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AMMONIA VARIATIONS IN OWERRI METROPOLIS AND ECOLOGICAL IMPACT

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ABSTRACT

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Ammonia emissions inventory is rarely reported in Nigeria and when at high levels is toxic to animals including humans. It is instructive to evaluate the levels of ammonia in metropolitan area as a priority to promote a clearer understanding of its distribution and interaction. The study investigated the levels of ammonia in different parts of Owerri Metropolis and its ecological impact. Ambient atmospheric NH3 concentrations have been measured for Owerri metropolis, away from point sources, for a period of three consecutive months in 2018 calendar year. Measured lowest mean NH3 concentrations have been in August at 0.04633 mg/L, which exceeded the critical loads and occupation exposure limits. There has been no significant change in the spatial variation in NH3 concentrations between the months albeit different locations varied significantly. The ecosystems where lichens and bryophytes are key species within the studied area may be under threat from loss of biodiversity while levels of human exposure to NH3 are completely unacceptable and require reducing and controlling measures. Hence, excess ammonia will induce elevated nitrification and denitrification driving higher greenhouse gas emissions.

Contribution/Originality: This study is one of very few studies which have investigated the levels of ammonia in a metropolitan area in Nigeria. The findings shows relatively high levels of ammonia, which if not controlled might increase to levels that disrupts human health and ecosystem balance.

1. INTRODUCTION

Ammonia (NH_3) is a colourless and pungent smelling gas having acute toxic potential ($NH4^{+}$). A volatile alkaline gas formed from reduced nitrogen gaseous pollutant in our environment, which has been gaining growing attention from the public and regulatory agencies (Sather et al., 2008). This is partly due to its ability to form ammonium based fine particulate aerosols that induces visibility interruption and adverse health effects (Robarge, Walker, McCulloch, & Murray, 2002). According to Fangmeier, Hadwiger-Fangmeier, Van der Eerden, and Jäger (1994) when present as atmospheric ammonia, it promotes damage and death of sensitive species and equally contributes to nitrogen eutrophication and ecosystem acidification at high concentrations. As a consequent, the ecosystem becomes susceptible to drought, frosts, pest induced stress and Increase in soil pH following acidification. In humans, these effects on exposure are not only determined by its pollution level, but the time spent breathing the polluted air (O'kane, 1983). Although a variety of natural and human influenced sources have been identified as the main sources of ammonia emission, but natural sources constitute more than 95% of its levels in the atmosphere (Aneja, Chauhan, & Walker, 2000). The natural sources are mainly due to the biodegradation of organic matter, of plants and animals wastes and urine that leads to urea hydrolysis with subsequently ammonia volatilization (Pandolfi et al., 2012). Anthropogenic sources include industrial emissions, non-industrial fuel combustion, catalytic converters in petrol cars, incineration and cigarette smoking (Pyatt, 2003). The evolved gaseous ammonia undergoes chemical transformations in the atmosphere by reacting rapidly with acidic substances such as sulphuric acid (H_2SO_4), nitric acid (HNO_3), nitrous acid (HNO_2), hydrochloric acid (HCl) or sulphur dioxide (SO_2) to form ammonium salts as seen in equation (1) and (2). The salts often occur predominantly as fine particles $(NH_4)_2SO_4$ and NH_4NO_3 (Rattray & Sievering, 2001). Ammonia (NH_3) pollution has been widely studied in many developed countries of the world. For example, it is found to be a contributor to Beijing pollution by promoting both homogeneous and heterogeneous formation of NO_3^- and enhancing the night time formation of NH_4Cl (Zhao et al., 2016). In the USA, a report conveyed that ammonia reacts with nitric acid and sulfuric acid to form to form fine particles as shown in the equation below (CENR, 2000).

$$2NH_3 + H_2SO_4 \rightarrow 2NH_4H{\bullet}SO_4 + NH_3 \rightarrow (NH_4)_2SO_4 \qquad (1)$$

$$NH_3 + HNO_3 \longleftrightarrow NH_4NO_3 \qquad (2)$$

Hence, majority of aerosol ammonia are of sulphate origin been favoured over nitric and mainly circulates in US cities. Moreover, winter conditions promote $PM_{2.5}$ concentrations in several Midwestern locations in the US with large sensitivity to NH_3 emissions. Except that semi-natural ecosystems will only be achieved if NH_3 emissions are drastically reduced (Pinder, Gilliland, & Dennis, 2008).

