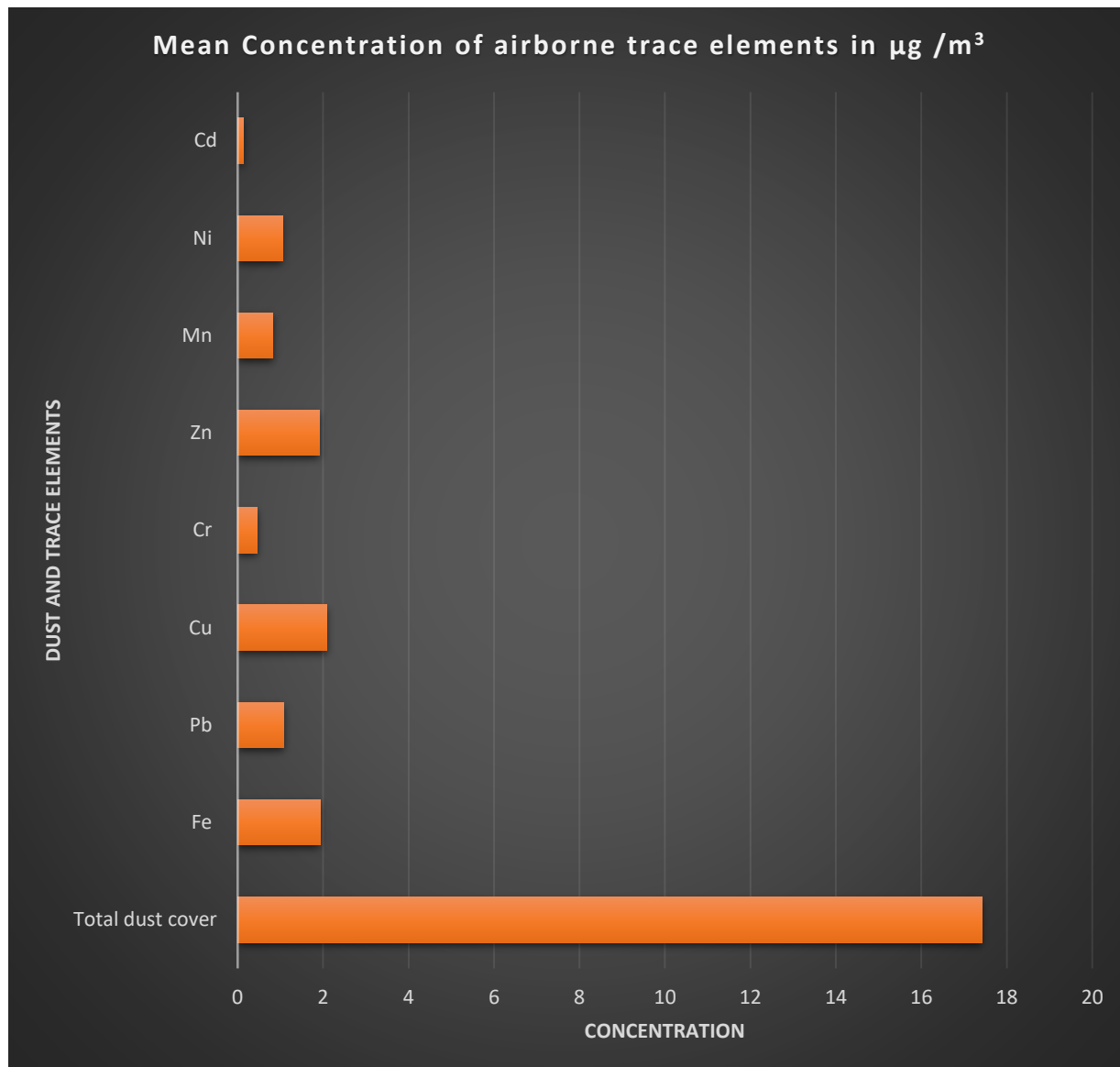


Fig. 5: Chart of mean concentration of airborne trace elements in $\mu\text{g}/\text{m}^3$

4. Conclusion

Particulate matter of aerodynamic diameter of less than $2.5 \mu\text{m}$ (PM_{2.5}) is a recognized carcinogen and a priority air pollutant owing to its respirable and toxic chemical components. This study determines the seasonal concentration of suspended particulate matter, SPM in Calabar ambient air, it can be shown that the atmosphere shows seasonal variations of trace metal concentration between the dry season and the wet season with the dry season indicating higher concentrations.

The study found that there was heavy presence of dust particles especially during the dry season of the year putting inhabitants, especially the sensitive population, at more risk during this time of the year. The air at this time appears to be hazy and foggy reducing visibility to a few

meters at the height of the dry season in December and January. This is attributable to the North East trade winds which blow dust particles from the Sahara Desert. The wet season also experiences thick dust collections on open surfaces. Authors found that this could be due to the heavy quarrying activities and the location of two large cement factories such as Dongote cement and Larfage cement companies located at the outskirts of the city.

The characterization of the dust samples reveals that they contain some carcinogenic metals such as cadmium and Nickel. The findings indicate that the concentrations of trace metals in SPM demonstrate seasonal-dependence and a strong tendency to trigger cancer and non-cancer health risks in Calabar. We note that incidences of cancer cases have been reported to be on the

increase recently. Also common are cases of respiratory infections, heart attack and deep organ failure due to trace metal poisoning. Elevated metals concentration of common trace metals of concern showed the following average values: Lead (Pb = 1.075), Nickel (Ni = 1.047), Manganese (Mn = 0.826), Zinc (Zn = 1.919), Copper (Cu = 2.087), Iron (Fe = 1.925), Chromium (Cr = 0.457) and Cadmium (Cd = 0.142).

It can be observed that though Nigeria has no regulatory measures for ambient air concentration, the values of trace metals, identified all exceed WHO regulatory threshold values. The SPM average concentrations varied between $9.98 \mu\text{g}/\text{m}^3$ and $19.71 \mu\text{g}/\text{m}^3$ with a mean value of $15.379 \mu\text{g}/\text{m}^3$ in the wet season and between $16.06 \mu\text{g}/\text{m}^3$ and $24.69 \mu\text{g}/\text{m}^3$ with a mean value of $19.465 \mu\text{g}/\text{m}^3$ in the dry season of the year.

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