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Evaluation of Trace Metals in Particulate Matter from the Ambient Air of Calabar Metropolis, Cross River State, Nigeria

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Abstract:- This study measured and compared the levels of trace metals (Pb, Cr, Cu, Ni, Mn, Fe, Cd and Zn) in air borne suspended particulate matter (SPM) collected between August-September (wet season),2020 and January-February (dry season), 2021 at ten locations (CRUTECH, Ekpo-Abasi, Mayne Avenue by Atamunu, Etagbor by Jimco, Watt Market, Calabar Post Office, Marian Market, Diamomd Hill/MCC, Port Complex/NPA, Federal Housing by NTA) in Calabar metropolis, Cross River State, Nigeria. The samples were collected by gravity settlement method, using high density polyethylene (HDPE) containers with 10cm diameter funnel. About 50cm^3 of 0.1mg/L solution of $CuSO_4$ algaecide was added to prevent algae growth. The set up was mounted on a flat elevation, at least 6 meters high and supported at the base and exposed for a period of 30days with constant checking. Samples were collected and taken to the laboratory for storage and analysis. The study was done in two phases, wet and dry seasons. A descriptive analysis of UV visible spectrophotometer was used. Based on the analysis, the SPM concentrations varied from 13.020 µg/m^3 minimum to 22.025µg/m^3 maximum according to location. The total mean dust cover was 17.422 µg/m^3. Spectroscopy results shows that the air basin at all location sites contain concentrations of trace metals<15µg/m^3. Higher concentration of Cu (2.087± 0.455 µg/m^3) was recorded at Port Complex/NPA location and of Fe (1.925 ± 0.264 µg/m^3) while Zn is (1.919 ± 0.541) respectively. Paired independent t-test at p≤ 0.05 (df=19, n =20) confirmed significant seasonal variations in the concentration of the metals with higher concentrations during the dry season. Enrichment factor (EF) analysis was adopted to identify the source and the contributions to particulate matter. The result revealed that the background atmosphere in the studied stations was highly affected by anthropogenic pollution in the order of minimum to maximum concentrations by location and demonstrated that high heavy metals concentrations occurred but with significant EF values during the dry season. These results are useful for effective environmental pollution monitoring in Calabar metropolis air basin. It is therefore recommended that burying of refuse should be encouraged instead of burning, only road-worthy vehicles should be allowed to ply the roads, bush-burning should be completely discouraged and environmental impact assessment must be carried out before establishment of any industry.

Keywords:- *Particulate Matter, Ambient Air, Trace and Heavy Metals, Suspended Particulate Matter.*

I. INTRODUCTION

Particulatematter is a non-gaseous concentration in the atmosphere which represents an index of diverse classes of substances often referred to as aerosols[1][2].These materials which are both solids and liquids are suspended particles and could be airborne for long period of time. They are classified by their sizes, which are invariablyresponsible for the kind of effects they create in the environment. Particulate matter is often chemically diverse and could contain a variety of trace metals among others, that are responsible for their toxicity to the ecosystem [3][4]. Particulate air pollutants are a major problem in developing countries due to excessive use of fossil fuels, especially petroleum, coal with wood and flaring of gas[1].

[5][6] in separate researches, discovered that particulates cover could reduce visibility and disrupt traffic including air travels in extreme casesand also disrupt sunlight to plants which need this for their photosynthesis activities. These small particles in the atmosphere also influence climate. Their role is exactly opposite to that of the greenhouse effects. The greenhouse blanket, according to [7], causes the earth to warm up because they interfere without-going radiation (long wavelength radiation) whose escape cools the earth by drawing away energy into outer space.In contrast, particulate matter, interfere with incoming radiation from the sun. Sunlight that would otherwise warm the earth is reflected back into space by dust and this results to a cooler earth [8].

Particulates also serve as nucleus around which tiny particles or water vapour is formed [9][10]. As earlier said, that in urban environment, dust particulates are prevalent, their origin is from many different sources which include volcaniceruption, dust storm, mining activities and land clearing, othersare industrial processes which involve refining of petroleum and coal, chemical Plants, smoke stacks, construction industries and automobile exhaust emission etc. All these make substantial contribution to the quality of particles in the atmosphere.In a given ecosystem, there are inter- relationships between trace metals in air, soil and plants. Trace metals are metallic elements which constitute less than 1% concentration or found in small or minute quantity in a given ecosystem [11].

Metallic trace elements released from anthropogenic sources enter the environment and follow normal

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biogeochemical cycles. The implication could be very wide including contamination of the ecosystem [9]. Most Nigerian urban cities are confronted with challenge of the environmental problems especially atmospheric pollution arising from suspended particulate matter. Concern about air pollution in urban regions is receiving increasing importance worldwide, especially pollution by trace metals and particulate matter [2]. In the urban environment, dust particulate cover has been widely known to reduce visibility and disrupting traffic including air travels in extreme cases [12]. In many urban areas, dusty particulate matter in a large scale is associated with dust haze that greatly disrupts air travels during harmattan weather and other climatic effects. For example, [10][11] wrote that, "particulate matter tends to form blankets that shield the land from warming sunlight when excess UV-radiation from the sun is screened from the earth surface (a kind of greenhouse effect). On a Global scale, particulate matters (PM) also influence directly or indirectly the Earth's radiation energy balance and can subsequently impact on global climate change [13]. Atmospheric particulates are reported to affect ecosystems and materials adversely. [8] assert that atmospheric particulate matter is considered as a prime pollutant of concern for urban cities not only because of the adverse health effects, but also for the reducing atmospheric visibility.

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 [14]. PM_{10} particles (the fraction of particulates in air of very small size<10UM) are of major current concern, as they are small enough to penetrate deep into the lungs and so potentially pose significant health risk [9]. Air borne particulate matter (PM) is considered to be the most significant environmental pollutants, that exist in various amount and as such is used to monitor the levels of environmental pollution [4,15]. Recent studies on the health problems associated with exposure to PM containing heavy or trace metals with an aerodynamic diameter of 10μM or less (PM_{10}) have been linked to both long-term and short-term effects, such as a decline lung function, increase in respiratory problems, chronic pulmonary diseases, heart diseases, lung cancer, damage to other organs and premature death along with a rise in mortality [16].

The results of the long-term studies confirm that the adverse health effects are mainly due to particulate matter especially small particles- less than 10microns in diameter, PM_{10}. The particulate may include a broad range of chemical species, ranging from metals to organic and inorganic compounds [17].Among the inorganic compounds, most important ones are the 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 sourcesand produce the largest emissions of trace metals such asArsenic(As), Manganese (Mn), Cobalt(Co), Cadmium (Cd), Copper (Cu), Nickel (Ni), Iron (Fe), and Zinc (Zn) [12]. [18] suggested that airborne particulate matter with elevated metals concentration may have a serious impact on human health which mostly includes respiratory disease and damage to other organs.

Within the European programme for monitoring and evaluation of the long-range transmission of air pollutants, (EMEP), measurements of PM_{10} and heavy metals are highly toxic species that have been introduced. These observations are influencing the environmental legislative authorities all over the world to update and modify their air standards [19][20].The recommended guidelines for maximum PM_{10} concentrations are $50\mu g/m^3$ (24h average) whereas $20\mu g/M^3$ for annual average concentration.

II. TRACE METALS AND THEIR EFFECTS

Inorganic component of particulate matter which is mainly trace metals is very important because they are natural constituents of the earth crust and are widely distributed in environmental matrices. At elevated concentrations, all the metals are harmful to living being including humans. The urban population is exposed to airborne toxic metals that often are well above natural background level.Trace metals are elements that occur at very small quantities less than 1% concentration but are nonetheless important for many biological processes.Heavy metal refers to metallic chemical element that has relatively high density which is usually toxic even at low concentrations. Human activities such as industrial production, mining, agriculture and transportation, release high amount of both trace and heavy metals into the surface and ground water, soils and ultimately to the Biosphere.Some of the trace metals considered in this study include lead (Pb), Iron (Fe), Zinc (Zn), Copper (Cu) manganese Mn, Nickel (Ni) chromium (Cr) and Cadmium (Cd).

