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Spatial Distribution and Toxicity Assessment of Pollution Indices of Nitrogen IV Oxide in Ambient Air of Oil Producing Communities of Egbema Imo State

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***Abstract*—** *Palme's tubes where used to trap Nitrogen iv oxide (NO_2) in ambient air of oil producing communities of Egbema, Imo State where the Spatial distribution and toxicity assessment of pollution in six Locations where harvested, for six months. The assessment indices were ascertained using analytical instrument such as UV/Visible spectrophotometer, where samples from dry seasons in these locations where obtained. Highest concentration and average mean spread of NO_2, in these locations are: 111.50µg/m^3 and 66.20µg/m^3 at AQEWH, while 14.51µg/m^3 and 29.18 µg/m^3 spread was lowest at AQAFS and AQOWH locations respectively. Total concentration of NO_2 spread was also recorded as highest at 397.20µg/m^3 in AQEWH and 175.08µg/m^3 is lowest in AQOWH, while its toxicity potential concentrations were 1.32µg/m^3 and lowest at 0.58µg/m^3 in AQOWH locations respectively. Using statistical principal component analysis (PCA), which is widely used technique in meteorology and climatology, it indicates that AQEWH location has the largest variation spread of NO_2, while AQOWH and AQAFS has the lowest variation spread which represents, 83.8% and 93.7%, total variability respectively during dry season. Since long – term or chronic exposure to these pollutants on humans and environment has serious health implications, such as cardiovascular, gastrointestinal effects, chronic asthma, carcinogenic effects and chronic obstructive pulmonary disease, with responsiveness respiratory symptoms, there is every need to regularly monitor and conduct environmental air quality assessment of locations with high human activities to ascertain the level of exposure of pollutants to knowing their toxicological permissible limit*.

***Keywords*—** *Variation, toxicity, concentration, nitrogen iv oxide*.

I. INTRODUCTION

Pollution is the presentation of pollutants into the climate that cause mischief or uneasiness to people or other living beings that harm the climate. Pollution is the expansion of any substance or type of energy to the climate at a rate quicker than the climate can oblige it by scattering, breakdown, reusing or capacity in some innocuous structure. Pollution is an exceptional instance of environment annihilation. It is a synthetic pulverization as opposed to more clear physical obliteration. (Drummand,2018).

Air Pollution

Is the arrival of synthetic compounds and particulates into the air. Regular vaporous toxins incorporate carbon monoxide, sulphur dioxide, chlorofluorocarbons (CFCs) and nitrogen oxides created by enterprises and engine vehicles. Photochemical ozone and exhaust cloud are made as nitrogen oxides and hydrocarbons respond to sunlight, (Ravindra et al, 2008). Particulate issue or fine residue is described by their micrometer size PM_{10} to PM_{25}. It might cause maladies, sensitivities and even passing to people; it might likewise make hurt other living life forms, for example, creatures and food crops, and may harm the normal or assembled climate. Both human activity and regular cycles can create air pollution. Indoor air pollution and poor metropolitan air quality are recorded as two of the world's most noticeably awful poisonous pollution issues in the metalworker Institute report 2008. As indicated by the 2014 World Health Organization report, air pollution in 2012 caused the death of around 7 million individuals around the world, (IEA,2019).

Fig. 1: Air pollution in US,1973.

Nitrogen Dioxide

Nitrogen dioxide or NO_2 is an intermediate in the industrial synthesis of Nitric acid. In high temperature it is reddish-brown gas, with sharp billing odour and is prominent air pollutant. The chemistry of NO_2 is oxidation of Nitric oxide by oxygen in air.

$$2N0 + 0_2 \longrightarrow 2N0_2$$

$N0_2$ is formed in most combustion process using air as the oxidant. At elevated temp, Nitrogen combines with oxygen to form Nitric oxide.

$$0_2 + N_2 \longrightarrow 2NO$$

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The chemistry of NO_2 has been investigated extensively at 150^0c. $N0_2$ decomposes with release of oxygen via endothermic process.

$2NO_2 2NO + O_2 \longrightarrow$ (DH = 14K 5/mol). It serves as an oxidizer because of the weakness of N-O bond, $N0_2$ is a good oxidizer. It combusts consequently and explodes at this with many compounds such as hydrocarbons.