However, there seem not to be sufficient interest about NH_3 emission and its effects in developing countries such as Nigeria and needs to be investigated (Aneja., Stahel, Rogers, Witherspoon, & Heck, 1978; Olszyna, Bairai, & Tanner, 2005). In determining the concentration of ammonia in urban air, Richard, Canales, Flocchini, and Morales (2014) utilized Ogawa passive samplers by absorbing ammonia on two replicate cellulose pads coated with citric acid forming ammonia citrate. Their findings established that agricultural activities significantly contribute to the presence of ammonia based fine particle aerosols in the atmosphere (Klein, Olson, & McKinney, 1985).

In addition, at high concentrations exposure to ammonia could affect the quality of life, personal comfort and well-being in urban cities as noted by Hsieh and Chen (2010). Some of the health side effects of NH_3 include; impairment of respiration and irritation of the eyes, nose and throat (Pyatt, 2003). Hence, this research paper will investigate the levels of ammonia in different parts of Owerri Metropolis and its ecological impact.

2. MATERIALS AND METHODS

2.1. The Study Area

The study area is Owerri, the Capital city of Imo state, Nigeria, located in Southeastern Nigeria on longitude 6^0 50' to 7^0 50 E' East and on latitude 4^0 45' to 7^0 15' N. Owerri is a rapid developing urban city with beehive commercial, residential and administrative activities. Three local government areas make up Owerri city namely Owerri municipal, Owerri North and Owerri West. It has an estimated population of about 400,000 with an area of approximately 100 square kilometers (Okoro, Uzoukwu, & Chiomezie, 2014). It is bordered by Otamiri River in the east and Nworie River in the South. The Otamiri water shed covers about 10,000 km with an annual rainfall of 2250-2500 mm. The watershed is mostly covered by depleted rainforest vegetation, with mean temperatures of 27 ^{0}C all through the year (Osuagwu, Nwachukwu, Nwoke, & Agbo, 2014). A detailed description is obtained in the map Figure 1 below showing owerri municipal at the central map and bordered on the left by Owerri west and on the right by Owerri North.

Figure-1. Map of Owerri city showing study areas.

2.2. Sampling Strategy

In this study, nine different locations were selected for NH_3 monitoring. The locations were: Municipal, Naze, Nekede, Egbu, Akwakuma, Avu, Irette, Umuguma and Uratta. They sampling locations of Naze, Avu, Nekede and Irete are in Owerri west, while umugumma, uratta and egbu are in Owerri north. Owerri Municipal is the central city and has several congestion points. Therefore, the allocation of the sampling sites in each location was based on random and representative sampling to comprise the major areas of anthropogenic activities. In addition, each site consists of a major market, clustered urban settlement and traffic congestions during work hours. Field Sampling of NH_3 was conducted at the different sites within the study locations shown in Figure 1. Five hundred and forty (540) samples were taken and averages reported. Five different sampling points was selected for each location from August 2018 to October 2018, with rainy days excluded. The value determined reported were averages recorded. On each sampling day, NH_3 gas monitor was deployed for 6 hours at sites and the gas monitor operated on 09:00–15:00 daily-cycle at all the sampling sites.

2.3. Instrumentation

The concentrations of ammonia in the locations were measured using portable in-situ gas monitor made by Crowcon gas instruments, with model number 1458C. The monitor is calibrated in mg/L with detection limit of 0.001 mg/L. Ammonia is lighter than air, so the monitor was positioned in the breathing zone, four to six feet above ground level, or the emission sources. The monitor contains an in-built electrical transducer known as the sensor. The sensor is made of SnO_2 semiconductor, which operates on the principle of conductance change due to chemisorptions of gas molecules to the SnO_2 sensing layer. When the monitor was switched on, SnO_2 crystal becomes heated and oxygen (O_2) is adsorbed on the surface with a negative charge. This increases the sensor resistance while preventing electric current flow. With its high electron affinity, O_2 attracts free electrons inside SnO_2 thus forming potential barrier at the grain boundaries as shown in Figure 2 below. Therefore, in the presence of NH_3 gas on the sensor, the surface density of adsorbed O_2 is decreased as it reacts with NH_3 gas. Then electrons are released into SnO_2 and current flows through the sensor dropping the resistance of the sensor (Azad, Akbar, Mhaisalkar, Birkefeld, & Goto, 1992). The concentration of NH_3 gas is detected by measuring the resistance of the sensor via direct digital read out.