It was also known that mining, smelting and quarrying activities have created local environmental effects throughout the world and in the past have led to acute or chronic intoxication due to the emission of trace metals such as lead (Pb), arsenic (As), cadmium (Cd), and mercury (Hg). Lead (Pb) is known for its toxic effect in the body. It's cumulative and long-term exposure have been known to cause serious health hazards which include inhibition of the synthesis of hemoglobin and also adverse effects on kidney etc.Iron (Fe) and Zinc (Zn) are also regarded as essential metals and has been found to be poisonous at high concentration,accumulation of heavy metals including Pb, Zn, and Cu in Urban air can be attributed to vehicle exhausts, industrial discharges, oil lubricants automobiles parts, corrosion of building materials, atmospheric deposition.

Exhaust fumes from all combustion engines combine to produce local adverse effects on the health of people especially automobile users and pedestrians. People living along highways, high traffic congested areas, production industries, automobile workshops are usually at high risk of heavy metals poisoning. The worse sufferers are traffic policemen, who are particularly close to the fumes of

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automobile exhaust. Dust consist of solid matter particulate in the form of fine powder lying on the ground, on the surface of objects or blown about by natural or mechanical forces.The presence of metals in dust has been identified as useful indicators for contamination in surface soil, cements and dusts environments.

Generally, the degree of concentration and accumulation of heavy or trace metals in environmental indices depend on the type of heavy metals and the activities taking place in a particular area. It is a fact that street dust is an important pathway in the exposure of people to toxic elements. The ingestion of dust particles with high concentration of potentially toxic metals possess a potential threat to human health.

In Nigeria, 5-10% of allergen cities for atmospheric total suspended particulate matter was attributed to Harmattan dust haze [21]. Heavy metals are persistent pollutant that can be biomagnified in the food chain, becoming increasingly dangerous to humans and wild life. Then, assessing metal pollutants in different component of the ecosystem have become an important task in preventing risk to natural life and public health [22]. Exposure to metals in the air is capable of causing a myriad of human health effects, ranging from cardiovascular and pulmonary inflammation to cancer and damage of vital organs. Contemporary research into air pollution is revealing that the metals components of particulate matter (PM) are contributing significantly to adverse health effects, even at low concentrations found in ambient air. Metals such as Cd, Ni, and Pb are known examples of elements that exact pronounced negative health effect from inhalation and have been reserved from birth/occupational and ambient air exposure.Cadmium (Cd) has been widely dispersed into the environment through the air by its mining and smelting as well as other man-made routes which include usage of fertilizers, presence of sewage and various industrial uses such as Ni Cd batteries, plating, Pigment and Plastics [10]. Cd may find its way into human population through food and beverages, drinking water, air and cigarette smoking [23]. Cd fumes can damage the olfactory organs, chronic exposure produces variety of effects on kidneys, lungs, heart, bones (Asteomalacia and Osteoporosis in humans and animals, and gonads. [6] have reported work showing that lead in air and dust are not the only sources of pollutants. About 10% of ingested lead may be absorbed by the stomach, while 20 to 50% of the lead in air may be absorbed by the lungs. The small particle size of air borne lead aids its penetration into the lungs. It could be concluded therefore that lead in paint is an overwhelming source compared to lead in air.

III. MATHEMATICAL FORMULATIONS

- **Gravitational settling:** When particles in suspension are dilute, they tend to act independently, hence their behaviors are therefore said to be discrete with respect to each other. As a particle settles in a fluid, its body force f_g, buoyant force f_b, and drag force f_d act on it. Applying Newton's theory of gravitation in the direction of settling, the terminal velocity of a settling particle can be represented in the equations below.

$$f_g - f_b - f_d = ma \quad \text{....1}$$

Where

m =The mass of the particle

a = The acceleration.

f_g = Body force

f_b = Buoyant force and

f_d = Drag force

Calling, p_p the mass density of the particle p_w the mass density of water, v_p the volume of particle and g the acceleration due to gravity yields –

$$f_g = p_p g v_p \quad \text{.....2}$$

$$f_b = p_w g v_p \quad \text{....3}$$

Because particles will ultimately settle at its terminal settling velocity, the acceleration a, is equal to zero. By substitution,

$$(p_p - p_w) g v_p - f_d = 0 \quad \text{.....4}$$

The drag stress is directly proportional to the dynamic pressure, $p_w v^2/_2$, where v is the terminal settling velocity of the particle. Hence;

$$f_d = C_D A_p p_w v^{2/2} \quad \text{.....5}$$

Where

C_D = The coefficient of proportionality called drag coefficient and

A_p = The projected area of the particle that is causing the drag.

Substituting equation (5) in equation (4) and solving for the velocity of spherical particles of diameter d (from $A_p = \pi d^{2/4}$, d = diameter of spherical particle), we have

$$\mathrm{V} = \frac{4}{2} g \sqrt{\frac{(P_p - P_w)^d}{C_D p_w}} \quad \text{.....6}$$

The value of the coefficient of drag C_D varies with the flow regimes of laminar, transitional and turbulent flows.

IV. MATERIALS AND METHODS

- **Study Area:** The research area is in Calabar metropolis comprising of Calabar Municipality and Calabar South in Cross River State of Nigeria. The approximate geographical co-ordinates of the project is between $06^0.00$N – $06^0.15^0$N and $08^0.15^1$E – $08^0.\ 20^0$E. It lies within the tropics and therefore has a tropical climate, with two distinct seasons, the wet season and the dry season.The wet season begins in March/April and last till October, while the dry season starts from November – March. It has an annual rainfall of between 2700mm – 3500mmand a mean annual temperature of between 32^0C – 35^0C. The topography of the area is generally flat with

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minor undulations and micro–relief due to stream courses that drain into the Calabar and great Qua Rivers respectively.This area is predominantly made up of traditional household farmers, who use simple techniques of crop production to cultivate subsistence food crops such as maize, cassava and vegetables. Calabar is a riverine City with a population of between 500,000 to 600,000 people. Traditionally, the occupation of the natives were fishing and farming. In recent times, development and technology advancement has changed its status from agrarian to a civil service town. Calabar is located in the rainforest belt and is blessed with rich, productive soils which encourages crop production. The criteria for considering Calabar metropolis for this study is that, Calabar is generally pollution "free" with no serious petroleum activities. Although it is not heavily industrialized, it has moderate traffic density, farming and commercial activities.

- **Sampling Area**: The sampling area is Calabar Metropolis. Dust particulates were collected at 10 chosen stations based on geographical spread, commercial activities and industrialization. The stationsmapped out for sampling are as shown in the sketch map and listed in the table below.

Fig. 1 Map of Calabar metropolis showing sampling stations

- **Sampling Method:** The samples were collected by gravity settlement method, using high density polyethylene (HDPE) containers with 10cm diameter funnel. About 50cm^3 of 0.1mg/L solution of $CuSO_4$algaecide was added to prevent algae growth. The set up was mounted at each location on a flat elevation of at least 6 meters in height and supported at the base and exposed for a period of 30days with constant checking. Samples were collected and taken to the laboratory for storage and analysis. The study was done in two phases,wet and dry seasons. In wet season, samples were collected in the month of August to September. While in the dry season sample were collected in the month of January to February. These are seasonal variation analysis to check the level of contamination between the two seasons.