It also hydrolyzes to give Nitric acid and Nitrous acid. $2NO_2, N_2 0_4 + H_2O \longrightarrow HNO_3$. Thus reaction is one step in the Ostwald process for the industrial production of Nitric acid from ammonia. Nitric acid decomposes slowly to nitrogen dioxide which confers the characteristic yellow colour of most samples of this acid.

$$4HN0_3 \longrightarrow 4NO_2 + 2H_2 0 + 0_2.$$

Exposure caused by human are from the internal combustion engines burning fossil fuels. Outdoor $N0_2$ can be as a result of tight from motor vehicles. Indoors exposure arises from cigarette smoke, butane, kerosene heaters and stoves. Workers in industries where $N0_2$ is used are also exposed and are at risk for occupational lungs diseases. Chronic exposure to NO_2 can cause respiratory effects including air way inflammatory in healthy people and increased respiratory symptoms and increased asthma. $N0_2$ creates ozone which causes eye initiation and exacerbates especially asthma. Its toxicity shows gaseous $N0_2$ diffuses into the epithelial lining fluid of the respiratory epithelium and dissolves, chemically with antioxidant and lipid molecules in (Onidevarborma, 2015).

II. Sources of Environmental Toxicity

There are numerous wellsprings of ecological toxicity that can prompt the presence of poisons in air, food, and water. These sources are both natural and inorganic toxins. There can be so many point wellsprings of pollution, the channels from a particular manufacturing plant yet additionally non-point sources like elastic from vehicle tires that contain various synthetics and hefty metals that are spread in the climate. As an outcome, fundamental toxicological investigations incorporate estimations of the impacts of expanding dosages of a poison on a creature or some segment of that living being. The estimation is perhaps the best test of study of toxicology and its forecast and disclosure of constant, sub deadly cycle.

In 1920's, excessive introduction of laborers to tetraethyl lead (found in fuel) offered ascend to creation offices which cause roughly fifteen passings. Notwithstanding this revelation of the obvious risk of lead in gas and the worries of ordinarily ahead, thorough logical examinations were needed to illustrate, the unobtrusive, threats of persistent lead explosive. (Lin et al., 2008).

In portraying toxicity, one proportion of reaction is intense toxicity which is the measure of poison that will cause an unfavorable impact inside a relatively brief timeframe. Another proportion of reaction is ongoing toxicity, which is the drawn out reaction to a poison. In spite of the fact that a similar kind of portion reaction bends are utilized to quantify the persistent toxicity of poisons. Those estimations are harder to evaluate on the grounds that the reactions are regularly not so much about but rather more mind boggling. For instance, constant benzene toxicity causes lungs disease yet it might be a long time before that benzene-prompted malignancy shows up. Types of toxicity can likewise be described by the kind of unfavorable reaction that make contrasts in sensitivities which are utilized in settling the unfriendly impacts of a poison that are muddled by the variety in those impacts in various species. A few animal varieties are more sensitive to specific poisons than others and the impact of poisons on various tissue consistently fluctuate. There are likewise relatively huge contrasts in the sensitivities and impacts of poisons between individuals of certain species. Baby's hatchlings are more sensitive to neurotoxic impacts of lead then more established individuals since lead meddles with the improvement of focal sensory system which is framed during the initial not many long periods of life. At long last, sound individuals are commonly less sensitive to toxins than individuals with shortcoming resistant frameworks who are less competent and likewise dangers to their wellbeing, (Lin *et al.*, 2008).

III. Objectives of Study

While some outstanding works has not been done to ascertain the viability of assessment of NO_2, PAH and Trace Elements in Nigeria, is yet to gain wide spread acceptance:

- Aim of this research is to identify the most polluted areas or locations, as well as to compare the level of environmental burden in oil producing communities of Egbema Imo state.
- This study aims to understand the capabilities of using palmes tubes, and also to quantify the suitability of different taxa for monitoring airborne pollutants in our environment.
- This study focuses on determination and assessment of the quality of Ambient Air in Urban and Egbema oil producing areas of Imo State.
- To ascertain the spatial distribution and toxicity level of the NO_2 in all locations of Urban and Oil producing communities of Egbema for a period of six months.

