MONITORING NOX AND O3 IN URBAN ATMOSPHERE: A COLORIMETRIC APPROACH IN ILORIN, NIGERIA

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Abstract: This study presents an assessment of oxides of nitrogen (NOX) and total oxidants as ozone (O3) over the airshed of a typical average tropical equatorial city using a colorimetric approach. The concentrations of NOX and O3 were monitored at three urban site classes and a control site using a high-volume sampler for three years. The mean concentrations for all sites during the wet season (May - October) were 3.31 ± 0.40 ppb for NOX and 21.86 ± 2.47 ppb for O3, while the dry season (November - April) mean concentration values were 2.03 ± 0.23 ppb for NOX and 32.44 ± 5.13 ppb for O3. The mean value at the control site was an order of magnitude lower than the urban sites during the two seasons, except for the concentration of O3, which was higher during the dry season. Traffic density and trace gas concentrations showed a good correlation of 0.98 (P<0.05). NOX was confirmed to be a strong precursor for O3 formation. The influence of Harmattan dust in impeding the photochemistry of O3 formation from November to January (NDJ) months was observed. The overall concentration levels of NOX and O3 for the airshed were 2.67 ± 0.32 and 27.15 ± 3.8, respectively, which are within the limit of United States Environmental Protection Agency (USEPA) guidelines for air quality standards.

Keywords: oxides of nitrogen (NOX), ozone (O3), colorimetric approach, urban atmosphere, Harmattan dust, air quality standards.

1.0 Introduction

Atmospheric pollution is one of the most dominant problems associated with urbanization. Urban areas are associated with high density of industries and transport networks, among other infrastructure, which generate a wide range of air pollutants. The concentrations of oxides of nitrogen ($NO_X = NO + NO_2$) in the urban atmosphere are mainly associated with industrial boilers, and non-industrial fuel combustions by both stationary and mobile sources. In addition, some of these primary pollutants are involved in photochemical transformations in the atmosphere under favourable conditions to produce secondary pollutants. Pollutants, which are photo-chemically generated in the atmosphere, are commonly referred to as photochemical oxidants, in view of their formation pathways. Ozone is one of the most recognized parts of photochemical oxidants. Others include peroxyacetylnitrate (PAN), hydrogen peroxide (H_2O_2), and so on, usually in a web of multi-path photochemical

transformation processes. Ozone and PAN are known to be associated mainly with photochemical oxidation of NO_X and a range of non-methyl volatile organic compounds (NMVOC) in the atmosphere under

favourable photo-dissociation conditions (Thomas *et al*., 1974)

In most developed countries which have urban areas ranging from small to mega-cities, the formulation of polices that could bring about reduction of these pollutants concentrations levels are supported by routine monitoring and modelling, which have now remained essential programmes supported by government and private sector agencies. Experience from these countries indicate that a wide range of methods exist which are routinely deployed for either on-the-spot sampling, or for systematic observations which yield trends in atmospheric mixing values over time. The most precise of these techniques are those relying on infrared (IR), ultraviolet (UV) and other relevant atomic/molecular spectrometry techniques. These techniques have also been known to be very cost intensive, as well as demanding in both the level of human capacity support and maintenance requirements.

In the less developed countries, especially those in Africa, air quality monitoring and modelling are yet to become routine scientific activities, leading to data which are highly sparse or sometimes not at all in existence. The challenge therefore on scientists is to rise to the demand of providing the needed information to support policies, which could improve the management of urban and rural air quality. These challenges are in most cases, countered by the high cost of atomic and molecular spectroscopy-based analysers. The ability of these countries to deploy these precision techniques is known to be low. As proper management of total environment in these countries requires the acquisition and archiving of trends in atmospheric mixing values of air toxics in both rural and urban areas routinely, the development and application of less expensive but reliable and reproducible techniques have been advocated widely. The colorimetric method (Saltzman, 1954; Saltzman and Gilbert, 1959) is among the techniques, which have been established as adequate for the monitoring of NO_X and O_3. This technique form the basis of the measurements presented in this study.

The main objective of this study is to determine the concentrations of NO_X and O_3 and the mixing values of these gases, in the atmosphere of different urban locations in the city of Ilorin, Nigeria. These mixing values will then be compared with similar urban centre measurements elsewhere. The influence of air-shed photochemistry on the concentration of NOx and ozone during the seasonal transitions between Harmattan to Rain and Rain to Harmattan will be evaluated. Additionally, the concentrations of these pollutants will be compared with World Health Organization (WHO) or United States Environmental Protection Agency (EPA) maximum permissible limits and the implications to public health will then be discussed.

2.0 Materials and Methods 2.1 Study Area

The city of Ilorin is located on latitude 8 20'N and longitude 4 35'E, at an approximate altitude of 306 m above the mean sea level. The city is strategically located in the Guinea Savanna belt of Nigeria, at what may be described as the geographical and cultural confluence of the Northern and Southern parts of the country. As a result of its location, Ilorin experiences two major seasons during an annual cycle, the dry and the wet seasons. The persistence of either season is influenced by the absolute fraction of time during an annual cycle that the line of the Inter-Tropical Convergence Zone (ITCZ) or the Inter-tropical Discontinuity (ITD), as it is called in West Africa, is below or above its line of latitude.

The dry season (under the influence of the north-east trade winds, when the ITD is south of the city), on the average, starts around the middle of October and lasts until the middle of April of the following year, though more pronounced between mid-November and mid-February. Rains initiated by predominance of southwest monsoon winds about the remaining six months of the year in the area, when the ITD lies north of the city. The dry season period is characterized, not only by near absence of rain, but also by transport of dust haze from the Sahara Desert

into the region. The winds are generally cold because they form part of the Hadley cell, which is known to move equator-ward from the poles at ground levels, and pole-ward from the equator at upper levels. The Harmattan period, being wintertime in Europe, implies that very cold air, drafted across Europe through the Sahara, arrives in the subregion, carrying the Sahara dusts with it. The season is characterized by high atmospheric turbidity, which inhibits the penetration of a significant fraction of the incident solar radiation to the earth's surface.

In development terms, the city is semi-industrial in the sense that, although a relatively large urban centre geographically by national standard, there seems to be very little presence of large scale industries that could qualify as major point sources. Hence, apart from the few industries, which are sparsely located, the rest of the city is dominated by mobile sources from the expanse of road network across the city, and area sources, which are a mix of residential, commercial and, medium to small scale industries. As for other major cities in the country, no strict demarcation exists between industrial, residential and commercial areas. Most industrial areas have admixtures of commercial and residential premises. The converse holds for commercial and residential areas.