- **Gravitational Settling:** This refers to downward movement of particles resulting from gravitational attraction. The Newton's theory of gravitation is applied in this regard which states that any two particles of matter attract one another with a force directly proportional to the product of their masses and inversely proportional to the square of the distance between them.

The practical limit of particulate size to be removed by gravitational settling is 50µm, the size of about one-half the diameter of a human hair. Below this limit would require a large settling chamber and a long detention time. The principles of design are similar to that in water and waste water treatment, except that in the present case, air is involved instead of water. As in grit (sand or gravel) chambers, the flow-through velocity along the chamber should be maintained at less than 0.3mls.

List of Sample Stations and Environmental Significance

SITE	LOCATION	ENVIRONMENTAL SIGNIFICANCE
(1)	CRUTECH (control site)	Very low in traffic, industrial and commercial activities (chosen for control).
(2)	Watt market	Large Scale commercial activities with high traffic, (market area).
(3)	Calabar Post Office.	High traffic density with large scale commercial activities.
(4)	Ekpo – Abasi Junction	High commercial activities, solid waste disposal and high traffic movement.
(5)	Mayne avenueby Atamunu filling station	Busy traffic area and high commercial activities with high population density.
(6)	Etta Agbor by Jimco filling station	Busy traffic area, the university area with high traffic and high population density with small scale commercial and industrial activities.
(7)	Marian market	Large scale commercial activities with high traffic (market area).
(8)	Diamond Hill MCC	Flour mills factory location with high industrial activities.
(9)	Port complex NPA/EPZ	Shipping and general port activities with high industrial activities.
(10)	Federal Housing Estate, NTA location.	High population density area and high traffic density.

- PRE–TREATMENT AND DETERMINATION OF DUST PARTICULATE:
  Samples were pre–treated by removing extraneous materials that may be present and distilled water was added to facilitate filtration. They were then evaporated over steam bath to moist residue and transferred to an oven to complete evaporation at 105^0C. The residues were cooled in desiccators and weighed to nearest milligrams. The weights were then used to calculate the dust particulate cover.

- PRE–TREATMENT OF SAMPLE FOR TRACE METALS ANALYSIS BYACID DIGESTION.
  The residue obtained from each station was weighed into different 250ml flat bottom flask and 20ml concentrated Nitric acid (HNO_3) was added and allowed to stand for 1 hour. 15ml of concentrated perchloric acid ($HClO_4$) was also added. The mixture was digested on hot plate in a fume cupboard until the mixture turned yellow colourat end-point.It was then dissolved with1MHCl acid, filtered and the filtrate made up to 150ml with deionized water. Then 25ml of each pretreated sample was taken for analysis of trace metals.

- INSTRUMENT ANALYSIS (EXPERIMENTAL)
  Related parameters such as total dust cover, Lead (Pb), Nickel (Ni), Manganese (Mn), Zinc (Zn), Copper (Cu), Iron (Fe), Chromium (Cr) and Cadmium (Cd) were determined by spectrophotometric method using UV visible/3000 spectrophotometer model19600 at various wavelength as shown below. Samples were digested using perchloric acid ($HClO_4$) and Nitric acid (HNO_3).

- SPECTROPHOTOMETRIC ANALYSIS.
  For metal analysis, the major instrument use for the analysis was the spectrophotometer and this method is an accurate method for determining the concentration of substances in solution. It is regarded as refined filter photoelectric photometers which permit the use of continuous variable and more nearly monochromatic bands of light. As the name implies, it is a device for producing coloured light of any selected colour or wavelength. It is generally calibrated in wavelength (nm).

Spectroscopic process refers to the various instrumental techniques (methods used) in the determination/measurement of metallic elements that may be present in any given substance(s). These methods include:

A.A.S. – Atomic Absorption Spectrophotometer
F.E.S. – Flame Emission Spectrophotometer
I.R. – Infra-red Spectrophotometer
I.C.P. – Inductively Coupled Plasma Spectrophotometer
X-Ray Fluorescent Spectrophotometer
UV- Visible Spectrophotometer
Gas - Chromatographic Mass Spectrophotometer, Colorimeter etc.

The method used in this research work was the UV Visible Spectrophotometer. Spectroscopic process is a process which applies Beer-Lambert's Law, which is currently known as Beer's Law. This law states that the intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically.

Mathematically, this is written as:

$$I = I_0 e^{-kc} \quad \ldots\ldots 7$$

$$\frac{CX \log I_0}{I_t} \; or \; \frac{CX \log I_0}{I}$$

Where c is the concentration, k is constant and I is intensity of the incident light of wavelength (**λ).**

A Spectroscope is an apparatus for examining 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. This requires a more complicated and consequently more expensive instrument, a spectrophotometer. An optical spectrometer is an instrument possessing an optical system which can produce dispersion of incident electromagnetic radiation and with which measurements can be made of the quantity of transmitted radiation at selected wavelengths of the spectral range. Photometer is also a devise for measuring the intensity of transmitted.Radiation or a function of this quantity. When combined in the spectrophotometer, the spectrometer and photometer produce a signal that corresponds to the difference between the transmitted radiations of a reference material and the transmitted

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radiation of a sample at selected wave lengths. Fluorimetric analysis is a method of analysis in which the amount of radiation emitted is used to measure the concentration of theanalyte.

The variation of the color of a system with change in concentration of some components forms the basis of what the chemist commonly terms calorimetric analysis. The color is usually due to the formation of a colored compound by the addition of an appropriate reagent, or it may be inherent in the desired constituent itself.The intensity of the color may be compared with the intensity obtained by treating a known amount of the substance in the same manner.The chief advantage of colorimetric and spectrometric methods is that, they provide a simple means for determining minute quantities of substances. In general, the upper limit of colorimetric method is the determination of constituents which are present in quantities less than 1% or 2%. In spectrophotometry and colorimetry, when light, either monochromatic or heterogeneous, 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.

V. INSTRUMENT ANALYSIS

- **LEAD:**

Wave length: 520nm
Procedure: 25ml of pretreated sample of each station was added to 1 sachet of lead reagent powder pillow and swirled to mix. 25ml of deionized water was used as blank to zero the instrument. The concentration as determined at stated wavelength

- **ZINC:**

Wavelength: 620nm
Procedure: for Zinc analysis,25ml pretreated sample from each station was taken and reacted with 1 sachet of Zinc reagent added to pretreated sample using deionized water as blank and result read on the screen of DR/3000 spectrophotometer at stated wavelength.

- **IRON:**

Method: 1.10 phenanthroline
Range: 0 - 3. 000 mg/L (PPM)
Wavelength: 510nm
Procedure: 25ml of acid digested sample was reacted with ferrovet iron reagent powder pillow and swirled to mix and analyzed using DREL 3000 Spectrophotometer at the stated wavelength.

- **COPPER:**

Range: 500 – 10mg/L
Wavelength: 356nm
Procedure: 25ml of pretreated sample was taken and I packet of cuver 1(copper reagent) powder pillow was added and swirled to mix for 30 seconds and read at the screen of UV/ Visible 3000 spectrophotometer, using deionized water as blank. The concentration of copper was determined at the started wave length.

- **MANGANESE**

Method: per – iodate oxidation
Wavelength:550nm
Range: 0.20 – 00mg/L
Procedure: 25ml of pretreated sample was added to bugger powder pillow citrate type of manganese and 1 powder pillow of sodium per iodate was also added. The content was swirled to mix. Deionized water was used as blank and concentration of manganese determined.

- **CHROMIUM:**

Method: (1.5, Diphenyl carbohydrate)
Wavelength: 540nm
Procedure: 25ml of pretreated sample was added chromium reagent powder pillow and well mix to dissolve. A purple color will develop if chromium is present. Allow color development of the sample for 5 minutes; deionized water was used as blank and concentration of chromium was determined at started wave length.