IV. Justification of Study

- As the assessment of environmental hazards are gaining recognition globally in recent times, basically to some for alternative treatment or management of gases at various exploration sites and communities, it is very important we know the type and study the environment we are in.
- Many studies have shown the potential efforts put in place to make our environment free from harmful gases. Benefits from this technology show understanding the quality of our host community. The major importance of this study is to work out a good process to be used to determine the level of toxic gases evolved during exploration process. The global concern on energy arsis as well as air management, this study will be beneficial as it will focus on determining the parameters and level of gases toxicity in exploration sites of Egbema communities. An understanding of the well enlightened rural natives to explore the advantages or disadvantages of living within an exploration site. Equally, a good knowledge of controlling parameters and harmful exposures of these metals and gases will also be known and possible prevention or preventive measures will be addressed as well. Palmes tubes due to its features are most

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useful in monitoring NO_2 in air, while mosses plants (*pleurozium schreberi)* has the capacity to trap air pollutants to its self. Also the analytical tool used in this research x-rays the importance of GC- MS, AAS and UV-VIS Spectroscopy in assessment of air pollutants. The statistical method used is Principle component analysis, (PCA) which is a widely used technique in meteorology and climatology. It reduces the size of large datasets while minimizing any loss of information, with the aim of a better understanding. It is used to ascertain the variability of these pollutants in all locations of study. Therefore, the knowledge of the toxicity level of some of these gases and metals concentrations and their health effects will help both the oil companies and the host communities to know exactly the course of their problems in near future.

V. Materials and Methods

Apparatus/Equipment Used

- Palmes' diffusion tubes, Power of tweezers, Stirring rod, Beakers (250ml)
- Pipette (micro ml), Measuring cylinder (10ml), Volumetric flasks (25ml, 100ml)
- Paper tape, UV/visible spectrophotometer (JASCO), Grids (4x4 per mm^2)
- Petridish, 250ml Pyrex Conical Flask.

Chemicals / Reagents Used:

- Triethanolamine ($C_6H_{15}NO$).Dichloromethane, Hexane, Anhydrous sodium sulphate, Acetonitrile, Acetone Acid - Analytical grade acetone (C_3H_60) without purification, Sulphanilamide – Analar grade Sulphanilamide ($C_6H_{12}N_20_2S$), Sodium Nitrite – Analar grade sodium nitrite ($NaN0_2$) Naphtlylethylene Di-ammonium Chloride - (NEDA) ($C_{12}H_6C_{12}N_2$), Orthophosphoric acid-Analar grade Sulphuric acid, Nitric acid, Perchloric acid, Activated alumina, Nitric Acid.

Methodology

- Preparations of Saltzman's Reagents (Colour Development Reagent)
- Preparations of installation of $N0_2$ Diffusion tube
- Analysis of contents of $N0_2$ in Diffusion Tubes
- Samples are collected at two to three weeks every month.
- Five locations will be used, locations in the oil producing areas.
- NO_2 will be monitored with diffusion tubes for six months to cover dry seasons.
- Use of Spectroanalytical procedures e.g. UV/Spectrophotometry to determine the concentration of NO_2.

Palme's diffusion tube

This shows the typical components of a diffusion tube. These consist of an acrylic tube, two Stainless steel grids and two caps.

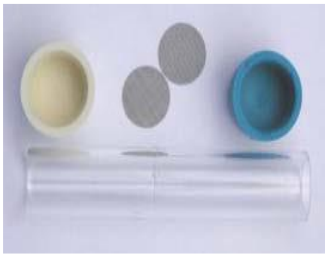
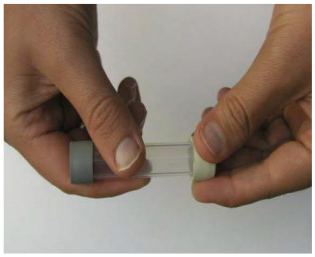


Fig. 2 Palme's diffusion tube (a)



Palme's diffusion tube (b)

Fig. 3: Deployment of Palme's diffusion tube

The required steel grids were cleansed with acetone and then dried properly. The samplers (tubes and caps) were washed with soap and dried. A mixture of two parts of acetone and one part of TEA (Triethanolamine, $C_6H_{15}NO_3$) was added in a 100ml beaker and stirred till clear homogenous solution was obtained.

