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DISPARITY IN TROPOSPHERIC AND TOTAL OZONE VARIABILITIES OVER THE TROPICS

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ABSTRACT
This study presents the analysis of tropospheric ozone data with focus on the boundary layer and that of total atmospheric ozone data with focus on the stratospheric layer as released by satellites. It was observed that total ozone concentration at the equatorial zones 5°N-5°S had a significant negative correlation of -0.80 with relative humidity at 100mb, and a stronger positive correlation of 0.92 with relative humidity at the earth surface at pressure of 1000mb. While tropospheric ozone recorded insignificant correlations of -0.15 with the relative humidity at 100mb, and 0.19 with the relative humidity at 1000mb. This observation suggested the contributions of anthropogenic activities in the lower troposphere to the variability of tropospheric ozone. Tropospheric ozone was also observed to have biannual peak seasonal variation while total ozone concentration recorded single-annual peak seasonal trend at the equatorial zones.
Emissions from fossil fuel combustion and other air pollutants are suggested as major contributors to tropospheric ozone variability.

Keywords: Total ozone, tropospheric ozone, anthropogenic emissions

INTRODUCTION
Ozone is of great interest to atmospheric scientists because it is a key factor in controlling the chemical composition of air quality and climate evolution of the troposphere. The troposphere is the lower part of the atmosphere characterized by decreasing temperature with altitude, significant vertical wind motion and water vapor content. At high concentrations tropospheric ozone has adverse effects on human health, terrestrial plants and outdoor materials (World Meteorological Organization (WMO), 1994; Tang and Madronich, 1995). Specifically, tropospheric ozone reacts readily with water vapor to form the hydroxyl radical (OH), which influences the concentration of many atmospheric pollutants. In many regions of the troposphere, hydroxyl radical (OH), nitric oxide (NO), nitrogen dioxide (NO2) and tropospheric ozone (O3) are coupled in various photochemical reactions at wavelength of about 420nm. In addition, the presence of carbon monoxide (CO), methane (CH4), and nonmethane organic gases also contribute significantly to these photochemical reactions in the troposphere. For instance OH reacts with CO, NO2, and CH4 to form carbon dioxide (CO2), nitric acid (HNO3) and methyl radical (CH3) respectively, all of which escalate atmospheric pollution (Jacobson, 2000).

\[ \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}, \]
\[ \text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3, \]
\[ \text{CH}_4 + \text{OH} \rightarrow \text{CH}_2 + \text{H}_2\text{O}. \]

In addition, ozone can absorb thermal radiation and subsequently influence the radiative budget of the troposphere by acting as a greenhouse gas (Fishman et al., 1979), especially in the upper troposphere. In the lower troposphere, ozone is known to contribute to crop and tree damages and human health impairment.

Tropospheric ozone is a colourless gas and the major component of smog. Tropospheric ozone is not emitted directly into the air but is formed through complex chemical reactions between precursor emissions of volatile organic compounds (VOC) and NOx in the presence of sunlight. These reactions are accelerated by sunlight and increased temperature. Ozone reacts with water vapour to produce hydroxyl radicals (OH), in the presence of sunlight, OH reacts with nitric oxide (NO) to form HNO3, an acidic compound capable of damaging crops and vegetation. Peak ozone levels typically occur during the warmer times of the year. Ozone causes health problems because it damages lung tissue, reduces lung function, and sensitizes the lungs to other irritants (APTI, 2004; Jacobson, 2000).

The behavior of tropospheric ozone is thus of significant importance. Tropospheric ozone has been widely studied in other regions (Logan and Kirchhoff, 1986; Volz and Kley, 1988; Oltmans and Levy, 1994) among others, but more reports on the behavior of tropospheric ozone in the West African region are still required. Logan (1985) reported that a summer maximum of tropospheric ozone cannot be found at lower latitudes.

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over Japan (Kagoshima, 32°N) where ozone decreases dramatically. This study is a comparative analysis of tropospheric ozone, stratospheric ozone and high altitude relative humidity’s variation over West Africa.