- **CADMIUM:**

Method: Dithizone
Wavelength: 520nm
Reagents:Sodium potassium tartrate solution, 40% sodium hydroxide, 1% cyanide solution, Hydroxylaminehydrochloride solution, Tartaric acid solution, Dithizone (0.01%), Carbon tetrachloride, Standard cadmium solution.
Procedure: Neutralize if necessary, 25ml of the sample with sodium hydroxide and transfer to a separating funnel. Add 1ml of sodium potassium tartrate, then 5ml 40% sodium hydroxide. Add 1% cyanide solution and 1ml of hydroxylamine hydrochloride. Mix well after addition of each reagent and then add 10ml of dithizone, shake for 1 Minute and run the dithizone, shake for 1 minute and run the dithozine into a second separating funnel which contains 25ml tartic acid solution, shake for 1 minute. Discard the carbon tetrachloride layer. Again add, 025ml hydroxylamine hydrochloride, 10ml dithizone, 5ml 40% sodium hydroxide and 0.05% Cyanide solution and shake for 1 minute. Filter the dithizone extract into a 50ml volumetric flask. Repeat the extraction with 10ml portion of dithizone until the final extract is colourless. Filter each portion into the flask. Dilute to the mark with carbon tetrachloride and determine the Cadmium concentration calorimetrically at the wave length of 520nm.

- **Determination of Nickel (Ni)**

Apparatus:25ml and 100ml volumetric flask, Spectrophotometer, 10ml pipette.
Reagents: NH_4OH Solution 1:1 (50ml of conc NH_3 solution mixed with 50ml of water), Iodine solution 0.05m, Dimethylglyoxime: dissolve 1g in 500ml of conc. NH_4OH and make to 1 liter with deionized water, Ammonium citrate, 1000ppm Nickel Standard Stock, Nickel working standard.
Procedure: Pipette 5ml of the sample into a 25ml flask,add 8ml of deionized water, 2ml of ammonium citrate, and

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2ml of iodine solution and 5ml of dimethyl glyoxime,read the absorbance at 530nm after 20 minutes

- **Calculations;**
  ppm= Instruments reading x conc. Of Standard x extract vol. x DF
  Absorbance of Standards x weight of sample x Aliquot taken

- **Data Analysis Techniques**
  In this study, the descriptive and quantitative method of analysis through data collected from primary source were used. "Charts such as time plots and tables were employed to aid in the proper actualization of the set objectives. The study adopted the analysis of variance (ANOVA) and the independent T-test and correlation coefficient modeling of time series variables which was described by the statistical packages.

VI. RESULTS AND DISCUSSION

Based on the results from the study area, this section presents the discussion of results on evaluation of trace metals in dust particulate from ambient air in Calabar metropolis. The research reveals that, anthropogenic sources of air pollution are related to particulate matter within the study area. The results graphically represent evidence of the analysis of the aim and objectives of the study in several forms.

Total Dust	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Cover/µg/m^3	9.980	19.47	15.82	13.38	12.53	12.89	16.79	19.71	18.62	14.60
Fe – µg /m^3	0.106	1.432	1.881	0.744	1.823	1.148	1.824	2.743	1.662	0.823
Pb - µg /m^3	0. 044	0.721	0.322	0.820	0.956	0.744	0.654	2.423	1.654	0.433
Cu – µg /m^3	0.113	0.384	0.392	1.201	1.902	0.785	2.113	2.677	3.420	0.504
Cr – µg /m^3	0.080	0.889	0.268	0.123	0.240	0.381	0.241	0.244	0.611	0.221
Zn – µg /m^3	0.043	0.122	0.181	0.120	0.981	1.830	1.021	1.762	1.670	0.192
Mn – µg /m^3	0.020	0.130	0.132	0.123	0.341	0.434	0.891	1.212	2.817	0.801
Ni – µg /m^3	0.021	0.142	0.131	0.142	0.723	0.770	1.640	2.514	2.832	0.872
Cd – µg /m^3	0.013	0.011	0.015	0.014	0.012	0.115	0.114	0.221	0.273	0.107

Table 1 :Correlation coefficients of total dust cover Vs. Trace metals in **WET SEASON**

Total Dust	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Cover/µg/m^3	16.06	24.58	18.25	17.28	16.30	17.03	19.83	24.69	22.14	18.49
Fe – µg /m^3	0.230	1.828	2.084	1.175	2.504	2.566	3.234	4.022	4.852	1.820
Pb - µg /m^3	0.140	0.904	1.303	1.201	1.243	0.922	1.023	2.477	2.723	0.801
Cu – µg /m^3	0.330	0.802	1.041	1.324	2.420	3.771	4.552	6.031	7.430	0.542
Cr – µg /m^3	0.214	1.022	0.610	0.552	0.743	0.401	0.513	0.612	0.840	0.342
Zn – µg /m^3	0.086	0.250	1.034	1.443	1.720	4.323	6.552	6.888	7.620	0.533
Mn – µg /m^3	0.056	0.140	0.182	0.245	0.360	0.788	1.424	1.984	3.680	0.765
Ni – µg /m^3	0.083	0.251	0.163	0.182	0.843	0.844	1.882	2.863	3.435	0.605
Cd – µg /m^3	0.016	0.028	0.063	0.042	0.081	0.206	0.221	0.430	0.721	0.141

Table 2: Correlation coefficients of total dust cover Vs. Trace metals **DRY SEASON**

METALS(Ug/m3)		WHO(1993)	NIS(mg/l)
Fe	-	1.00	2.00
Pb	-	0.050.01	
Cu	-	1.001.00	
Cr	-	0.050.05	
Zn	-	1.00 5.00	
Mn	-	0.05 0.05	
Ni	-	0.02 0.02	
Cd	-	0.10 0.01	

WHO AQGS (2005)

Table 3: Showing Threshold limit values (TLVs) for heavy metals in the air.

Air quality guidelines

- For PM 2.5; 20 µg/m^3 for the annual average and 25 µg/m^3 for the 24 – hour means (not to be exceeded for more than 3 days/year).

• For PM_{10}; 20µg/m^3 for the annual average and 50µg/m^3 for the 24 – hour means.

Based on the results in table 4 and figure 1 below, the descriptive statistics-mean, standard deviation, standard error, minimum and maximum limits were computed for the nine (9) study variables: total dust cover, the presence of Fe, Pb, Cu, Cr, Zn, Mn, Ni, Cd in air,represent the results shown in table 1 and 2 above. Table 3 above, is to compare the threshold limits value.