The grids were dabbed in the mixture and were laid on a tissue with a pair of tweezers. They were laid on the tissue with the convex side down. The dried steel grids were put inside the white coloured cap of the sampler with the help of a tweezers again with the convex side down. The acrylic tube of the sampler was pushed into the white cap and the other end closed with the red cap. The prepared tubes were stored in the dark and care was taken not to expose them to extreme heat or cold, (Palme et al 1976).

Sample collection of Nitrogen iv oxide

Sampling was carried with palmes tubes for a period of six months (during the dry season) Samples were collected in six locations, six samples from Oil producing communities of Egbema in Imo State, which is distributed across the study location areas. These comprised of AQEWFS, AQEWH, AQEOJ, AQOFS, AQOWH and AQAFS for Oil producing communities. At the sites, the red caps of each tube is removed f were the are exposed at a height of about 1 .9metres above the ground for two to three weeks where movement of the air was unrestricted.

At the end of the 2-weeks sampling period, the red caps of the tubes were replaced and the tubes removed from site (harvested) and brought to the laboratory for analysis. Care was taken when collecting the samples to prevent contamination or

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losses by utilising equipment and containers that wouldn't change the chemical composition of the samples in any way (Hristozova et al., 2014). After collection the samples were transported to the laboratory where they were analysed for NO_2 concentration. Prescribed precautions were taken in the handling and transportation of the samples (Goudarzi, 2015).

Preparation of Salztman's Reagent (Colour Development Reagent)

a) 10 grams of sulfanilamide ($C_6H_{12}N_2O_2S$) BDH Analar grade was dissolved in 25m1 of phosphoric acid (H_3P0_4) in a 500m1 volumetric flask. 150m1 of demineralized water was added and made up to the 500m1 mark.
b) 0.07 grams Napthylethylene di-ammonium chloride ($C_{12}H_{16}C_{12}N_2$), NEDA (merck art. 6237) was dissolved in 50ml demineralized water.
c) (a) And (b) were put together and 500ml of demineralized water was added. Altogether 0.5L + 0.5L + 0.05L =1.05Litres of the salztman reagent.

The working principle of Palme's tube

The diffusion process on which the working of the tube is based starts as soon as the absorbent (Triethanolamine and acetone) in the steel grid in the white cap end] of the tube catches the nitrogen dioxide (NO_2) away from the air. This will happen so efficiently that the concentration of NO_2 in the air at the grid can be assumed to be zero. Therefore, a concentration gradient arises from the open end of the tube to the metal grid. This concentration difference causes diffusion of NO_2 into the tube in accordance with diffusion process predicted by Fick's law (Palme *et a*l., 1976).

Fick's law states that diffusional flux is directly proportional to the coefficient of the diffusion of the gas in air and to the difference in the concentration across the diffusion barrier which is inversely proportional to the length of the diffusion path of the tube.

This is expressed mathematically as: JA = D/ (A/ L) C

VI. Statistical Analytical Methods

Principal component analysis (PCA) is a well-known data display method in multivariate analysis therefore, only a summary of the method is described below. A common method in climatology and meteorology is the PCA. In order to have a better understanding, it shrinks big datasets while minimising information loss. This can be done by creating new variables that are different from the original ones but constructed from combinations of them. The simplicity of the PCA technique lies in its restriction to linear functions of the original variables ending and interpreting the structure of the data,((Kannel *et al*., 2007). The objective of PCA is to find a small number, m, of linear functions of a set of N variables that successively accounts for the maximum amount of variation in the original variables.

This statistical approach is used to control and validate the implementation of measurement locations. The statistical approach consisted of data analysis by principal component analysis (PCA). Statistical methods such as PCA have been used in many studies aimed at the management of water monitoring networks and air quality management.