2.1.1 Choice of Sampling Sites

In the absence of clearly demarcated urban industrial, commercial and residential areas, it was not possible to identify sampling sites, which fits exactly into these major categories. In place of such urban classification scheme, the sampling locations were selected across the city to reflect the following categories of interest:

•High traffic volume/medium population density (HT-MPD) zones

•Medium traffic volume/High population density (MT-HPD) zones

•Industrial areas/Low traffic volume (IA-LT) zones, and

•Low population density/No traffic (LPD-NT) zone was used as control (CTR).

2.2 Preparation of Absorbing and Sampling Solutions

Total oxidants were determined by buffered potassium iodide solution method proposed by (Saltzman and Gilbert, 1959). Determination of oxides of nitrogen concentrations was based on the methods of ICMA (ICMA, 1972), which was an adaptation of the Saltzman (1954) colorimetric, azo-dye forming reagent. The application of these techniques to the monitoring required the preparation of the following range of reagents as sampling and absorbing solutions.

2.2.1 Preparation of 1% Neutral-Buffered Potassium Iodide solution

In order to prepare the neutral-buffered potassium iodide solution, 13.61 g of anhydrous potassium dihydrogen tetra-oxo-phosphate (V) $\{KH_2PO_4\}$, 14.20 g of anhydrous di-sodium hydrogen tetra oxo-phosphate (V) $\{Na_2HPO_4\}$, and 10 g of potassium iodide (KI) were successively dissolved in distilled water in a 1.0 litre volumetric flask. The solution was made up to 1 litre mark on the flask.

2.2.2 Preparation of Saltzman Solution

In order to prepare the colorimetric solution, azo-dye forming reagent, 5.0 g of anhydrous sulphanilic acid $\{HNC_6H_4SO_3H\}$ and 140 cm^3 of glacial acetic $\{CH_3COOH\}$ acid were added to 250 cm^3 distilled water in 1litre volumetric flask, the solution warmed and allowed to cool to room temperature. Twenty (20) cm^3 of a 0.1 % stock solution of N–(1-naphthyl) ethylene di amine di hydrochloride $\{2HClNH_2 (CH_2) 2NHC_{10}H_7\}$ and 1 % acetone $\{CH_3COCH_3\}$ was added to retain the colour. The volumetric flask was shaken thoroughly and the solution made up to the mark with distilled water.

The chemicals used in the preparation of sampling and absorbing solutions were all of analytical grade. The reagents had been stable prior to their use.

2.3 Sampling

The detailed of the air sampling set up used has been presented by (Abdul Raheem *et al.,* 2013). A vacuum pump draws air from the atmosphere into sampling solution in a bubbler tube at a mean flow rate of 1000 cm^3 per minute.

The volume of absorbing solution used was 30 cm^3 to ensure that enough sample dissolved in the absorbing solution based on their low concentration in the atmosphere. All joints in the sampling train were made airtight through the application of silicon grease. Sampling was undertaken at sixty-minute intervals, after which, the bubbler was removed carefully and the absorbent solution (sample) transferred into sample bottle for analysis. For NO$_x$ a fritted bubbler was used to improve collection efficiency. The method was authenticated by the use of a LaMotte air sampler (LaMotte, 2005) imported from LaMotte and Company U.S.A along with standard reagents for all the pollutants. In order to determine pollutant variability over daytime periods, air sampling was undertaken at each location over seven defined sixty minutes periods for any sampling day. The ten sampling periods were equitably spaced between approximately 6.00 am and 6.00 pm; a minimum of 60 samples were collected at each site per week for the trace gases monitored. The time of sixty minutes was found from trial samplings to be sufficient for the quantitative sampling of these gases without the absorbing solution being saturated. All samplings reported were carried out in triplicates. The sampling exercise lasted for 3 years between midNovembers to Mid-Februarys. Since road traffic is the common source cutting across all sites classes, the average traffic densities were determined for all sampling locations. Traffic counts were undertaken at hourly intervals. The minimum and maximum temperatures were between 23 ^{0}C and 34.3 ^{0}C (Abdul Raheem *et al.,* 2008), throughout the sampling time.

2.4 Establishment of Atmospheric Concentrations

While the absorbance of the samples and absorbing solutions were measured using Aquamate UV-Visible Spectrophotometer, the absorbance of O$_3$ were measured at 352 nm, while those of NO$_X$ measured at 550 nm using the same UV-visible spectrophotometer with 1 cm^3 cuvette. The results of the absorbance were measured for their equivalent concentrations using the standards prepared from iodine (I$_2$) solution for O$_3$. This provides a calibrated iodine solution equivalent to 1.92 µg of ozone per ml (Stanley, 1975, Dara, 2008). As ozone reacts with iodine ion in neutral buffer solution according to the following equation:

$$O3 + 3I- + H2O \longrightarrow I3- + 2OH- + O2 \qquad (1)$$

The tri – iodide ion liberated has an intense yellow colour. The standard solution was always prepared freshly when needed. Sodium di-oxo nitrate III (NaNO$_2$) standard solutions were prepared with the NO$_X$ absorbing reagent, which allowed the formation of red azo dye of which the absorbance was picked at 550 nm. The absorbances of the standards against their concentrations were used for calibration curve preparation which was used in deducing the respective concentration of the gas in the absorbing solutions (samples). As the standardization was based on the empirical observation that 0.72 mole of NaNO$_2$ produces the same colour as 1 mole of NO$_2$ (Hesketh, 1972). The concentration of each pollutant in the sampled air was finally established as the ratio of the mass in absorbing solution and total volume of air sampled during the period. Both calibration curves displayed very good linear correlations ($R^2 > 0.99$) between concentration of the pollutant of interest and the absorbance respectively for O$_3$ and NO$_X$ in the measuring range.