3. RESULTS AND DISCUSSION

Ammonia concentration levels over the three months period (August, September and October), for the nine locations are shown in Figure 2. The mean concentrations of NH_3 across the months ranged from 0.012 to 0.028 mg/L, while its mean concentration across the locations ranged from 0.019 to 0.028 mg/L. Also, observation shows that the concentrations of ammonia in all measured locations were below 0.3 mg/L, hence primary toxicity of NH_3 in plants within all regions will not arise because NHy^+ arises as soon as uptake exceeds assimilation capacity in plants (Fangmeier et al., 1994). The frequency distribution pattern of ammonia gas in municipal is seen in Figure 2 above. The distribution is skewed towards high frequency and high concentration with a mean and standard deviation of 0.028 ± 0.01 mg/L.

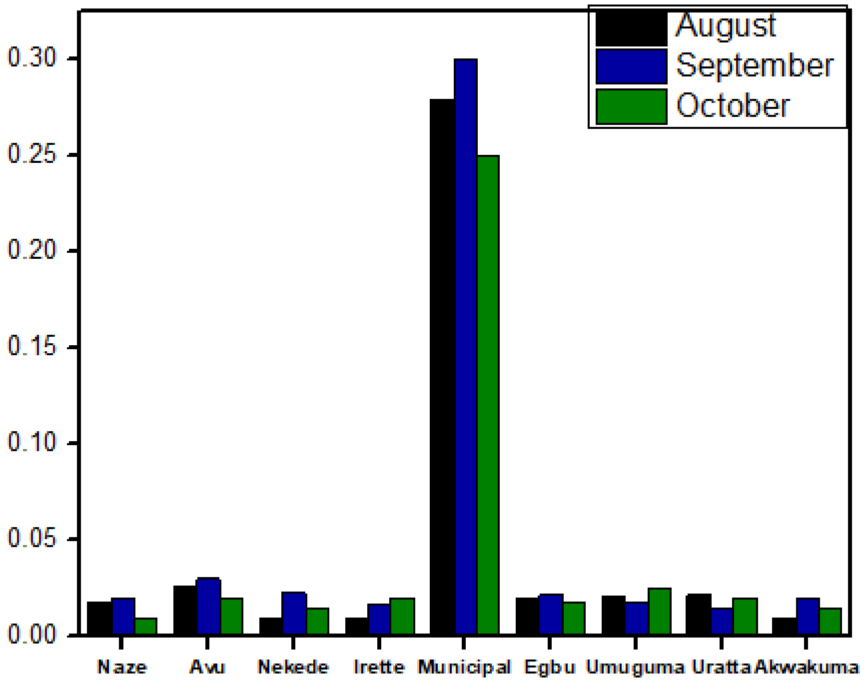

Figure-2. Column plot for NH_3 distribution in sampled locations.

The municipal ammonia concentration levels were significantly higher than other locations. This correlated with studies that characterized municipal with high population and traffic density in the midst of congested and high-rise buildings. This observed pattern could be because of ammonia emissions arising from road transportation network, uncovered decaying refuse dump and household combustion (Okoro et al., 2014; Osuagwu et al., 2014). The frequency distribution pattern of ammonia gas in other locations is skewed towards high frequency of lower concentrations with small mean values (0.012 ≥ 0.025) and standard deviations (0.01 ± 0.002) mg/L. These values may arise because most of the residents indulge in farming activities, bush burning, and landfill near the area. Also this pattern of distribution may be due to ammonia emission from fertilizer applications from farmlands and bush burning, household combustion, poultry and animal rearing operations (Sutton, Reis, & Baker, 2009)(CENR 2000).