Name of variables	Mean	Std. Dev.	Std. Error	Minimum	Maximum
Total dust cover	17.422	3.806	.851	9.980	25.580
Fe	1.925	1.179	.264	.104	4.852
Pb	1.075	.742	.166	.044	2.723
Cu	2.087	2.036	.455	.113	7.430
Cr	.457	.270	.060	.080	1.022
Zn	1.919	2.421	.541	.043	7.620
Mn	.826	.987	.221	.020	3.680
Ni	1.047	1.088	.243	.021	3.435
Cd	.142	.176	.039	.011	.721

Table 4 : Descriptive statistics of study variables (Whole samples, N=20)

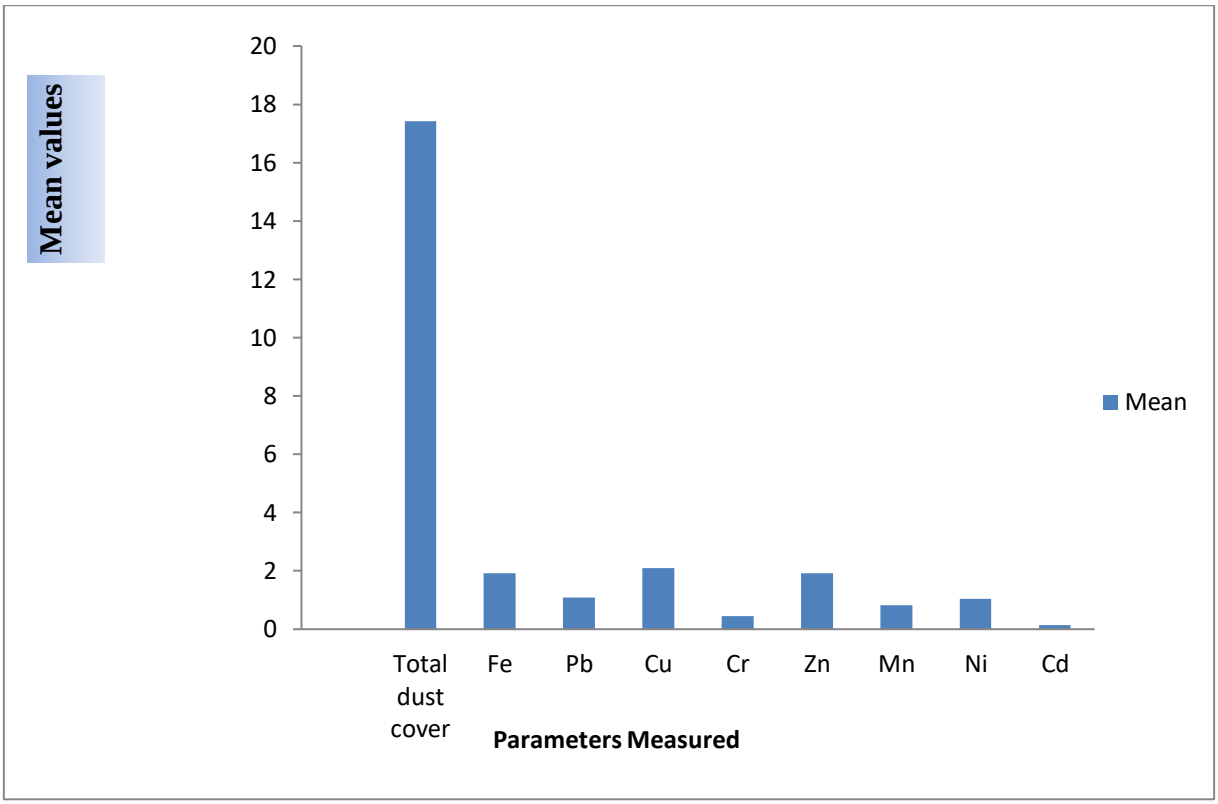

Fig. 1: Showing a bar chart of the Mean of all the parameters measured for both wet and dry season

The results in table 1 shows that the mean total dust cover ($\bar{x}$=17.422) with standard deviation (S = 3.806) is lower than the threshold value (µ = 20.000). For the presence of heavy metals in the air, the mean Cu ($\bar{x}$ = 2.08) which is the highest followed by Fe ($\bar{x}$=1.925) and the least was Cd ($\bar{x}$ =.142). Based on record, the mean Cd is a bid higher than the threshold value.

- Inter-variable correlation

The Pearson product moment correlation coefficient was computed for all possible pairs of the nine study variables, together with their corresponding P-values. Table 5 is the summary of the result.

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Location	N	Mean	Std. dev.	Std. error	Minimum	Maximum
Crutech	2	13.020	4.299	3.040	9.980	16.060
Watt market	2	22.025	3.613	2.555	19.470	24.580
Calabar post office	2	17.035	1.718	1.215	15.820	18.250
Ekpo Abasi junction	2	15.330	2.758	1.950	13.380	17.280
Mayne Ave. By Atemunu	2	14.415	2.666	1.885	12.530	16.300
Etagbo/ Jimco Oil	2	14.960	2.927	2.070	12.890	17.030
Marian Market	2	18.310	2.150	1.520	16.790	19.830
Diamond Hill/MCC	2	22.200	3.521	2.490	19.710	24.690
Port complex, NPA	2	20.380	2.489	1.760	18.620	22.140
Fed. Housing/NTA	2	16.545	2.751	1.945	14.600	18.490
Total	20	17.422	3.806	.851	9.980	24.690

Table 5: One-way ANOVA of total dust cover (TDC) by location of site, N=2

The result in table 5 shows that the total dust cover was highest at diamond hill/MCC ($\bar{x}$=22.200) followed by watt market ($\bar{x}$=22.025) and least is Crutech ($\bar{x}$= 13.020 see also fig.2) the result also showed that the p-value (.101) associated in the computed F-value (2.342) is greater than .05. As a result the null hypothesis with respect to total dust cover was not rejected. This means that there is no significant mean effect of location on total dust cover in Calabar.

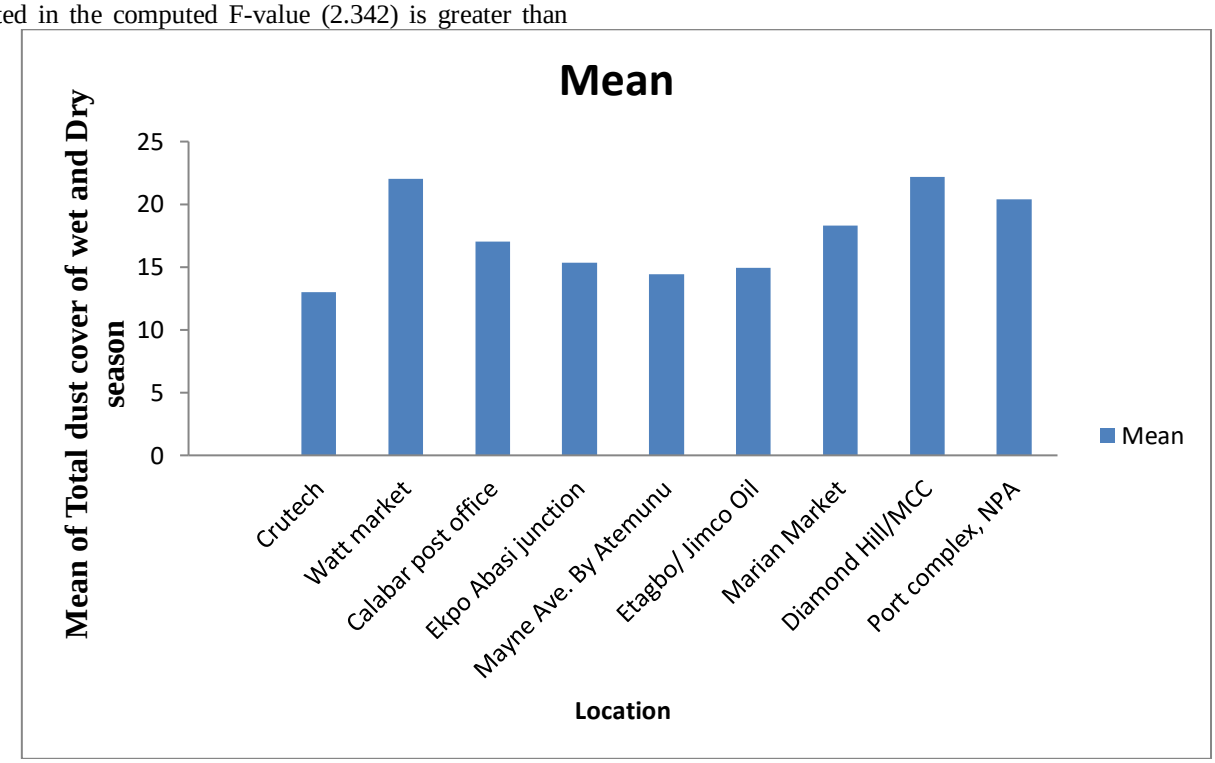

Fig. 2: Bar chart showing Mean of Total dust cover (wet and Dry season) per each location

