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NANOPARTICLES EFFECT ON ROOF-TOP COLORATION: AN ATTEMPT AT UNDERSTANDING THE NATURE OF DRY AIR DEPOSITION ON ROOFTOPS IN UYO METROPOLIS

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ABSTRACT

The study Nanoparticles Effect on Roof-Top Coloration: An Attempt at Understanding the Nature of Dry Air Deposition on Rooftops in Uyo Metropolis has been extensively undertaken. The study considered four different study areas in Uyo metropolis viz station 1 (University Main campus), station 2 (Use Offot on Nwanniba road), station 3 (:Ikot-Okubo on Abak road) and station 4 (Mbaibong on Oron road). Dry air sampling was carried out in the four stations using Attair 5x, and the condition of the roofs were noted and examined. The samples from the roofs were taken for SEM micrographs and scraped material from the roof was analysed using EDX-X-Ray Fluorescence. The suspended particulate matter in the dry air in all the four stations was also determined using High Volume Sampler. The various particle sizes of the SPM from the dry air which ranged from nano to micro –sizes were digested and analysed for some selected elements which included lead, iron, cadmium, zinc, copper, and sodium. The study revealed the nature of pollutants from the dry air in the four stations to be gaseous pollutants and suspended particulate matter (SPM). From the result of the work it was established that the SPM from the dry air had effect on the rooftops of buildings in Uyo metropolis as both the nano-size and micro-size of the SPM from the dry air were deposited on the rooftops leading to the coloration (dark-black) of the rooftops. The composition of the sampled dry air and the SPM was compared with that of the dark-black material to establish that the dark black deposit was actually from the dry air. The study also noted that the composition of the SPM may have some health implications since the lead content in station 3 was higher than specification from air quality standard of 0.00038 ppm. The scanning electron microscope micrograph of the rooftops, show the dark- black deposit as it covers the roof, with dark areas representing where the deposit was thick on the roof, and shining-light areas representing where the deposit was thin on the roof.

Keywords: Dry air, Particulates, Nano-size, Inhalable particles, Rooftops, Nature.

INTRODUCTION

When air is polluted, it carries the pollutant with it along the way some of the pollutants are deposited on things with which it comes into contact with. Living things also inhales the polluted air. When it rains the rain washes the pollutants unto roof-tops and down to the soil this explains the interrelationship mentioned by Bhatia (2008). Tice (1962) and Okedere and Elehinafe (2016) in their respective works have addressed the effect of air pollution from various sources and associated side effects on structures and living things.

Buildings in Uyo metropolis shortly on completion, the roof gets covered up with dark-black deposits. Plate I below is a typical example of the menace. For reflective roofing sheets they cease to be reflective as a result of this deposits. Jordan Woods (2017) of the Berkeley Laboratory notes that reflective roofs are needed for cool buildings (Woods, 2017). Aesthetics is very important in building structures; aesthetics is now being taken away in most structures shortly after completion by this menace which requires thorough investigation in order to be able to tackle it. The menace may even have health implication in which case the findings may be of value to the Federal Ministry of Health. In a recent publication by Ihom, (2014) and Ihom and Aniekan, (2014) the authors observed that WHO has released a report which said that ‘’ air pollution has become worse in many cities around the world in recent years, especially in Africa and South-East Asia. The UN agency’s report showed that nearly 90 per cent of the world population breathes air that is markedly above the limits recommended by the WHO. Experts from the agency identified car traffic, the burning of coal, oil and gas as well as badly insulated houses as the main culprits. The UN agency had said in April, 2012 that polluted air killed 3.7 million people under the age of 60 in 2012 (WHO, 2014). Similarly in a publication by Ola, *et al*, (2013) the authors observed after their work, which was aimed at indexing pollution in Jos Metropolis that the levels of H_2S, Carbon monoxide and particulate matter were above specified limits for quality air and therefore had some health implications on humans. Understanding the nature of this deposit which obviously is from the air is therefore very important.