3. Results and Discussion

3.1 Urban Sites Classification and Traffic volume Density

The specific urban locations and site classification by type of activity are presented in Table 1 together with the results of the hourly traffic counts undertaken at the various urban sites where sampling were undertaken. This shows urban site class HT-MPD, represented by the Post Office Roundabout where the highest traffic density of 2,976 and 1917 vehicles per hour were recorded respectively for both dry and wet seasons over the sampling period. The other two sites had 2202, 1240 and 474, 857 respectively while the background site, represented by the University of Ilorin Research Farm recorded few close to no traffic density throughout the sampling period. In order to relate traffic density with the diurnal variations in the monitored

**Table
1: The coordinates and description of sampling locations**

		ILORIN		
Location	Description	Coordinates		Average Traffic count per hour
1	Medium population density / High traffic volume	08°29"10.4'N, 004°33"51.6'E		1917[a] 2976[b]
2	High population density / Medium traffic volume	08°29"39.7'N, 004°32"48.1'E		1240[a] 2202[b]
3	Industrial area / Low traffic volume	08°27 "00.2'N, 004°32"16.0'E	857[a] 474[b]	
4	Low population density / Very low traffic volume	08°27"49.2'N, 004°39"42.3'E	2a 5b	

[a] Wet season [b] Dry season

Trace gas concentrations, the variation of pollutant concentrations with time of the day and average vehicular volume at all sites during dry and wet seasons is presented in Table 2 and 3 respectively.

Table 2: Variation of pollutants concentration with the time of the day and the vehicular volume at all sites during dry season

Site	Range	Mean	Range	Mean	Ave/veh/count
1	7.11 – 17.51	12.31 ± 2.3	0.78 – 3.86	2.32 ± 0.68	2976
2	16.36 – 71.43	43.89 ± 2.17	1.07 – 2.07	1.57 ± 0.22	2202
3	4.46 ± 22.28	13.37 ± 3.94	0.91 – 3.06	1.98 ± 0.47	474
4	37.45 ± 2.94	60.19 ± 0.06	1.35 – 3.14	2.24 ± 0.40	5

O_3 NO_x

3.2 Air-shed Concentrations of Trace Gases and Day-time Trends

The results of the daytime mean values of the assessment of atmospheric mixing values of the trace gases (NO_X and O_3) in the four urban site types for dry and wet seasons are presented in Table 2 & 3. The results indicate that even though the mean daily concentrations are close in values, significant differences exist among the three site classes. These differences are a reflection of the nature of activities in various areas. For instance, In the case of NO_x medium traffic volume and high population density (MT-HPD) zones and industrial area are higher than high traffic and medium population density (HT-MPD) area by an average of about 28 % while for O_3 high traffic and

medium population density (HT-MPD) and medium traffic and high population density (MT-HPD) are higher than Industrial area by 31 %. The concentration of the trace gases in the control site or background is however, approximately an order of magnitude lower than the other three sites except for O_3 where the value is even higher than the industrial area.

Table 3: Variation of pollutants concentration with the time of the day and the vehicular volume at all sites during wet season

| | O_3 | | NO_x | | |
Site	Range	Mean	Range	Mean	Ave/veh/co unt
1	7.47 – 17.15	12.30 ± 2.14	2.78 – 7.23	5.01 ± 0.98	1917
2	12.35 – 25.86	19.10 ± 2.99	3.08 – 5.97	4.53 ± 0.64	1240
3	28.33 – 52.32	40.33 ± 5.30	0.22 – 1.42	0.82 ± 0.27	857
4	8.26 – 23.15	15.71 ± 3.29	1.97 – 3.81	2.89 ± 0.41	2

The high O_3 concentration at the CTR site was associated with the time taken for the photochemical transformation of NO_X and VOC which are generated at urban sites. During this range of time, the parcels of air carrying the O_3 would have experienced advection in the downwind direction towards rural area, thereby producing higher values at downwind distances. This observation where rural areas have higher O_3 concentration than urban centres is an established urban-rural dispersion for atmospheric O_3 concentration (Wanner *et al.,* 1993; Baumbach and Vogt, 2003). The overall city average for Ilorin from the sites sampled is estimated to be approximately 27.15 ppb for total oxidants and 2.67 ppb for NO_X. These are comparable with values of O_3 and NO_X measured in Lagos in 1993 based on state of the art UV-fluorescence and Chemiluminescence's techniques, and which were respectively in the range 4 to 102 ppb for O_3 and 5 to 45 ppb for NO_X, including periods of episodic events (Akeredolu *et al.,* 2004).

The daytime trends in concentrations of oxides of nitrogen (NO_X = NO + NO_2) in the four sites are presented in Figure 1.
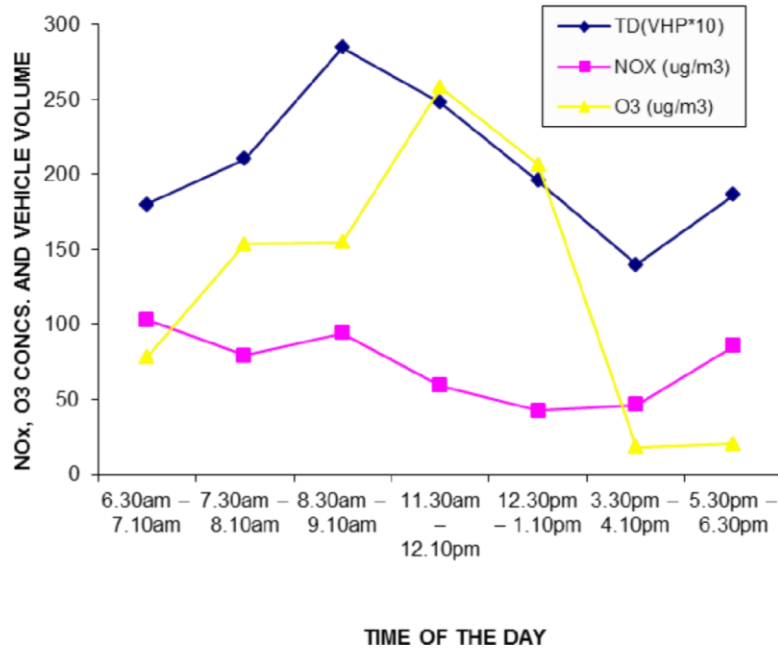
Figure 1: Diurnal Variation of Traffic Density with Trace Gas Concentrations for HT-MPD Sites