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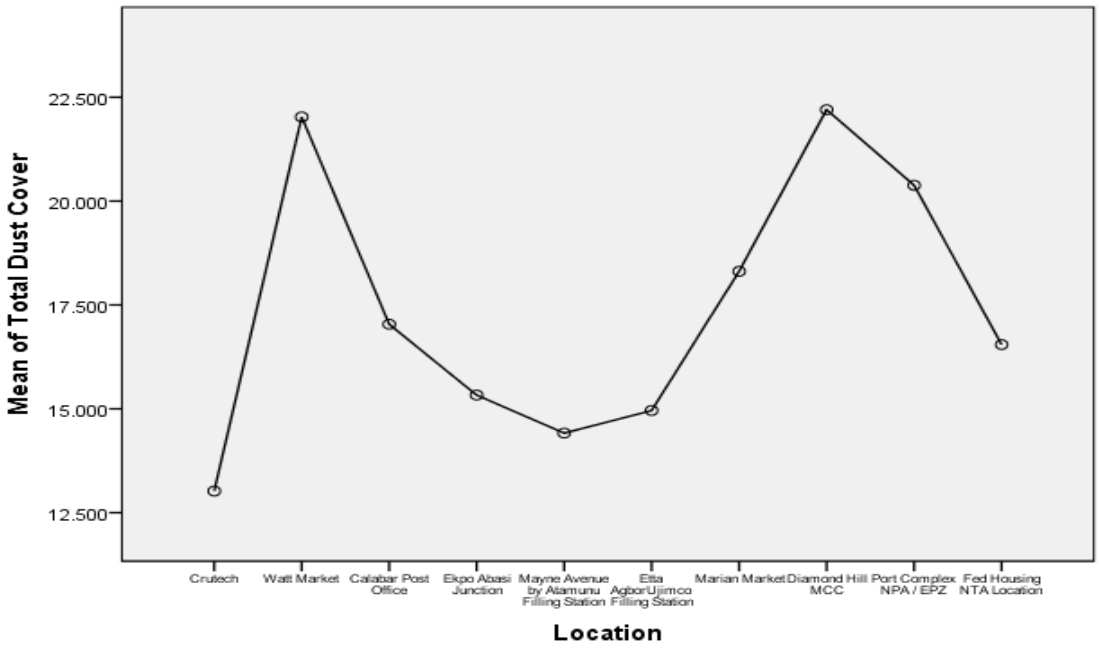

Fig. 3: Trend analysis showing Mean of Total dust cover (wet and Dry season) per each location

Variable name	N	season	mean	Std. dev.	Mean diff.	t-value	P-value
Total dust cover	10 10 20	Wet Dry total	15.379 19.465 17.422	3.270 3.257 3.806	4.086	12.163*	.000
Fe	10 10 20	Wet Dry total	1.419 2.432 1.925	.742 1.347 1.179	1.013	3.531*	.006
Pb	10 10 20	Wet Dry Total	.877 1,274 1.075	.691 .774 742	.397	3.573*	.006
Cu	10 10 20	Wet Dry Total	1.349 2.824 2.087	1.124 2.505 2.036	1.475	3.028*	.014
Cr	10 10 20	Wet Dry total	.330 .585 .457	.245 .240 270	.225	5.210*	.001
Zn	10 10 20	Wet Dry Total	.792 3.045 1.919	.751 3.000 2.421	2.253	2.996*	.015
Mn	10 10 20	Wet Dry Total	.690 .962 .826	.845 1.140 .987	.272	2.546*	.031
Ni	10 10 20	Wet Dry Total	.979 1.115 1.047	1.021 1.203 1.088	136	1.889	.091
Cd	10 10 20	Wet Dry total	.090 .195 .142	.095 .223 .176	.105	2.482*	.035

Table 6: Paired sample t-test for significance of heavy metals in air due to season.

*Significant at .05 level. P<.05

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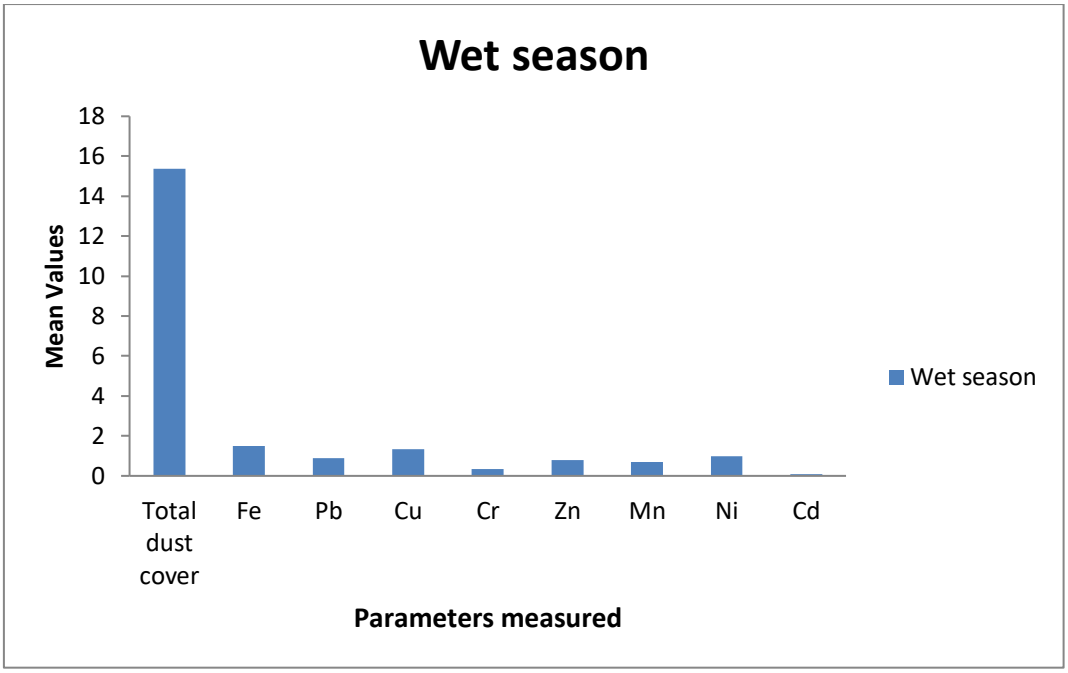

Fig. 4: Comparative Bar Chart showing mean values of all the parameters under study for Wet season