Plate I. Dark-Black Deposit on Colored Roofs in a Housing Estate in Uyo Town

The quantity of atmospheric deposition depends on the amount and types of air pollutants emitted in the vicinity and upwind of a site (Foster, 1998), and the length of time between precipitation events (Thomas and Greene, 1993). A recent study of the Puget sound Basin evaluated heavy metals, polycyclic hydrocarbons (PAHs), and other compounds in wet and dry atmospheric depositions. This study found that concentrations of the chemicals of concern in the highly urbanized area sampled were an order of magnitude greater than outside the urban area (Brandenbergen, *et al.*, 2011).

Particulate matter is the sum of all solid and liquid particles suspended in air many of which are hazardous. This complex mixture contains for instance; dust, pollen, soot, smoke, and liquid droplets. These particles vary greatly in size, composition and origin. Particles in air are either, directly emitted for instance when fuel burns and when dust is carried by wind, or indirectly formed, when gaseous pollutants previously emitted to air turn into particulate matter.

There are many global challenges facing the world today. They range from finding sustainable renewable energy sources, reducing pollution, supplying uncontaminated drinking water, reducing the use of pesticides and herbicides, improving agricultural outputs to feed an increasing population, and predicted changes in world climate resulting from global warming. Nanotechnology and nanoscience have the potential to deliver solutions to many, if not all, of these global challenges, although it had been known for sometime that submicron-scale materials displayed some unusual and exotic properties, it was not until the advent of the scanning probe microscope that the nanometer-scale world was truly discovered. In this new world, matter at the nanometer scale, (1-100nm, where 1 nm is equivalent to 1 x 10^{-9} m) was found to have significantly different properties compared to those of the equivalent material at the macroscopic scale (Poinern, 2015). To put the nanoscale in right perspective, an atom is around 0.2 nm in diameter; a red blood cell is approximately 7500nm in diameter. Since the discovery of the buckyball, other fullerene molecules ranging from C70 all the way to C300 have also been found in some minerals, meteorites, and even carbon soot. Buckyballs have a diameter of 0.71nm (Poinern, 2015).

Air is a mixture of gases and suspended particulate matter. The components of the mixture also have various sizes ranging from macroscopic to nanoscale- size and even beyond. The suspended particulate matter sizes range from nanoscale to macroscopic scale. Several activities produce nanoscale particles that are released to the atmosphere. The striking of match stick, burning of fossil fuel, vaporizing of graphite, arc welding, meteorites, carbon soot, smoke, kerosene stoves etc. all these produces various forms of particulate carbon at the nanoscale that are released to the ambient air in the form of suspended particulate matter (SPM). Where the degree of release of these SPM is high the effect can be noticed on the rooftops when the SPM settles on the rooftops. Adhesion of SPMs to the roofs can be enhanced in the presence of moisture which makes the SPM sticky. Nanoscale SPM thus have an effect on rooftops particularly the dark-black deposit seen on rooftops in cities with highly polluted air as a result of fossil fuel burning and other industrial activities. The black colour of the deposit is normally associated with the presence of carbon SPM from soot and smoke (Dara, 2007; Asanusung, 2014; John, 2016).

The objective of this research work is to understand the nature of dry air deposition on rooftops in Uyo metropolis occasioned by the mixture of nanoparticles in the suspended particulate matter.

MATERIALS AND METHOD

Materials

The materials used for this research work included the following: the sampled air in dry season, dark-black deposit from the rooftops, chemicals used for the analysis and specimens cut from the rooftops.

Equipment

The equipment used for the work included Attair 5x Multigas detector, EDX-X Ray Fluorescence, Scanning Electron Microscope, High Volume Sampler, scissors, petri dish, filter paper, analytical weighing balance, electric oven, desicator with silica gel, thongs, sample collectors and ladder.