NO_X exhibits an early morning maxima between 6.30 and 7.10 am. However, a second maximum appears to show up between 9 and 10 am, which gives way a little later and remains low until late in the evening when the value starts to increase.
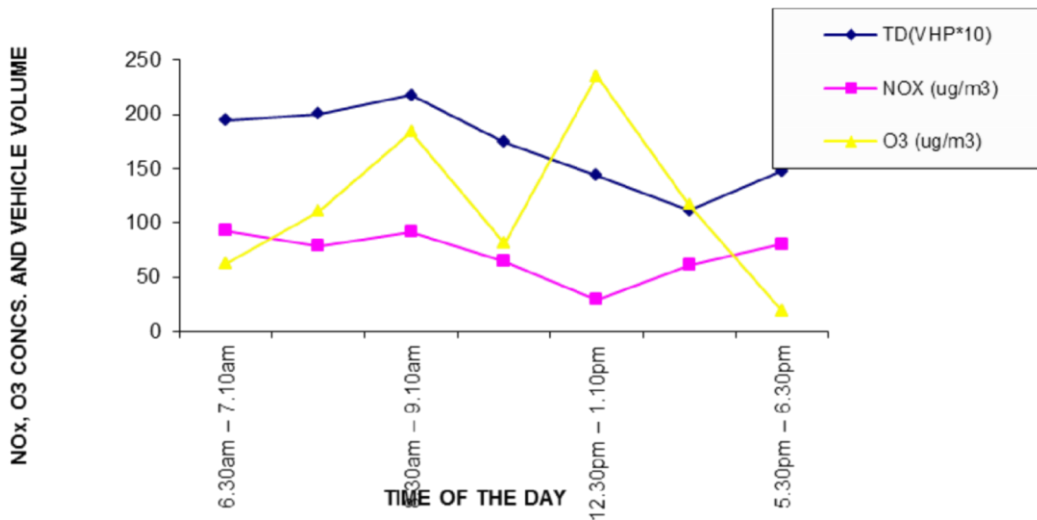

Figure 2: Diurnal Variation of Traffic Density with Trace Gas Concentrations for MT-HPD Sites The daily mean values for the three urban sites are equal, while the background station or control site is also, nearly an order of magnitude lower than the urban sites. The observed trends in the NO_X values may be affected by a combination of factors. Figures 1 to 3 indicate that some weak correlation appears to exist between NO_2 and traffic density for HT-MPD and MT-HPD sites, while being anti-correlated with traffic for the IA-LT sites. Indications are that the early morning peak is most likely dominated by NO emissions, which become photochemically transformed in the late morning and afternoon to NO_2. The weak correlation with traffic may be indicative that other urban sources (industrial, diesel and gasoline generators, and for IA-LT sites, residential burning of firewood and charcoal)

combined with potential emissions from savannas burning (which are rampant during the Harmattan season) may have higher source strengths than traffic.

The trends in measured atmospheric concentration of total oxidants (presented as O_3) at the four sites are presented in Figure 5, unlike the trends for NO_X, total oxidants concentrations
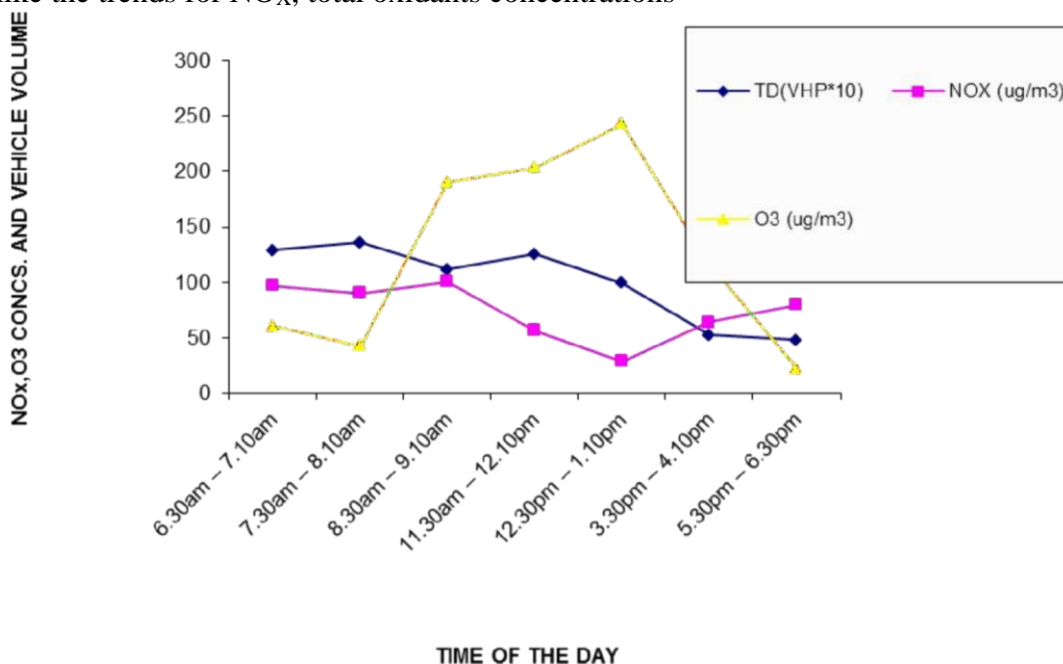

TIME OF THE DAY

Figure 3: Diurnal Variation of Traffic Density with Trace Gas Concentrations for IA-LT Sites appear to have low values in the morning but increases gradually during the day reaching a peak in the midafternoon before eventual gradual decrease to minimum values in the evening.

Figures 1 to 3 indicate that O_3 has an inverse-correlation with traffic density during daytime and reduces towards zero values during the hours when the sun is switched off. These are clearly indicative of the strong influence of solar radiation in the photochemical processes leading to O_3 formation (Abdul Raheem *et al.,* 2008). Since O_3 is not emitted by urban sources, but through photochemical transformation, the observed profile has expected should be strongly correlated with the trends in surface penetration of solar radiation. It is also evident that O_3 is anticorrelated with NO_X in all urban sites classes (Figures 1 to 3), which demonstrates the precursor-role of NO_X in O_3 formation. This could be confirmed by overall regression equations 2 and 3 obtained from regression results showing constants with O_3 as dependent variable for Ilorin data during wet and dry seasons (Tables 4 and 5)

$$[O_3] = 30.76 + 1.09[SO_2] - 3.11[NO_x] \qquad (2)$$
$$[O_3] = 60.48 - 4.25[NO_x] - 2.71[SO_2] \qquad (3)$$

Table 4: Regression results showing constants with O_3 as dependent variable for Ilorin dry season data