Differentiating between Stratospheric and Tropospheric Ozone

The atmosphere can be divided into different layers: troposphere, stratosphere, mesosphere, thermosphere, exosphere, ionosphere and magnetosphere. The troposphere extends up to about 16 km in the tropics but to about 9.7 km in the temperate latitudes (Jacobson, 2000). Above the troposphere is the stratosphere, ozone is found both in the stratosphere and the troposphere. The ozone molecules in these two layers are chemically identical as they both consist of three oxygen atoms and have the same formula O₃. Ozone in the stratosphere or natural ozone is formed as a result of the action of ultra violet radiation in the upper atmosphere with oxygen molecules. Highest natural ozone concentration is found within the altitude range of 25 – 32 km (Jacobson, 2000). This is the layer where there exists sufficient oxygen density and sufficient solar intensity to yield maximum ozone concentration. At higher altitude, though solar intensity is higher, oxygen density is low and vice versa at lower altitude. Tropospheric ozone (low-lying ozone) is a by-product of urban air pollution emitted from the combustion of fossil fuel in vehicles, industries etc. In the presence of high solar radiation, these emissions react with other atmospheric gases like oxides of nitrogen (NOₓ) at different chemical stages to produce ozone. It is generally agreed that tropospheric ozone has increased considerably as a result of these photochemical reactions (Roelofs and Lelieveld, 1997; Jacobson, 2000). While stratospheric ozone plays a beneficial role by absorbing and thus preventing the biologically harmful UV-B and UV-C rays from reaching the earth’s surface, tropospheric ozone (low-lying ozone) is destructive and dangerous. Ozone in direct contact with life-forms is highly toxic as it readily reacts with other molecules. Several studies have confirmed the harmful effects of tropospheric ozone with respect to crop production, forestry, and human health. Besides, it has adverse effect on visibility range especially in the urban centre. This is commonly referred to as photochemical smog (Jacobson, 2000). Tropospheric ozone reduces the quality of air in urban centre by reducing the concentration of oxygen atoms in the urban air through its very sporadic photochemical reactions. This has been observed to compound the problem of atmospheric stagnation in the urban region. Atmospheric stagnation occurs when the ventilation rate is very low because of lack of air motion. This usually occurs in the weak pressure gradient near the centre of an anticyclone with a warm core, thus resulting in very little air movement near the centre. Atmospheric stagnation coupled with high level low-lying ozone in urban air produces a lot of discomfort for the urban dwellers. Heavy tropospheric ozone pollution is often manifested as eye and lung irritation experienced at hot spot during peak-periods or rush-hours (Boube et al., 1994). These double roles of ozone result in two environmental issues of importance in the science world. There is a general concern on the increase of low-lying ozone in the boundary layer of the troposphere, which is resulting in photochemical smog and other air pollution related problems especially in urban centres. There is also the wide spread interest and concern on the depletion of ozone concentration in the stratosphere. This paper focuses on the former.

Photolysis of ozone near the earth surface

Near the earth’s surface, ozone production proceeds from the photolysis of nitrogen dioxide (NO₂) whereas up in the stratosphere, ozone production proceeds after the photolysis of molecular oxygen. In the presence of fossil fuel emissions in form of carbon monoxide (CO), methane (CH₄), nonmethane organic gases and early morning ultra violet radiation (hν) in the frequency range λ ~ 420 nm, photolysis occurs which escalate the concentration of ozone near the earth’s surface. Photolysis of ozone, followed by reaction with water vapor, produces hydroxyl radical (OH), the primary atmospheric oxidant in the troposphere (Logan, 1985). These oxidants are responsible for paints’ discoloration, atmospheric staining and streaking observed on buildings, vehicles, structures and other monuments. Below is the photochemical reaction chain which leads to the production of hydroxyl radical (OH), and eventually to tropospheric ozone (O₃):
\[ CO + O \rightarrow CO_2 + H \]
\[ H + O_2 \rightarrow HO_2 \]
\[ NO + HO_2 \rightarrow NO_2 + OH \]
\[ NO_2 + hv \rightarrow NO + O_2 \]
\[ O_2 + O_2 + M \rightarrow O_3 + M \]

**Method of Data Acquisition**

The ozone data used in this study was retrieved from the archives of Total Ozone Mapping Spectrometer (TOMS) satellite owned by NASA, while the average monthly relative humidity at 100mb was obtained from another of NASA online data archives TOVAS. Relative humidity at the 100mb pressure level was chosen because it coincides with an average altitude of about 17km, the average altitude of the upper troposphere at the equator.

Using the equation below,
\[ P(z) = P_0 \cdot e^{-z/H_p} \]

- \( P(z) \) = pressure at the surface
- \( z \) = height in km
- \( H_p \) = pressure scale height = 7.29 km

At altitude \( z = 16.9 \) km, pressure is 99.8 mb which was approximated to 100 mb. Average height of the troposphere at the equator is about 17 km.

**RESULT AND DISCUSSION**

Trends in tropospheric ozone as suggested by theoretical calculations and those of observed data as revealed by satellite at equatorial zone 5°N-5°S were studied (Figure 1). Under natural circumstances, tropospheric ozone constitutes about 10% of the total ozone concentration while the remaining 90% resided in the stratosphere and formed the ozone layer. Figure 1 revealed that observed tropospheric ozone exceeded the theoretical deduced values all year round at the equatorial zone studied. The deduced tropospheric ozone recorded an annual singular peak which maximized around July/August with an estimated value of 27 DU while the observed satellite tropospheric ozone recorded a biannual seasonal trend.