The result of the two-way ANOVA without replication is presented in Table 1 below. Now there two hypotheses: the columns represents the sampled months of August, September and October while the rows represents the nine different locations.

ROW: Since the p-value is less than the alpha value of 0.05 %, then the different places had no significant effect and common hypothesis can be rejected. In addition, since the F-value is greater than F-critical, the null hypothesis can be rejected, as there is significant statistical difference in the mean value of parameters (locations).

Table-1. ANOVA plot for NH_3 distribution in sampled locations.

ANOVA						
Source of variation	**SS**	**df**	**MS**	**F**	**P-value**	**F-Critical**
Rows	0.177916	8	0.022243	269.2073	1.41×10^{-15}	2.591096
Columns	0.000299	2	0.000149	1.807363	0.196021	3.633723
	0.001322	16	8.26×10^{-5}			
Total	0.179567	26				

This statistical argument is valid because the highest mean across location was 0.2766 at municipal while the lowest mean was 0.0150 at akwakuma, equivalent to 5.4 % of 27.

COLUMN: The p-value (0.196) is greater than 0.05 % alpha value, therefore the effects of the different months were significant and the common hypothesis cannot be rejected. Also, the F-value at 1.807 was less than the F-critical value of 3.633, then null hypothesis cannot be rejected and there is no significant difference in the calculated mean. This statistical argument strongly holds because the highest mean value across months was 0.05156 in August while the lowest was 0.04367 in October, equivalent to 85 % of 51.

3.1. Ecosystem Impact

Applicable information from studies on the impacts of nitrogen on natural and semi-natural ecosystems was incorporated into the existing European database on empirical critical levels. Critical levels are defined as concentrations of pollutants in the atmosphere above which direct adverse effects on receptors, such as materials, plants, human beings and ecosystems, may occur according to present knowledge. Critical loads, refers to the mass transfer to a receptor, and critical levels, which are based on concentrations. These concentrations can be used to determine deposition although deposition varies with ecosystem type and meteorology. It is needed to assess impacts of air pollution on ecosystems and on organisms respectively. The values for critical load exposure and occupational exposure are presented in Tables 2 and 3 below. In Table 2, 8 μg/m³ concentration of ammonia directly affects human health through the formation and inhalation of secondary particles. Also at 1 μg/m³ levels, lichens and bryophytes form a key part of the ecosystem, while at 3 μg/m³ all other vegetation forms a key part of ecosystem integrity. From the study, all locations sampled were considerably higher than all critical load threshold values. Accordingly, what Table 3 describes is that at such levels, a significant contribution to ill-health of workers/workforce may arise. Such cases may increase at home via certain domestic cleaning products, animal housing and slurry handling in agriculture.

Table-2. Critical load of NH_3 concentrations.

Ecosystem	**Concentration /threshold (μg/m³)**	**Concentration/ threshold (mg/L)**
Lichens and Bryophytes are key ecosystems	1	1×10^{-6}
Lichens and Bryophytes are not key to ecosystem	3	3×10^{-6}
Human health impacts	8	8×10^{-6}

Source: Doyle, Cummins, Augustenborg, and Aherne (2017).

Table-3. Occupational exposure limits to NH_3 concentrations.

Exposure duration (hours)	**Concentration (μg/m³)**	**Concentration (mg/L)**
8	17,000	0.017
15 mins	27,000	0.027

Source: Doyle et al. (2017).

The implication is that lichens and bryophytes are not critical to the sampled areas, neither was any vegetation growth critical to sampled area having exceeded their threshold. In addition, the health impact threshold was also exceeded. This relationship reflects the correlation between organic and mineral NH_3 variability in the land and observed atmospheric NH_3 concentration and NH_3 uptake. Because fast-growing species adapted to high nutrient availability thrive in a nitrogen-rich environment and subdue species, which are more sensitive or uncommon On the other hand, the levels of NH_3 at municipal area (0.23 mg/L) exceeded the occupational exposure limits. However, the duration levels will relatively vary among individuals. This therefore calls for an immediate critical action by the government and concerned agencies, which should include three key areas as follows. Regulation can be applied at different levels, such as setting targets and levels of emissions. Secondly, disseminating information about how to effectively implement new techniques and interventions. Finally, Incentives can provide financial motivation to individuals, companies and organizations to take particular actions and support regulatory initiatives. At other sampled areas, it was only Avu alongside Irette at 0.015 mg/L and Nekede at 0.016 mg/L that were lower than occupational exposure limit of 0.017 mg/L. However, the values are closely successive to each other. The other sampled areas exceeded occupational exposure limit with Umuguma highest at 0.021 mg/L. This correctly identified umuguma as another commercial and residential area next to municipal and larely contaminated with NH_3 gas.