Model	Unstandardized Coefficients		Standardized Coefficients	t	Sig.
	B	Std. Error	Beta		

	B	Std. Error	Beta	t	Sig.
1 (Constant)	60.479	10.016		6.038	.000
NOX	4.248	3.158	-.192	1.345	.187
SOX	-2.709	.842	-.460	-3.219	.003

Table 5: Regression results showing constants with O₃ as dependent variable for Ilorin rainy season data

Model	Unstandardized Coefficients		Standardi zed Coefficien ts		
	B	Std. Error	Beta	t	Sig.
1 (Constant) SO2	30.755	4.001		7.686	.000
NOX	1.087 -3.111	2.366 .994		.459 -3.129	.649
					.003
			.074		
			-.507		

3.3 The trend of total oxidant and titration effect

When NO₂ is exposed to UV light ($\lambda < 424nm$), oxygen atom and NO molecule are generated through the NO₂ photolysis reaction. As a result, O₃ is formed as the product of the reaction between O and O₂

$$NO_2 + h\upsilon \rightarrow NO + O \qquad (4)$$
$$O + O_2 \rightarrow O_3 + M \qquad (5)$$

Except when going through the O₃ production cycle, the NO from reaction equation 4 can react with O₃ to regenerate NO₂ as in equation 6

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (6)$$
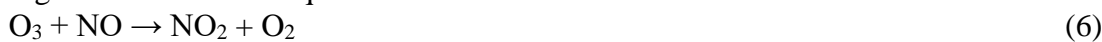
Equations 4 – 6 represent the photochemistry state for O₃, NO and NO₂. Reaction equation 6 is known as titration reaction. Nevertheless, in the case of a fixed O₃ production rate, a decrease in NOₓ emission will reduce the NO available for the titration reaction and, consequently, affect the O₃ – NO – NO₂ equilibrium in the photostationary cycle (Chou *et al.,* 2006)

Figure 4: Mean Daily Mixing Ratios of O₃, Noₓ and O₃+Noₓ of Ilorin Town during Rainy Season
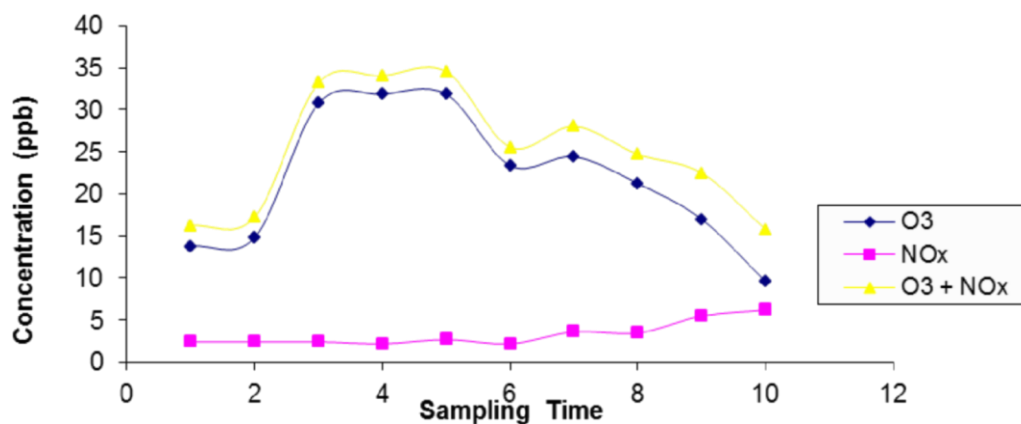
Figures 4 & 5 illustrate the analysis of total oxidants as estimated by $O_3 + NO_2$ instead of O_3. The values are the daily hourly averages of the mixing ratios throughout the period. Contrary to the findings of Chou et al., (2006), $O_3 + NO_2$ show the same seasonal variation with ozone, particularly $O_3 + NO_2$ during wet season. These enhance the seasonal variation with the maxima during the dry season. However the seasonal cycle of ozone / oxidant with dry season maximum and wet season minimum as shown is in accordance with results by other authors (Pissimanis *et al.,* 2000; Monks, 2000). It was observed that the dry season maximum is due to the long range transport of the polluted continental air masses and the prevalence of photochemical reactions. The wet season minimum is as a result of the low ozone concentration in the air masses transported from the regional transboundary.

Figure 5: Mean Daily Mixing Ratios of O_3, No_x and O_3+No_x of Ilorin Town during Dry Season
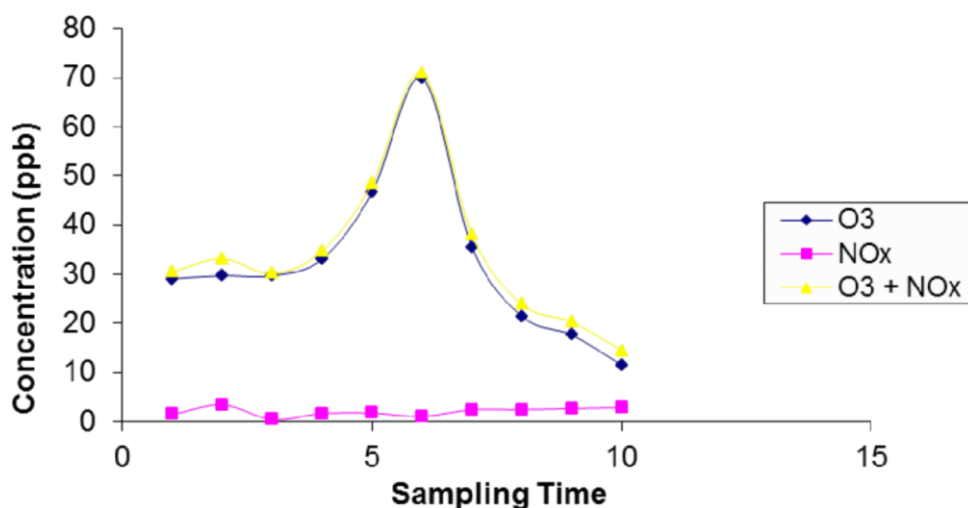
3.4 Implications for Atmospheric Photochemistry of Ilorin Urban

It is well known that NO_X and hydrocarbons serve as precursors in presence of solar radiation for formation of total oxidants. An illustration of the diurnal trends in solar radiation in a typical site in South West Nigeria, which shares the same climatic conditions as Ilorin, is presented in Figure 6 [Obioh's personal communication]. This indicates that solar radiation is initiated at approximate 7.00 hours local time, reaches its peak around mid-day and then gradually reduces to zero at approximately 19.00 hours local time, in what may be closely related to a Gaussian distribution.