The Study Area

The study area of this research work is Uyo metropolis. Uyo is the capital of Akwa Ibom state. It is a major oil producing state in Nigeria, with a lot of gas flaring activities going on from the oil exploiting companies. The population of Uyo according to the 2006 Nigerian census which comprises Uyo and Itu is 436,606. The metropolitan area covers an estimated area of 168 km^2 (65sq.mi). Uyo is a fast-growing city and has witnessed some infrastructural growth in recent years. It is located on coordinates $5^0$2`N and $7^0$56'E.

The average annual rainfall in the study area is between 2000-4000mm with the period of fall usually between April and October. The rainfall reaches its peak in the months of June and September, while the dry period falls between November to March. The relative humidity of the area varies between 75% and 95% with mean annual temperatures of about 26 to 36 ^oC. Fig.1 is the map of the study area. The samples for the work were taken in different areas of the metropolis covering, Use Offot on Nwanniba road (station 2), University of Uyo, main campus on Nwanniba

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road (station 1), Ikot-Okubo on Abak road (station3), and Mbaibong on Oron road (station 4). The town is characterized by high usage of generators as a result of incessant power failure from the national grid and high vehicular traffic typical of a growing metropolis.

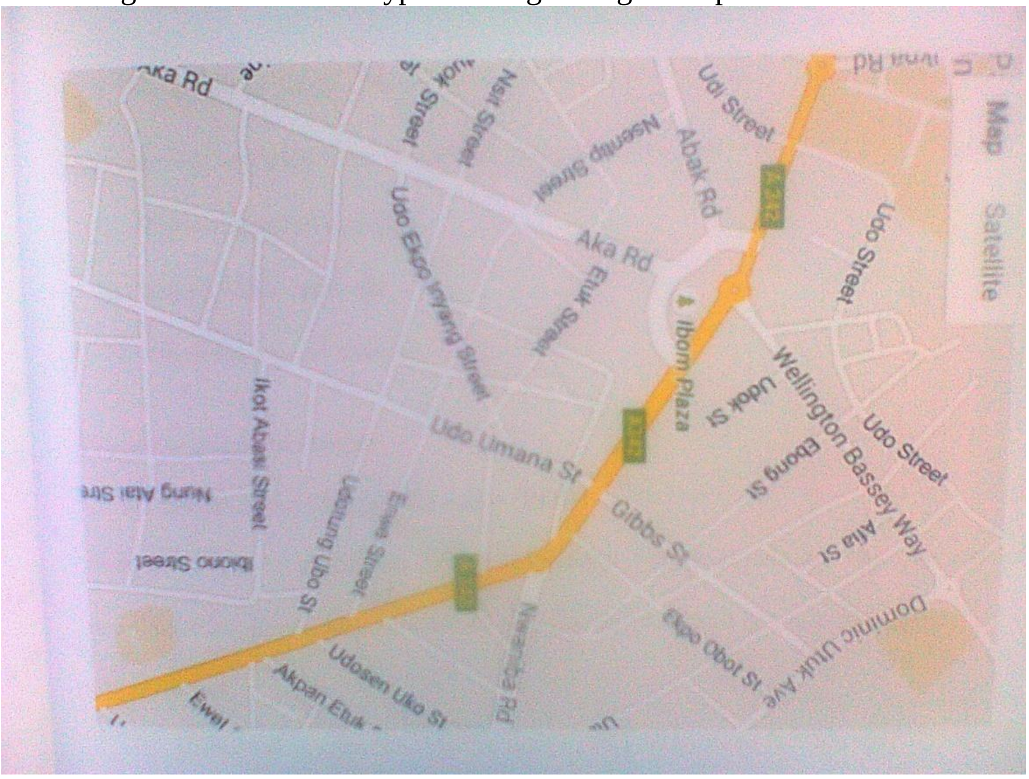

Fig.1: The Map of Uyo Metropolis the Study Area
Source: www.goggleearth.com

Method

Air sampling in the four stations was made possible through the use of Attair 5X Multigas detector. The device is equipped with catalytic sensor that detect a variety of gases in the atmosphere and displays the reading. Plate II show the technologist sampling the air at station 1 (University of Uyo, Main campus). The sampling of the dry air took place 7th of December, 2016 during the dry season period in Uyo metropolis.