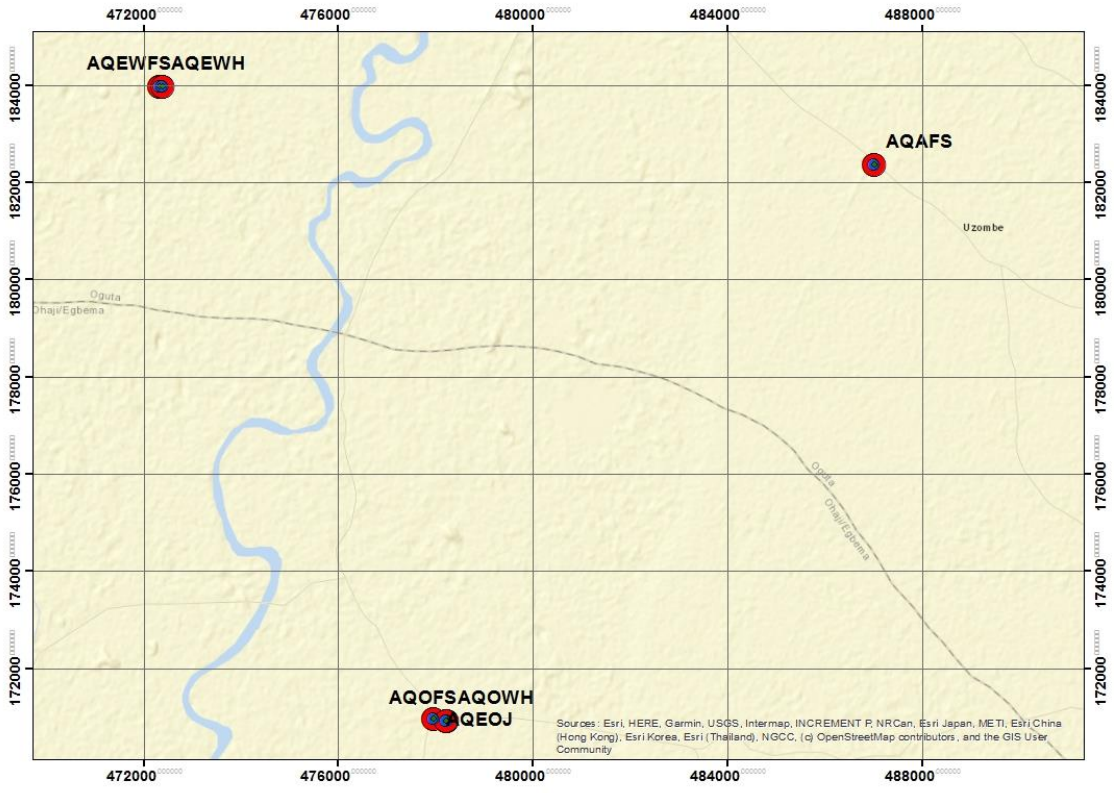

Fig. 4: Map of sample Locations in Egbema Oil producing area of Imo State

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TABLE 1: Concentration of Nitrogen IV Oxide Analysis (µg/m^3) (DRY SEASON).

S/N	Sample Name	Oct 2021	Nov 2021	Dec 2021	Jan 2022	Feb 2022	March 2022	Activities
1	AQEWFS	19.47	39.01	71.41	67.78	65.81	25.85	O E & G F
2	AQEWH	22.54	34.75	75.40	77.07	76.18	111.50	O E
3	AQEOJ	18.95	40.85	43.35	44.25	46.32	15.93	E A & V M
4	AQOFS	19.47	52.07	57.21	53.90	58.90	32.30	O E & G F
5	AQOWH	14.55	16.77	34.55	38.54	36.11	34.54	O E
6	AQAFS	21.19	37.13	59.23	61.26	52.52	14.51	O E & G F

TABLE 2: Toxicity Potential (PT) of Nitrogen IV Oxide (Dry Season – Oct 2021 – March 2022)

S/N	Location	Value estimated (µg/m^3)	Threshold limit (µg/m^3)	Toxicity potential (µg/m^3)
1	AQEWFS	48.22	50	0.96
2	AQEWH	66.20	50	1.32
3	AQEOJ	34.94	50	0.69
4	AQOFS	45.64	50	0.91
5	AQOWH	29.18	50	0.58
6	AQAFS	40.97	50	0.82

TABLE 3: Av. Mean NO_2 recorded for dry season (µg/m^3) Oct 2021 – March 2022)

S./N	Sample Name	Total Concentration	Average Mean
1	AQEWFS	289.32	48.22
2	AQEWH	397.20	66.20
3	AQEOJ	209.64	34.94
4	AQOFS	273.84	45.64
5	AQOWH	175.08	29.18
6	AQAFS	245.82	40.97