Figure 6: Diurnal Trends in Solar Radiation Levels at Ile-Ife, SW Nigeria
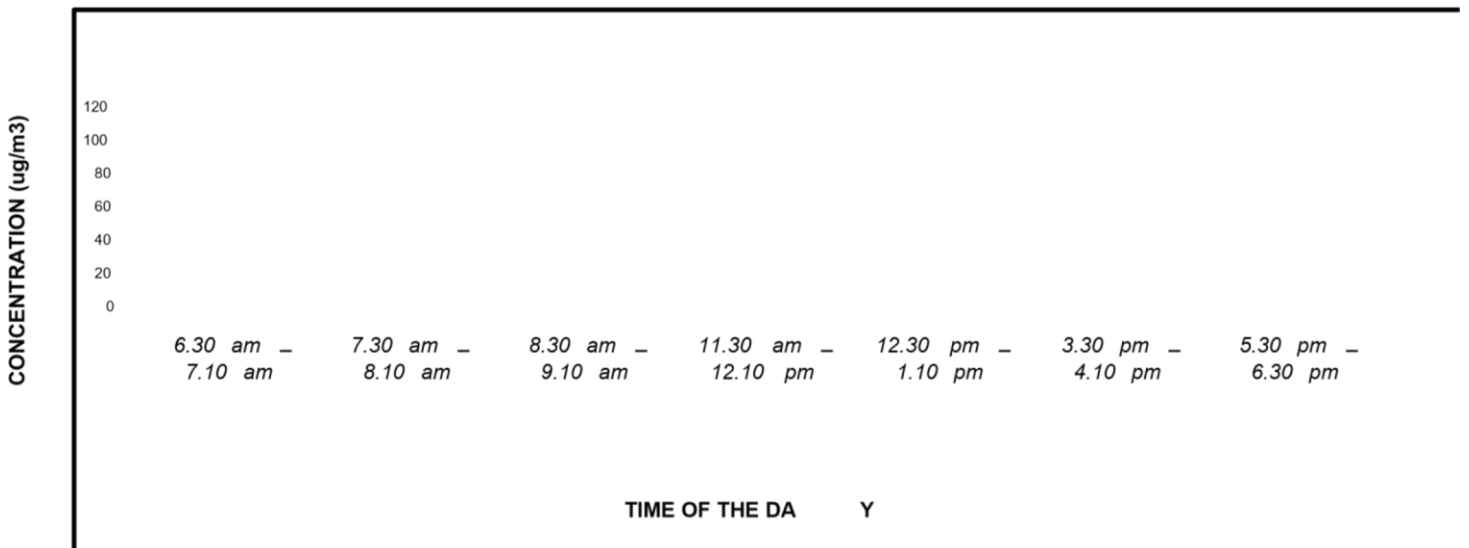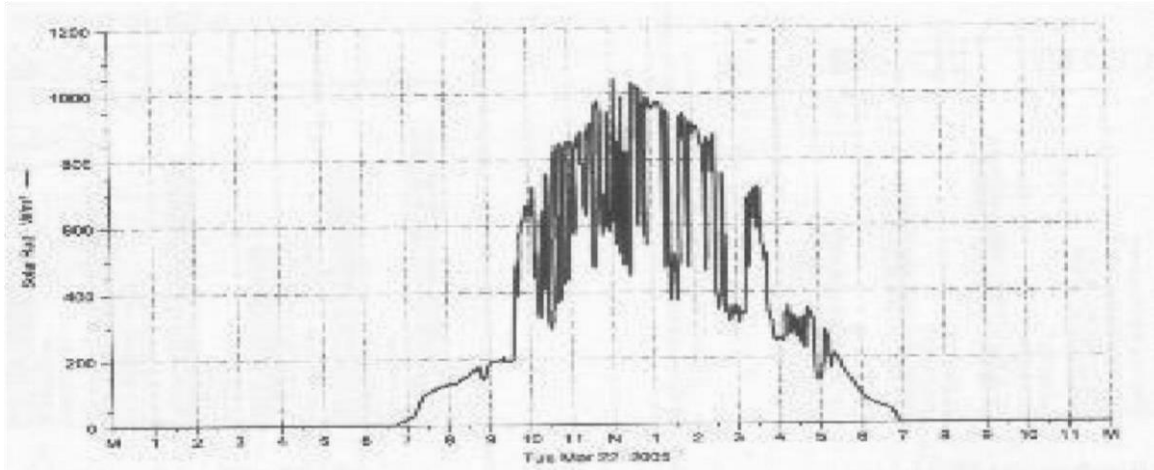
NOX

HT-MPD   MT-HPD

IA-MT   CTR

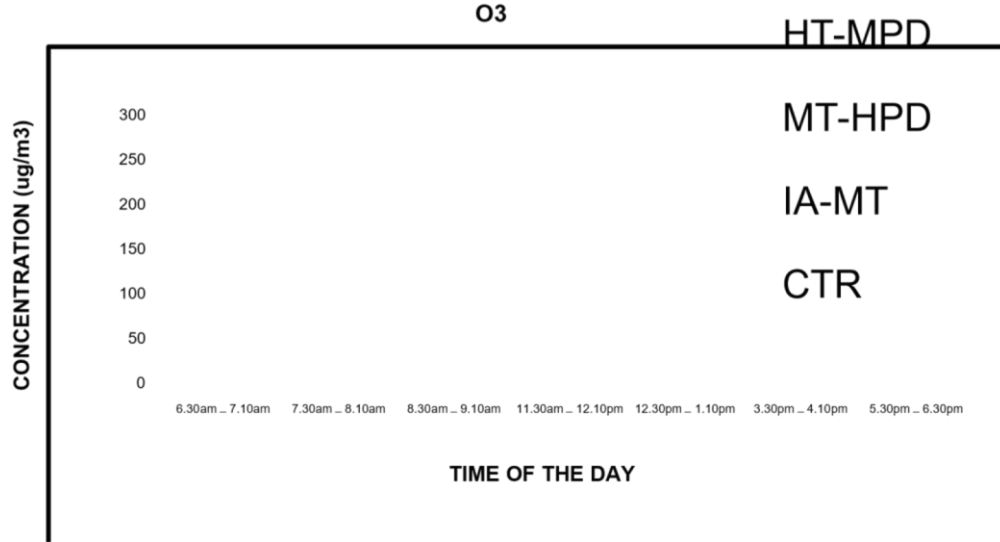**Figure 7: Day-time NO$_X$ Trends in Identified Urban and Control Sites**