The air sampling was closely followed by suspended particulate matter (SPM) determination. The method used for this analysis was filtration technique and the equipment used was the High Volume Sampler. The SPM was determined according to specifications by Ambient Air specification methods and American Society for Testing Materials (ASTM). The sampled SPM was then digested with mixed acids and subjected to elemental analysis at the Ministry of Science and Technology laboratory, Uyo. The dark-black deposit on the rooftops was scraped for analysis using EDX-X Ray Fluorescence. Specimens were equally cut from the roofs for SEM analysis using Scanning Electron Microscope.

Plate II: Show the technologist sampling the air at station 1 (University of Uyo, Main campus)

RESULTS AND DISCUSSION

Results

The results of this research work are as presented in Tables 1-2. Table 1 is the quality of the dry air which was sampled in the dry season in four different locations of Uyo metropolis. Table 2 is the elemental composition of the suspended particulate matter which was measured in dry season in four different locations of Uyo metropolis. Table 3 is the air quality standard Table. Table 4 is the EDX-X-Ray Fluorescence analysis of the dark-black deposit on the rooftops of buildings in Uyo metropolis. Plate III is the SEM micrograph of the dark-black deposit on the rooftops in Uyo metropolis.

Table 1: Dry Air Quality from Four Different Stations in Uyo Metropolis

S/No	Parameter	Station 1	Station 2	Station 3	Station 4
1	SO_X (ppm)	< 0.01	< 0.01	< 0.01	< 0.01
2	NO_X (ppm)	< 0.01	< 0.01	< 0.01	< 0.01
3	CO (ppm)	< 0.01	< 0.01	< 0.01	0.02
4	CO_2 (ppm)	279.0	274.0	272.0	272.0
5	H_2S (ppm)	<0.01	<0.01	<0.01	<0.01
6	SPM ($\mu g/m^3$)	1.34	0.83	0.68	0.91

Table 2: Elemental Analysis of Suspended Particulate Matter (SPM) from Four Stations in Uyo Metropolis

S/No	Parameter	Station 1	Station 2	Station 3	Station 4
1	Lead (Pb) mg/l	<0.0001	0.0001	0.001	0.0002
2	Iron (Fe) mg/l	0.0007	0.0009	0.0008	0.0009
3	Copper (Cu) mg/l	0.0026	0.0027	0.0028	0.0027
4	Zinc (Zn) mg/l	0.0023	0.0029	0.0026	0.0031
5	Cadmium (Cd) mg/l	<0.0001	0.0001	0.0003	0.0002
6	Sodium (Na) mg/l	0.0001	0.0001	0.0002	0.0003

Key: **Station 1:** University of Uyo, main campus on Nwanniba road, **Station 2:** Use Offot on Nwanniba road, **Station 3**:Ikot-Okubo on Abak road **Station 4:** Mbaibong on Oron road.

Table 3: Ambient Air Quality Standards

Pollutant	**time weighted average**	**Residential, Rural and mixed used area**
Sulphur dioxide (SO_2)	Annual average 24hrs	60µg/m^3 (0.023 ppm) 80µg/m^3
Oxides of Nitrogen (NOx)	Annual average 24hrs	60µg/m^3 80µg/m^3
Carbon Monoxide (CO)	Annual average 1 hr	2.0mg/m^3 4.0 mg/m^3
Suspended Particulate Matter (SPM)	Annual average 24 hrs	140µg/m^3 200µg/m^3 (0.077ppm)
Respirable Particulate Matter (size less than 0µm) RPM	Annual average 24 hrs	60µg/m^3 1000µg/m^3 (0.38 ppm)
Lead (Pb)	Annual average 24 hrs	0.75µg/m^3 1.00µg/m^3 (0.00038 ppm)
SOx	Annual average 24 hrs	80µg/m^3 (0.03ppm) 365µg/m^3 (0.14 ppm)
H_2S	Annual average	-
CO_2	24 hr	600 ppm
Oxidants	1 hr	160µg/m^3 (0.08 ppm)