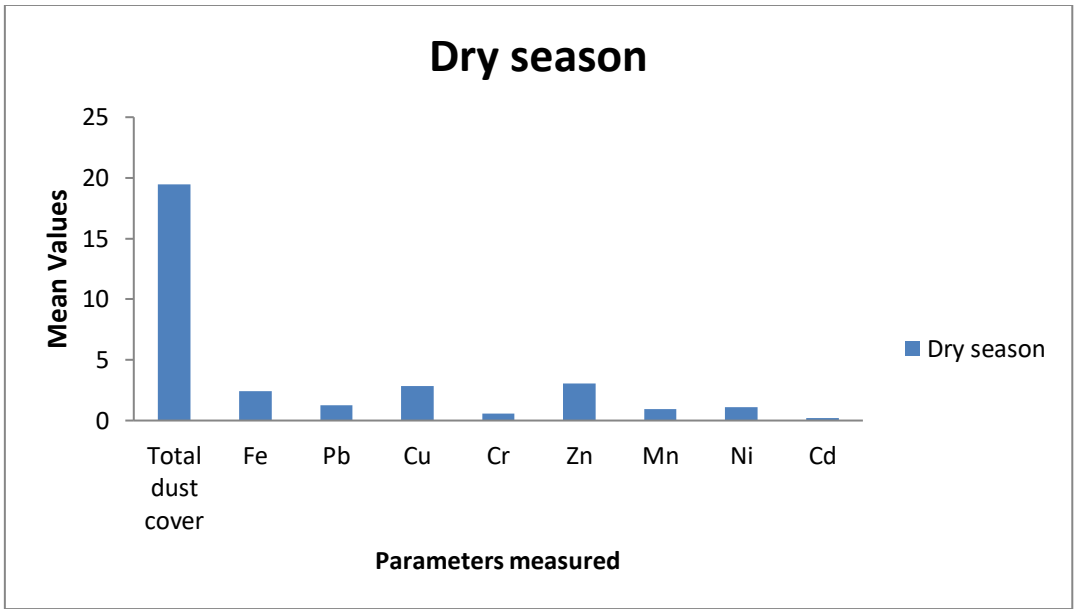

Fig. 5: Comparative Bar Chart showing mean values of all the parameters under study for Dry season

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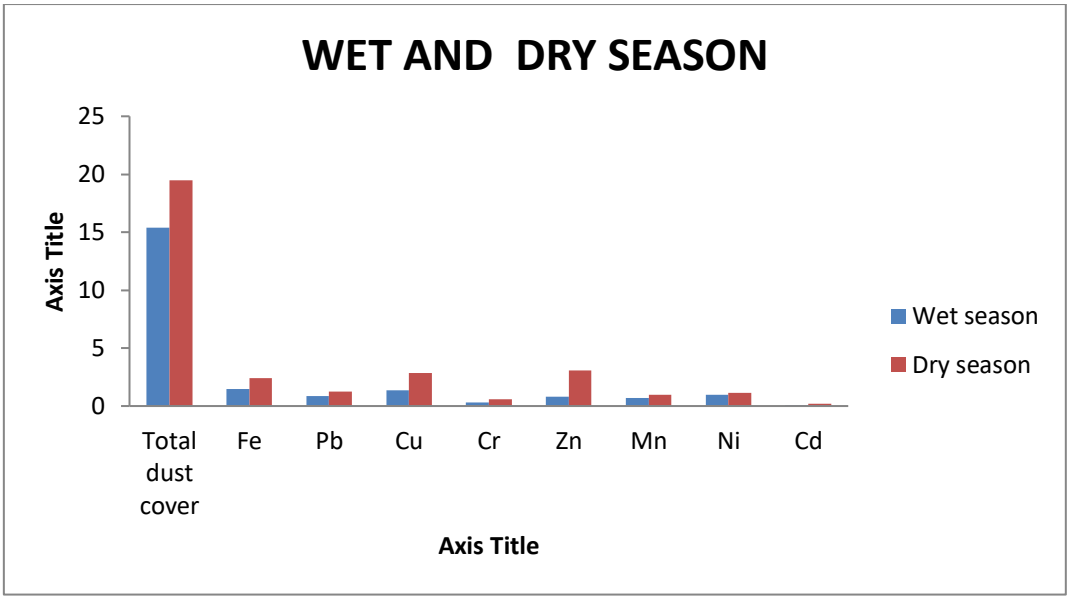

Fig. 6: Comparative Bar Chart showing mean values of all the parameters under study for wets and Dry season

The result in table 6 indicates that all the observed mean values are greater than their corresponding threshold values including mean Cd ($\bar{x}$= .142, μ = 0.100). The P-values (.000 ≤ p ≤ .028, associated with the computed t-values ($\bar{x}$= 2.387 ≤ t≤ 8.721) for TDC, Fe, Pb, Cu, Cr and Ni are less than .05. Consequently, the null hypothesis was rejected for these variables. The p-values (.106, .158 & .296) associated with the computed t-values (1.697, 1.479 & 1.074) for Zn, Mn and Cd respectively are greater than 0.05. The null hypothesis was not rejected for these variables (Zn, Mn and Cd). This means that for these variables the observed mean and the values are not significantly different from their respective threshold values.

VII. DISCUSSION

The results of the dust particulate and trace metals studied for each station due to season (wet and Dry) are given in table 6 and fig. 1 to 6. The mean values for each air quality characteristic studied for the metropolis are given in table 1 to Table 6, which is been represented in fig. 1to fig. 6. The result shows that the mean total dust cover ($\bar{x}$= 17. 422 ± 3. 808) is lower than the threshold limit value (μg = 20.000) for the presence of trace metals in the air. The mean Cu ($\bar{x}$=2. 087) was the highest followed by Fe ($\bar{x}$= 1.925) and the least was Cd ($\bar{x}$= 0.142). Only the mean Cd was low when compared with its threshold limit value (TLV).

The levels of all the observed mean values of trace metals are significantly higher than their TLV except mean Cd ($\bar{x}$= 0.142, μg = 0.100). The P-values (0.000≤ P ≤ 8.721) for TDC, Fe, Pb, Cu, Cr, and Ni are less than 0.05. The p-values (0.106, 0.158 and 0.296) associated with the computed t-values (1.691, 1.479 and 1.074) for Zn, Mn and Cd respectively are greater than 0.05. This means that for these variables, the observed mean values are not significantly different from their respective threshold values. This implies that the average Calabar metropolis air was significantly polluted with Pb as at the time of this study, due to vehicles exhausts emissions and Leaded fossil fuel combustion. Fe being the second highest concentration recorded may be due to the level of quarrying activities around Calabar vicinity. The quarries between Awi, Nsan, Okom-ita, Etomkpini, Mfamosing and the Cement factory (UNICEM) may contribute to high level of Fe. Generally, the dust particulate cover for the various location were low and not significant ($p<0.05$) but the distribution varies widely (fig.1). The highest level of 22.200 μg/m^3 was measured at site Diamond Hill/MCC followed by 22.025 μg/m^3 at Watt market area. The lowest of 13.020μg/m^3 was recorded for CRUTECH as control. These were expected and are the business area of the metropolis with many and various kinds of commercial and industrial activities (Flour Mill/Chicken Feed). The watt market also has the highest level of traffic in the Metropolis due to high population density and holds the terminal points for most commercial vehicles in and out of the Metropolis. The high traffic concentration is bound to increase vehicles exhaust emission which is one of the greatest sources of air particulate matter. CRUTECH area on the other hand is quite remote from the central business districts and no major industrial and commercial activities and hence has the lowest dust particulates matter. These explain its choice as the control point. The levels measured in other sites falls within these two extremes (Table 3).Diamond Hill/MCC which recorded the highest measurement of 22.200μg/m^3 was due to Flour Mill/ Chicken Feed processing plant present there. On the whole, the low level of atmospheric dust particulate cover during this study, the mean for Calabar metropolis of 17.422 ± 3.808μg/m^3.is negligible compared to National Standard of 250μg/m^3[24].

The trace metal levels and distribution in the atmosphere generally followed the similar pattern of the dust particulate but with a wide variation between the wet season and the dry season respectively and between locations (fig. 1-6) and they vary with dust particulate. The highest level of trace metals of 2.087mg/m^3 was recorded for Cu at the Port Complex (site 9). This appears realistic considering the chipping and general Port activities, the area has also recorded relatively high level of some other trace metal; Fe

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1.925, Pb 1.075, Cr 0.457, Zn 1.919, Mn 0.826, Ni 1.047, Cd 0.142ug/m^3.

These were all higher than the metropolis average level (table 1). Though the average level of the trace metals for Calabar metropolis show high contamination, they do not indicate pollution in the air, as there where below, their TLVs for safe air (FEPA 2000). However, there is cause to worry over these levels as heavy metals could be easily biomagnified through the food chain of pollution level in a particular ecosystem, like the aquatic or terrestrial environments, when they settle [25].