Figure 8: Day-time O$_3$ Trends in Identified Urban and Control Sites

The diurnal O$_3$ trends presented in Figures 1 to 3, 7 and 8 are illustrative of the strong correlation between solar radiation levels and O$_3$ concentration. The implication of NO$_X$ in the photochemistry of O$_3$ formation is presented in Figures 9, 10, 11 and 12. From these figures, it is apparent that NO$_X$ values are high in the morning hours in response to the early and mid-morning high traffic, with much less presence of O$_3$.
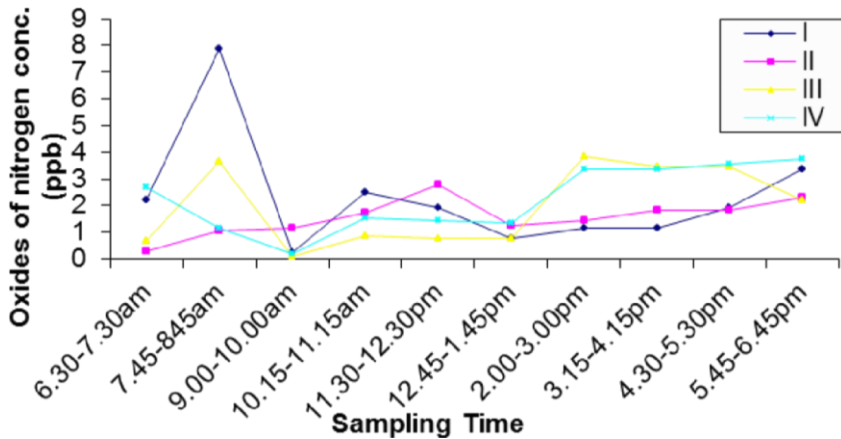

Figure 9: Time Variation of Daily Average Concentration of Oxides of Nitrogen in Ilorin Town during Dry Season
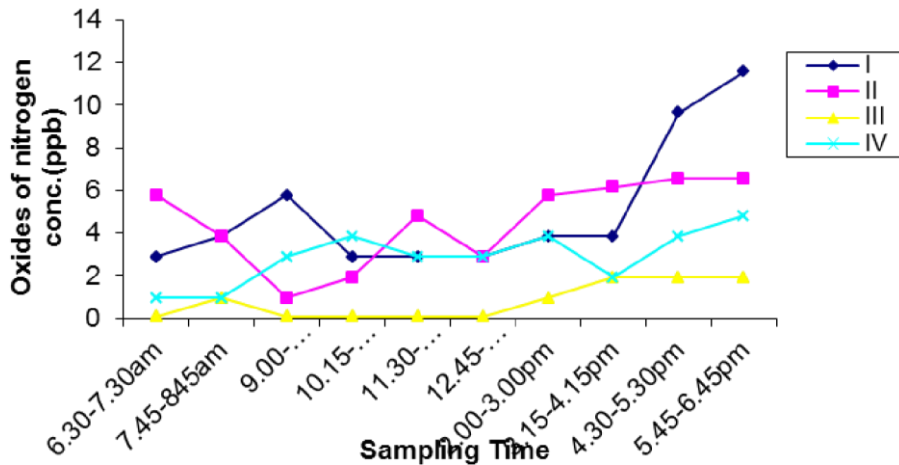
Figure 10: Time Variation of Daily Average Concentration of Oxides of Nitrogen in Ilorin Town during Wet Season

However, in the afternoon hours, even with the late afternoon high traffic, the values of NO_X remain low. At the same time, the value of O_3 that was low in the morning 11 and 12 is now showing significantly high values. This indicates that much of the NO_X emission during the day had been photo-oxidized to O_3, thus confirming a widely known urban photochemical process.
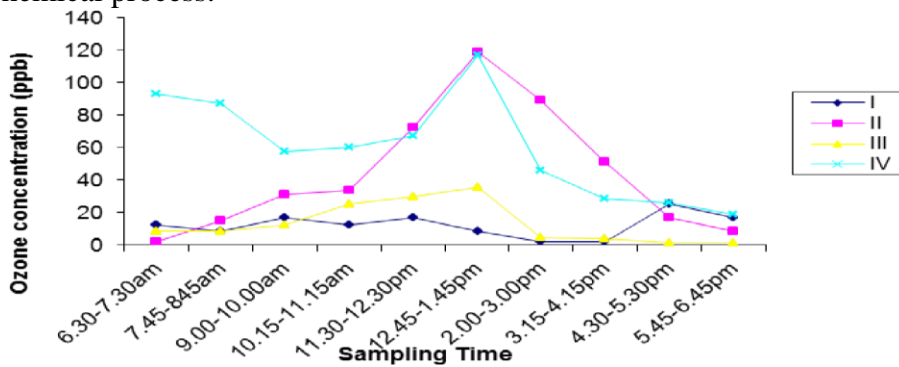

Figure 11: Time Variation of Daily Average Concentration of Ozone in Ilorin Town during Dry Season
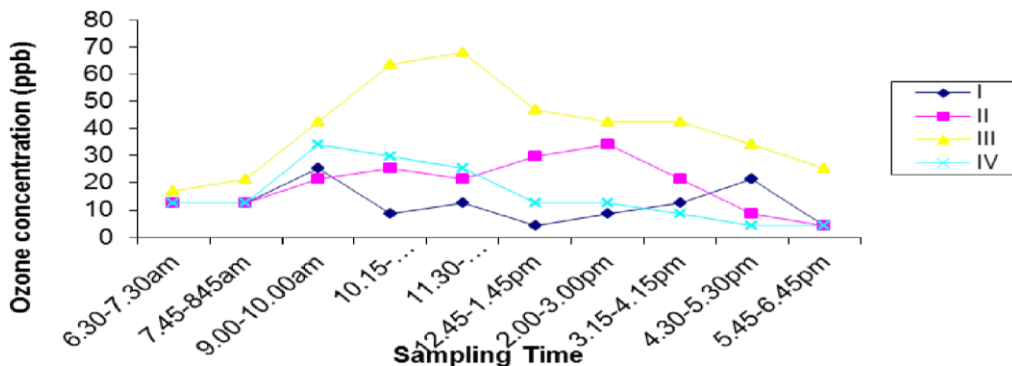