Table 4: Chemical Composition of Dark-Black Material Scrapped from Roof-Tops (Analysed at NMDC Jos)

Parameters (in %)

S/No	**Sample**	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	V_2O_5
1	**Blackish powder from roof-top**	16.00	43.80	1.20	2.71	3.20	1.62	2.93	0.11

Cr_2O_3	MnO	Fe_2O_3	NiO	Co_2O_3	CuO	ZnO	Br	Rb_2O	SrO
0.10	0.31	10.55	0.05	ND	0.09	0.22	0.07	0.03	0.05

ZrO_2	Yb_2O_3	Re_2O_7	PbO	Carbonaceous and volatile matter
0.20	0.001	0.06	0.11	16.59

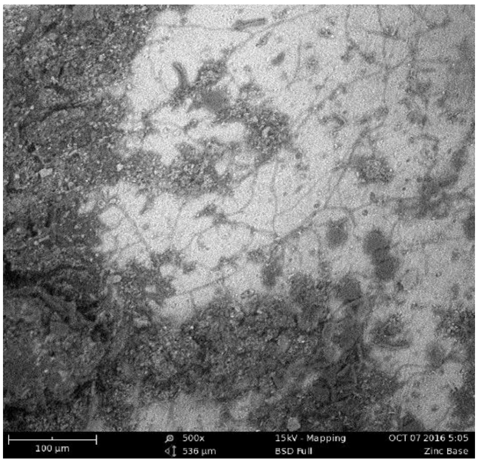

Plate III Scanning Electron Microscope (SEM) Micrographs of dark-black Deposit on Zinc-Coated base roofing sheet. The light areas have low deposit of the material; the substrate is still shining and the dark areas have large deposit of the material; the substrate is covered

DISCUSSION

Table 1 is the Dry Air Quality from Four Different Stations in Uyo Metropolis. Looking at the composition of the pollutants it can be observed that when compared with standard specification for air quality in Table 3, for residential, rural and mixed used area, none of the pollutants in the four stations exceeded the standard; except for the SPM that exceeded standard specification of 0.077 ppm for the micro-size SPM and 0.38 ppm for the nano-size SPM. Well this is expected because the wind speed was high at this time because of the harmattan - period that was being experienced in Uyo as of the time of this research.

Comparing Table 1 and Table 4 which is the Chemical Composition of Dark-Black Material Scrapped from Roof-Tops it will be observed that SOx have reported in the composition of the dark black deposit on the rooftops. From the composition of the dark-black deposit on the rooftop it can also be seen that the suspended particulate matter; both the micro-size and nano-size inhalable suspended particulate matter has reported on the rooftops resulting in the dark-black deposit. SPM is normally made up of dust, smoke, metals, soot, bacteria, fly ash, PAHs, carbon, etc in micro and nano-scale sizes (Dara, 2007). Table 4 shows the value of Al_2O_3 as 16% and SiO_2 as 43.8% this compounds must be from the dust component of SPM since dust is made up of majorly alumino-silicates. Table 4 also show the value of carbonaceous and volatile matter as 16.59% this must be from the SPM components of soot, fly ash, PAHs and carbon in micro and nano-sizes (Tice, 1962; Dara, 2007; Bhatia, 2008; Okedere and Elehinafe, 2016).