VIII. SUMMARY/CONCLUSION

This section presents the primary empirical findings ofevaluation of trace metals in particulate matter from the ambient air of calabar metropolis using the terminal velocity of a settling particle which is represented in the equation $V = \frac{4}{2} g \sqrt{\frac{(P_p - P_w)^d}{C_D p_w}}$. Sample of SPM for one year (August-September, 2020 for wet season and January-February, 2021 for dry season) has provided information of the levels of trace metals in the atmosphere of Calabar metropolis and also further our understanding of anthropogenic pollution in the metropolis.The particulate matter (PM_{10}) concentrations were lower than the values of 250µg/m^3 annual average stipulated by the national air quality regulating agency (FEPA, 1991).The seasonal variation of Fe, Pb, Cu, Zn, Cd, Cr, Mn and Ni showed high concentration during dry season.Enrichment factor (EF) proved useful in identifying the sources and their contributions to particulate matter and indicate that, the background atmosphere in the studied stations is highly affected by anthropogenic pollution, in the order, Port Complex/NPA > Diamond Hill/Mcc> Watt Market > Marian Market >Calabar Post Office > Etta-Agbor/Jimco Oil >Mayne Avenue by Atamunu> Federal Housing/NTA >Ekpo-Abasi Junction > CRUTECH and demonstrate that, high heavy metal concentration occur but with significant EF values during the dry season.

IX. RECOMMENDATIONS

- Bury instead of burning refuse should be encouraged.
- Only road – worthy vehicles should be allowed to ply the roads.
- Bush – burning should be completely discouraged.
- Environmental impact assessment must be carried out before establishment of any industry.
- Implementation of environmental laws must be followed strictly.
- The use of improved machinery should be encouraged, so that there will be high level in combustion efficiency.
- Tree planting to trap carbon emissions should encourage within the study area.

REFERENCES

[1.] Abiddle (2009), Human Right Violation and Environmental Degradation in the Niger. Delta in Elizabett porter and Baden offord (eds)'' Activating Human Rights, Oxford, Barne, New York.

[2.] Kabamba, M; Basosila, N; Malaji. C; Mata, H Tuakuila (2016). Toxic Heavy metals in Ambient Air of Kinshasha, Democratic Republic of Congo. Journal of Chemistry 3 (2).

[3.] Wellenius, G. A., Coull, B. A., Godleski, J. J., Koutrakis, P., Okabe, K. & Savage, S. T. (2018). Inhalation of concentrated ambient air particles exacerbates myocardial ischemia in conscious dogs. *Environmental Health Perspectives*, 111, 402–408.

[4.] Ismail I, Laiman R. Ahmad H (2011) Study of particulate matter (PM_{10}) concentration and elemental composition at Damansara – Puchong highway, Internet Conf on Biol Environ and Chem. Singapore.

[5.] Gobo, A., Richard, G. &Ubong, I. (2010). Health impact of gas flares on Igwuruta/Umuechem Godson, A. R., Sridhar, M. K. &Bamgboye, E. A. (2009). Environmental risk factors and health outcomes in selected communities of the Niger Delta Area, Nigeria. *International Journal of Public Health*, (129) 183-191.

[6.] Uquetan, U. I., Essoka, P. A., Egor, A. O., Osang, J. E. &Bawan, A. M. A. (2016), Case study of the effects of oil pollution on soil properties and growth of tree crops in Cross River State, Nigeria.*International Journal of Scientific & Engineering Research*, 7 (1), 1145-1156.

[7.] Barry J.L. and Horton F E, (1974). Urban Environmental Management, Planning for Pollution Control, Prentice Hall Inc. Englewood Cliff New Jersey : 377 pp.

[8.] Quinn, P. K. & Bates, T. S. Regional aerosol properties: Comparisons of boundary layer measurements from ACE 1, ACE 2, aerosols99, INDOEX, ACE asia, TARFOX, and NEAQS. *Journal of Geophysical Research-Atmospheres* **110**: 1-24. D14202 (2005).

[9.] Guittikunda, K., Sarath and Ramani V. Kopakka (2014). Source emisions health impacts of Urban air Pollution in Hyderabad, India air Quality Atmosphere and Heath, 195 – 207.

[10.] Godson, R. E., Sridhar, M. K. &Asuzu, C. M. (2010). Environmental risk factors and hospital-based cancers in two Nigerian Cities. *Journal of Public Health Epidemiology*, 2, 216–223.

[11.] Ewona, I. O., Osang, J. E, Obi, E. O.,Udoimuk A. B.&Ushie, P. O. (2013). Air quality and environmental health in Calabar, Cross River State, Nigeria. *Journal of Environmental Science, Toxicology and Food Technology,* 6, (6), 55-65.

[12.] Magas O.K, Gunter J.T, & Regens, JL (2007). Ambient air pollution and daily pediatric hospitalization for asthama Environmental science and pollution Research 14, 19 – 23 http://dx.doi. Org/10 . 1065/ espr 2006. 08.333

[13.] IPCC, (2001), Intergovernment Panel on Climate Change, third assessment report. Cambridge university Press, Cambridge UK.

[14.] Sun, Q., Yue, P., Kirk, R. I., Wang, A., Moatti, D., Jin, X. L, Schecter, A. D., Lippmann, M. & Gordon, T. (2018). Ambient air particulate matter exposure and tissue factor expression in atherosclerosis. *Inhale Toxicology*, 20, 127–137.

[15.] Sulaiman N. Abdullah M, Chieu PLP(2005) Concerntration and composition of PM_{10} in outdoor and indoor air indusrial area of Balakong Selangor, Malaysia.
[16.] Miller K.A et al (2007) long term exposure to air pollution and incidence of cardiovascular events in women New England.
[17.] Park, S. K., Neill, M. S., Vokonas, P. S., Sparrow, D. & Schwartz, J. (2005). Effects of air pollution on heart rate variability. *International Journal of Innovative and Environmental Health Prospective*, 113, 304–309.
[18.] Mavroidis I. &chaloulakou mA. (2010) Characteristics and expected health implications of anuual PM_{10} concentrations in atherns, Greece international J. of Environ. And poll, 41, 124 – 139
[19.] World Health Organization (WHO) (2006), Air quality Guidelines for particulate matter, ozone, Nitrogen dioxide and Sulphur dioxide. Global up – date 2005, Geneva, Switzerland.
[20.] United States Environmental Protection Agency (USEPA) (2008), National Ambient Air Quality Standards (NAAQS).
[21.] Weli, E. V. (2014). Atmospheric concentration of particulate pollutants and its implications for respiratory health hazard management in Port Harcourt Metropolis, Nigeria. *CivicEnvironmental Research*, 9, 11–17.
[22.] Yakubu, O. H. (2017). Addressing environmental health problems in Ogoni land through implementation of United Nations environment program recommendations: Environmental management strategies. *Environments*, 4, 28 - 31.
[23.] Okuo, JM: Okolo Po (2011). Levels of As, Pb, Cd, and Fe in Suspended Particulate matter (SPM) in Ambient air of Airtisan workshops in Benin City, Nigeria, Bayero Journal of Pure and applied Sciences 4 (2) : 97 – 99.
[24.] FEPA. 1991 Federal Environmental protection Agency interim Guidelines and Starndards for industrial effluents, Gaseeous Emissions and Hazardous wastes management in Nigeria: 238 pp
[25.] Ogri, O.R, Obi – Abang, M. &Uyana D. A. (2000) . Trace metals in dust particulates from Calabar Municipality, Nigeria Global Journey of pure and applied sciences 4 (2), 97 – 99.