TABLE 4: Toxicity Potential (PT) of Nitrogen IV Oxide (Dry Season)

S/N	Location	Value estimated (µg/m^3)	Threshold limit (µg/m^3)	Toxicity potential (µg/m^3)
1	AQEWFS	48.22	50	0.96
2	AQEWH	66.20	50	1.32
3	AQEOJ	34.94	50	0.69
4	AQOFS	45.64	50	0.91
5	AQOWH	29.18	50	0.58
6	AQAFS	40.97	50	0.82

VII. Statistical Analysis of NO_2 Concentration

It is good to note that AQEWH location has the largest variation (spread) of Nitrogen iv Oxide during the dry season while AQOWH location has the lowest spread of Nitrogen iv Oxide in the dry season. Hence, Nitrogen iv Oxide is most volatile in AQEWH location and this is evident in the value of the range.

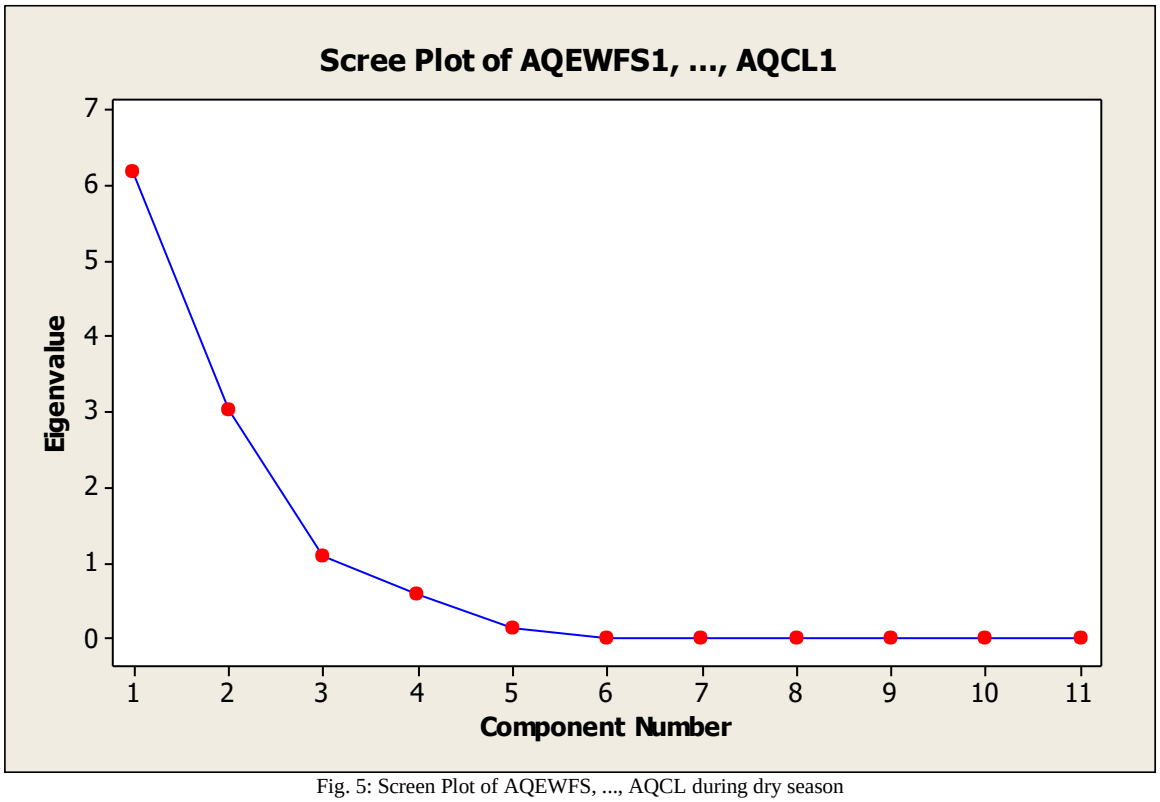

Fig. 5: Screen Plot of AQEWFS, ..., AQCL during dry season

Together, the first two and the first three principal components represent 83.8% and 93.7%, respectively, of the total variability in the NO_2 during the dry season. Thus, most of the data structure can be captured in two or three underlying dimensions. The remaining principal components account for a very small proportion of the variability and are probably unimportant. The Screen plot provides this information visually.