Table 2 is the Elemental Analysis of Suspended Particulate Matter (SPM) from Four Stations in Uyo Metropolis. Comparing the analysed parameters in Table 2 with standard specifications for metals in ambient air it can be seen that in most of the stations the parameters are below standard specification and therefore poses no much health danger, however the lead (Pb) content in station 3 is above the safe level of 0.00038 ppm for residential, rural and mixed used air quality. Lead is a poisonous metal just like cadmium there may be need for relevant agencies of government to investigate the health implications of this metal in stations where its value is high. According to Okedere and Elehinafe (2016) Particulate matter is the sum of all solid and liquid particles suspended in air many of which are hazardous. This complex mixture contains for instance; dust, pollen, soot, smoke, and liquid droplets. These particles vary greatly in size, composition and origin. Particles in air are either, directly emitted when fuel burns and when dust is carried by wind, or indirectly formed, when gaseous pollutants previously emitted to air turn into particulate matter.

Diesel engines emit air pollutants such as particulate matter; a known air pollutant with deleterious effect on public health. Due to these health concerns, several authorities have set exposure limits or guidelines for DPM (direct particulate matter). In Nigeria, limit for ambient total suspended particulate matter is put at 250 $\mu g/m^3$ for an averaging period of 24 hours. The increasing interest in the study of toxicity of DPM is due to associated human health concerns. The article on toxicity potential stipulated that negative health effects are commonly associated with numerical value of toxicity potential that is greater than 1.00 (Okedere and Elehinafe, 2016).

Most of the metals in Table 2 have all reported in the composition of the dark black material from the rooftops given in Table 4. The metals are from the metals component of the SPM which was digested and analysed. The metal particulates were of various sizes ranging from micro to nano-sizes. The effect of the various nanoparticles and micro-particles on rooftops in Uyo metropolis is shown in Plate III. Plate III is the Scanning Electron Microscope (SEM) Micrographs of dark-black Deposit on Zinc-Coated base roofing sheet. The light areas have low deposit of the material; the substrate is still shining and the dark areas have large deposit of the material; the substrate is covered. The dark-black colour is from the soot, PAHs, smoke and carbon component of the SPM. This covers the substrate and prevents it from corrosion attack for many years. It however takes away the aesthetics and beauty of the building. The problem is therefore more of aesthetic than the ability of the roof to perform and shade away rain, wind, and sun. Studies however have shown that the dark-black stains on the rooftops reduces the ability of the roofs to reflect light thereby increasing the heat within the buildings (Dangelo, 2016).

When air is polluted, it carries the pollutant with it along the way some of the pollutants are deposited on things with which it comes into contact with. Living things also inhales the polluted air. When it rains the rain washes the pollutants unto roof-tops and down to the soil this explains the interrelationship mentioned by Bhatia (2008). Tice (1962) and Okedere and Elehinafe (2016) in their respective works have addressed the effect of air pollution from various sources and associated side effects on structures and living things. The quantity of atmospheric deposition depends on the amount and types of air pollutants emitted in the vicinity and upwind of a site (Foster, 1998), and the length of time between precipitation events (Thomas and Greene, 1993). A recent study of the Puget sound Basin evaluated heavy metals, polycyclic hydrocarbons (PAHs), and other compounds in wet and dry atmospheric depositions. This study found that concentrations of the chemicals of concern in the highly urbanized area sampled were an order of magnitude greater than outside the urban area (Brandenbergen, *et al.*, 2011).

CONCLUSION

This work titled ''Nanoparticles Effect on Roof-Top Coloration: An Attempt at Understanding the Nature of Dry Air Deposition on Rooftops in Uyo Metropolis'' has been carried out and the following conclusions drawn

i. The work has noted that the dark-black deposit material on rooftops comes from the dry air which is made up of gases and suspended Particulate Matter (SPM)
ii. The SPM was a mixture of nanoparticles and micro-particles
iii. The SPM was found to be responsible for the dark-black coloration of the rooftops in Uyo metropolis.
iv. The nature of the dry air deposition has been understood since the parameters of the dry air that were analysed; most of them were equally found in the chemical composition of the dark-black deposit on the rooftops

v. The dry air composition has reasonable amounts of particulate metals indicating pollution to some extent, relevant government agencies may need to investigate the health implications.

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