Figure 12: Time Variation of Daily Average Concentration of Ozone in Ilorin Town during Wet Season
Thus NOx dominated the polluted air shed in Ilorin in the morning to mid-afternoon, and by O_3 in the late

afternoon. The atmospheric turbidity during the Harmattan season is generally known to be high, inhibiting optimal surface penetration of solar radiation. As a result, the rates of atmospheric photochemical kinetic processes are expected to be low. This implies that O_3 production currently recorded may be lower than the atmospheric concentrations outside the peak Harmattan season. To enable the quantitative evaluation of the potential role played by Harmattan aerosol in the O_3 photochemical production process, the typical seasonal variability of solar radiation level during an annual cycle in Ilorin is presented in Figure 13.

Figure 13: Typical Seasonal Trends in Meteorological Parameters over Ilorin, Nigeria
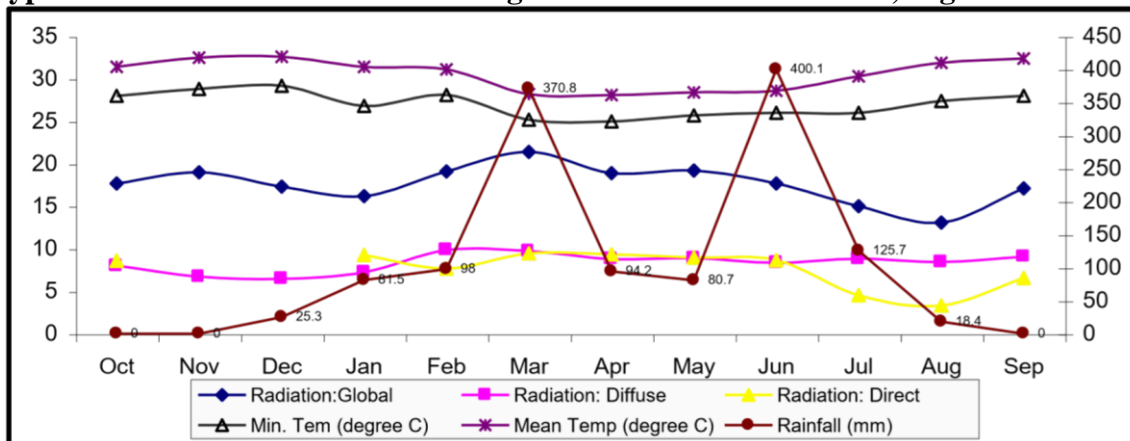
 (Source: NIMET, Ilorin)

This indicates that global solar radiation is minima during the DJF and JJA months during periods when atmospheric aerosols and clouds dominate and provide some shield to the surface penetration of solar radiation. As a result of poor surface solar radiation penetration, limited photochemical reactions dominate these two seasons (Harmattan and wet seasons). The transition periods between Harmattan to Rain (March) and Rain to Harmattan (November) appear to be more favourable to total oxidant formations (Abdul Raheem *et al.,* 2013).

3.5 Comparative Analysis of Implications for Human Health

From the available data of mean levels of NOX and O_3 in Ilorin urban and control sites, the comparative assessment of the level of pollution in the city with some of the known cities of the world has been undertaken as a means for inferring potential health implications of ambient concentrations of NO_X, and O_3. The overall average level for the city, using all the data at our disposal was estimated to be 27.15 ± 3.8 ppb total oxidants and 2.67 ± 0.32 of NO_X. The Ilorin city oxides of nitrogen and ozone concentration levels compared with NAAQS standards as shown in Tables 6. The value obtained for Ilorin may be considered high in view of its limited industrial and transport infrastructure.

This is illustrative of the need for early establishment of local emission factors, identification of reduction strategies which would have to be implemented as a long-term program to reduce the adverse impact of these potential high ambient concentrations on human health as the city strives to improve its industrial and social service infrastructure some of which are directly implicated in the emission of these trace gases.

Table 6: National Ambient Air Quality Standard compared to Ilorin ambient air shed NOx and Ozone concentrations

Pollutant/ Concentration (ppb)	Average Time	NAAQS (primary/secondary	Form	Source
Ozone / 70	8-hour	Primary /Secondary	Annual 4th highest daily maximum 8hour concentration average over 3 years	US EPA, (2017)
NO$_2$ / 100 53	1-hour 1-year	Primary Primary/Secondary	98th percentile of 1hour daily maximum concentration, average over 3 years Annual mean	US EPA, (2017)
O$_3$ /100	8-hour	Primary/Secondary	8-hour mean	WHO, 2005
NO$_2$/ 200 40	1-hour 1-year	Primary/Secondary	Annual Mean	WHO, 2005
O$_3$ / 27.15 ± 3.8 NOx / 2.67 ± 0.32	1-hour		3-year average	This Study

4 Conclusion

The study has provided estimates of the mean concentrations of two trace gases, day-time trends and the potential contributions to the atmospheric photochemistry in the city's air-shed. Results show colorimetric / spectrophotometric technique could be used to obtain results needed to support air quality management as well as some level of understanding of the source strengths, air-shed photochemistry and potential impacts. In particular, it has been confirmed that NOx plays a strong precursor role in the formation of surface O$_3$ in the city. It is also established that some weak correlation exists between NO$_x$ and traffic density for HT-MPD and MTHPD sites, while being anti-correlated with traffic for the IA-LT sites. Indications are that the early morning peak is most likely dominated by NO emissions, which become photochemically transformed in the late morning and afternoon to NO$_2$. For O$_3$, it is demonstrated that there is an inverse-correlation between O$_3$ concentrations and traffic density during daytime. The O$_3$ values reduce towards zero values during the hours when the sun is switched off, which clearly indicate the strong influence of solar radiation in the photochemistry of O$_3$ formation (Abdul Raheem *et al.,* 2013). The observed profile as expected should be strongly correlated with the trends in surface penetration of solar radiation. It is observed that solar radiation penetration to the surface is minimum

during the Harmattan season when the atmospheric aerosol content reaches maximum values and minimum during seasonal transitions between Harmattan to Rain (March) and Rain to Harmattan (November).

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