Finally, across the months, the average values were significantly higher than occupational exposure limits and critical load of NH_3 concentrations. Subsequently, this demands a critical action to reduce and control this air pollutant within all sampled areas or there may be loss of biodiversity. Similarly, Problems may arise for many plant species in natural and semi-natural ecosystems, as they can only compete where nitrogen is in low supply. Finally, Ammonia pollution also influences species composition through soil acidification and leaching of soil nutrients. For example in strongly acidic soils with $pH < 4.5$, a build-up of exchangeable NH_4^+ occurs and inhibiting nitrification. This in turn induces accumulation and results in the displacement of essential growth cations Ca^{2+}, Mg^{2+} and $K^+$from cation exchange sites and their subsequent leaching from the soil (Doyle et al., 2017; Guthrie et al., 2018).

4. CONCLUSION

Air pollution alerts have become nearly daily occurrences in Owerri metropolis that we cannot escape from it as seen from our present study. Although, the concentrations of ammonia gas detected throughout the study areas revealed high levels enough to cause serious health problems and disruption of ecosystem, however, permanent ammonia monitoring gas network will greatly assist to overcome this city pollutant. Finally, ammonia is rarely measured routinely; additional deposition monitoring is needed in these under-sampled regions in order to assess the impacts to sensitive terrestrial and aquatic ecosystems.

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REFERENCES

Aneja, V. P., Chauhan, J., & Walker, J. (2000). Characterization of atmospheric ammonia emissions from swine waste storage and treatment lagoons. *Journal of Geophysical Research: Atmospheres*, *105*(D9), 11535-11545.Available at: https://doi.org/10.1029/2000jd900066.

Aneja., V., Stahel, E., Rogers, H., Witherspoon, A., & Heck, W. (1978). Calibration and performance of a thermal converter in the continuous atmospheric monitoring of ammonia. *Analytical Chemistry*, *50*(12), 1705-1708.Available at: https://doi.org/10.1021/ac50034a036.

Azad, A., Akbar, S., Mhaisalkar, S., Birkefeld, L., & Goto, K. (1992). Solid-state gas sensors: A review. *Journal of the Electrochemical Society*, *139*(12), 3690-3704.

CENR. (2000). Committee on the environment and natural resources air quality research subcommittee atmospheric Ammonia: Sources and fate a review of ongoing federal research and future needs. 1-13. Retrieved from: https://www.esrl.noaa.gov/csd/aqrsd/reports/ammonia.pdf.

Doyle, B., Cummins, T., Augustenborg, C., & Aherne, J. (2017). Ambient Atmospheric Ammonia in Ireland, 2013-2014, Report No 193.1-62. Retrieved from: https://www.epa.ie/pubs/reports/research/air/.

Fangmeier, A., Hadwiger-Fangmeier, A., Van der Eerden, L., & Jäger, H.-J. (1994). Effects of atmospheric ammonia on vegetation—a review. *Environmental Pollution*, *86*(1), 43-82.Available at: https://doi.org/10.1016/0269-7491(94)90008-6.

Guthrie, S., Giles, S., Dunkerley, F., Tabaqchali, H., Harshfield, A., Ioppolo, B., & Manville, C. (2018). Impact of ammonia emissions from agriculture on biodiversity: An evidence synthesis.1-60. Retrieved from: https://royalsociety.org/~/media/policy/projects/evidence-synthesis/Ammonia/Ammonia-report.pdf.

Hsieh, L.-T., & Chen, T.-C. (2010). Characteristics of ambient ammonia levels measured in three different industrial parks in Southern Taiwan. *Aerosol and Air Quality Resarch*, *10*(6), 596-608.Available at: https://doi.org/10.4209/aaqr.2010.06.0044.