VIII. Discussion on Nitrogen IV Oxide (NO_2) Results

Experimental studies have shown that NO_2 can in prolonged periods remain in lungs of humans and animals for a long period of time. Between concentrations of 1880 – 9400 µg/m^3, there may be evidence of disorder in breathing and ventilator function. This will also increase the breathing frequency according to (EPA, 1993). The lowest concentration of NO_2 recorded at 30minute exposure (560µg/m^3) showed a direct effect on pulmonary function in asthmatics. This showed that result recorded in AQEWH (397.20µg/m^3) i.e. total concentration of dry season, will have similar health effects.

Many studies have shown long – term effects of NO_2 in adults (Bergmnd *et al*.,1993) There is also evidence of high respiratory symptoms (bronchitis) being dissociated with high level of NO_2 exposures. It is observed that NO_2 may increase respiratory illness in children (5 – 15 years). This is worrisome because repeated respiratory illness in children causes lungs damage in later life (Glezen, 1989). NO_2 has a stinging, suffocating odour where many authors have placed it at 100 µg/m^3 to 410 µg/m^3, (Bergmnd *et al.*,1993).

NO_2 health impact assessment exposure evaluation according 10 annual mean concentration are in the range of 0.4 – 9.4 µg/m^3, which is lower than the results gotten in our experiments which also shows that there is really NO_2 emission and NO_2 consequences in all locations of this research work. Short term exposure effects indicate that animal toxicology with exposure of $N0_2$ at less than 1880 µg/m^3 has rarely no health side effects (Drye *et al*; 1989). Healthy people at exposed NO_2 in two hours concentration of 4700 µg/m^3 experiences pronounced decrements in pulmonary function but people don't get affect at 1880 µg/m^3NO_2exposure according to (Drye *et al*; 1989). This shows that our results were for monthly not hours and it gives a clearly picture that the level of exposure will be very minimal. Also a study showed that people with 3 hours' exposure of NO_2 who has chronic obstructive pulmonary disease is affected at concentration of 560 µg/m^3 if obtained within six months, which shows that our locations are relatively safe from high concentration of NO_2 in hours. If the P- value is significant under 0.05 levels, hence we reject the null hypothesis that the difference between the mean of NO_2 in wet and dry season is equal to zero. This result indicates that there is NO_2 concentration in dry season of Imo State. This shows that for over a period of time concentration in the locations under review will surely have similar health effects on humans within these areas.

In conclusion, toxicity potential (PT) of NO_2, show a temporal variation with relatively higher concentration of these pollutants measured in Dry season periods, for example NO_2 toxicity level during dry season where AQEWH has highest toxicity potential level with lowest toxicity levels found in AQOWH of oil producing communities of Egbema.

IX. Conclusion

Despite the large number of acute controlled exposure studies on humans, several of which used multiple concentrations, there is no evidence for a clearly defined concentration–response relationship for nitrogen dioxide exposure. For acute exposures, only very high concentrations (1990µg/m^3) affect healthy people. Asthmatics and patients with chronic obstructive pulmonary disease are clearly more susceptible to acute changes in lung function, airway responsiveness and respiratory symptoms.

At 200µg/m3 or 400 µg/m^3, there is evidence to suggest possible small effects in the pulmonary function of asthmatics. Should the asthmatic be exposed either simultaneously or sequentially to nitrogen dioxide and an aeroallergen, the risk of an exaggerated response to the allergen is increased.

Air Quality Locations of Nitrogen IV Oxide

Locations of Oil / Urban Areas	Air Quality Denotations
SHELL B.P EGBEMA WEST FLOW STATION	AQEWFS
SHELL B.P EGBEMA WEST WELL HEAD	AQEWH
OBIKE EGBEMA SHELL B.P JUNCTION	AQEOJ
OBIKE EGBEMA SHELL B.P FLOW STATION	AQOFS
OBIKE EGBEMA SHELL B.P WELL HEAD	AQOWH
ADDAX IZOMBE FLOW STATION EGBEMA	AQAFS

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