Klein, J., Olson, K., & McKinney, H. (1985). Caustic injury from household ammonia. *The American Journal of Emergency Medicine*, *3*(4), 320-320.Available at: https://doi.org/10.1016/0735-6757(85)90055-5.

O'kane, G. (1983). Inhalation of ammonia vapour: A report on the management of eight patients during the acute stages. *Anaesthesia*, *38*(12), 1208-1213.Available at: https://doi.org/10.1111/j.1365-2044.1983.tb12527.x.

Okoro, B., Uzoukwu, R., & Chiomezie, N. (2014). River basins of Imo State for sustainable water resources management. *Journal of Civil and Environmental Engineering*, *4*(1), 1-8.Available at: https://doi.org/10.4172/2165-784x.1000134.

Olszyna, K. J., Bairai, S. T., & Tanner, R. L. (2005). Effect of ambient NH3 levels on PM2. 5 composition in the Great Smoky Mountains National Park. *Atmospheric Environment*, *39*(25), 4593-4606.Available at: https://doi.org/10.1016/j.atmosenv.2005.04.011.

Osuagwu, J., Nwachukwu, A., Nwoke, H., & Agbo, K. (2014). Effects of soil erosion and sediment deposition on surface water quality: A case study of Otamiri River. *Asian Journal of Engineering and Technology*, *2*(5), 438-442.

Pandolfi, M., Amato, F., Reche, C., Alastuey, A., Otjes, R., Blom, M., & Querol, X. (2012). Summer ammonia measurements in a densely populated Mediterranean city. *Atmospheric Chemistry & Physics*, *12*(16), 7557-7575.Available at: https://doi.org/10.5194/acp-12-7557-2012.

Pinder, R. W., Gilliland, A. B., & Dennis, R. L. (2008). Environmental impact of atmospheric NH3 emissions under present and future conditions in the Eastern United States. *Geophysical Research Letters*, *35*(12), 1-6.Available at: https://doi.org/10.1029/2008GL033732.

Pyatt, F. (2003). Potential effects on human health of an ammonia rich atmospheric environment in an archaeologically important cave in Southeast Asia. *Occupational and Environmental Medicine*, *60*(12), 986-988.Available at: https://doi.org/10.1136/oem.60.12.986.

Rattray, G., & Sievering, H. (2001). Dry deposition of ammonia, nitric acid, ammonium, and nitrate to alpine tundra at Niwot Ridge, Colorado. *Atmospheric Environment*, *35*(6), 1105-1109.Available at: https://doi.org/10.1016/s1352-2310(00)00276-4.

Richard, T. A., Canales, M., Flocchini, R. G., & Morales, R. G. (2014). Urban atmospheric Ammonia in Santiago City, Chile. *Aerosol and Air Quality Research*, *14*(1), 33-44.Available at: https://doi.org/10.4209/aaqr.2012.07.0189.

Robarge, W. P., Walker, J. T., McCulloch, R. B., & Murray, G. (2002). Atmospheric concentrations of ammonia and ammonium at an agricultural site in the Southeast United States. *Atmospheric Environment*, *36*(10), 1661-1674.Available at: https://doi.org/10.1016/s1352-2310(02)00171-1.

Sather, M. E., Mathew, J., Nguyen, N., Lay, J., Golod, G., Vet, R., & Callison, R. (2008). Baseline ambient gaseous ammonia concentrations in the Four Corners area and eastern Oklahoma, USA. *Journal of Environmental Monitoring*, *10*(11), 1319-1325.Available at: https://doi.org/10.1039/b807984f.

Sutton, M. A., Reis, S., & Baker, S. M. H. (2009). Atmospheric ammonia: Detecting emissions and environmental impacts. Samantha Eds (1st ed., pp. 123-180). The Netherlands: Springer Science and Business Media B.V.

Zhao, M., Wang, S., Tan, J., Hua, Y., Wu, D., & Hao, J. (2016). Variation of urban atmospheric ammonia pollution and its relation with PM2.5 chemical property in Winter of Beijing, China. *Aerosol and Air Quality Research*, *6*(16), 1378-1389.Available at: https://doi.org/ 10.4209/aaqr.2015.12.0699.