**Biannual Seasonal Tropospheric Ozone trend**

The observed tropospheric ozone indicated a biannual seasonal trend which peaked first around February/March and also around August/September with averages of 41 DU and 42.5 DU respectively. The first peak coincided with the dry season in the West Africa sub-region when precipitation is at its minimum and temperature is high. During the dry season air pollutants that serve as ozone precursors accumulate over a certain period, since there is no rain to wash them off the atmosphere. It can be suggested that the increase in ozone precursors coupled with long hours of intense sunshine enhanced the increase in the production of low-lying ozone observed. The second peak in August/September coincided with the raining season in the sub-region. The raining season is characterized with high atmospheric dynamics and strong vertical air mixing which allowed for maximum transfer of stratospheric ozone into the troposphere. This season is also characterized by maximum total ozone concentration. The first observed tropospheric ozone low occurred in May/June and the second in November with average values of 36.2 DU and 38.7 DU respectively. The May/June observation may be explained as follow, the accumulated ozone precursors in the atmosphere had been gradually depleted by the commencement of the raining season, while on the other hand, the atmospheric dynamics has not reached its peak for maximum downward transference of ozone from the stratosphere into the troposphere. The November low could also be associated with reduction in the vertical transport of ozone from the stratosphere into the troposphere, while the accumulation of anthropogenic generated ozone from air pollutants are yet to reach its peak.
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Biosphere-Atmosphere Link and Excess Observed Tropospheric Ozone.

Besides the difference in seasonal variation between the observed and the deduced tropospheric ozone, the observed exceeded the deduced all year round (figure 2) with an average value of 15 DU for eight months of the year, 10.5 DU in April/May/June, and 13 DU in November. The excess in observed values over the deduced, was attributed mainly to fossil fuel emissions and biomass burning, and linked partly also with the biosphere emission into the atmosphere within the latitudinal zone 5°N-5°S studied. Previous researches found out that certain plants, mammals and insects all of which are major composites of the biosphere, emit considerable amounts of organic hydrocarbons in form of isoprene gas (C_{5}H_{8}), (Nandita and Iyer, 2006). Detective works in some American cities found out that tropospheric ozone level failed to decline appreciably even after strong anti-pollution measures had been enforced upon the cities. They discovered that oak trees in particular produce enormous volume of volatile organic hydrocarbons which react photochemically with nitrogen oxides to escalate the concentration of tropospheric ozone. This led to the incrimination of such trees as oaks and poplar and their replacement with pine trees in cities (Nandita and Iyer, 2006). High concentration of isoprene only poses danger when it is found alongside high concentration of nitrogen oxides (NO\(_x\)) the most prevalent urban air pollutants. In the presence of medium or high NO\(_x\), isoprene escalates the production of low-lying ozone in the urban air through the following reaction (Makar and McConnel, 1992): Oxidation of isoprene by OH and NO\(_x\) produces alkylperoxides radicals (RO\(_2\)), which in turn reacts with nitrogen oxide (NO) to produce RO and NO\(_2\):

\[
RO\(_2\) + NO \rightarrow RO + NO\(_2\)
\]

In the presence of sunlight NO\(_2\) photolysis to release free oxygen atom into the atmosphere which react with abundant oxygen molecules (O\(_2\)) to produce ozone (O\(_3\)).

\[
NO\(_2\) + h\nu \rightarrow NO + O
\]
\[
O + O\(_3\) + M \rightarrow O\(_3\) + M
\]

Thus latitudes 5°N-5°S the zone where the tropical rain forest region falls may be assumed to have enhanced tropospheric ozone production through the medium of biosphere-atmosphere exchange.

To further confirm the strong connectivity of tropospheric ozone trend with activities within the boundary layer of the troposphere at the equatorial zones 5°N-5°S, the relative humidity over the region at 100mb altitude was compared with the total ozone concentration and the observed tropospheric ozone (Figures 3 and 4). The study showed that stratospheric ozone had a strong negative correlation of -0.8 with relative humidity at 100mb, while tropospheric ozone recorded no significant correlation with the relative humidity. The 100mb correspond to about 17km altitude which is the approximate altitude of the upper troposphere. This result confirms the influence of anthropogenic emissions and other natural organic gases in the lower troposphere as major contributor to tropospheric ozone trends.

CONCLUSION

Tropospheric ozone recorded biannual seasonal variation which peaked first around February/March and next around August/September. The total ozone concentration peaked once annually around July/August. Insignificant correlation between the observed tropospheric ozone and the relative humidity at 100mb indicated the contributions of other factors outside the upper troposphere and stratosphere on the variability of tropospheric ozone. One of the major factors is fossil fuel emission.

When these emissions are reduced to the barest minimum through the embracing of renewable energy sources, tropospheric ozone levels is expected to reduce significantly. Reduction in tropospheric ozone will substantially bring about improvement in the local air quality and thus contribute positively to both health and vegetation subsistence. This should also lead to reduction in radiative forcing on the atmosphere, ozone being a greenhouse gas.
REFERENCES


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Figure 1: Tropospheric ozone concentration at latitudes 5°S - 5°N (2003-2005)

Figure 2: Average differences between observed and deduced tropospheric ozone at latitudes 5N-5S
Figure 3: Total ozone concentration at latitudes 5S - 5N (2003-2005)

Figure 4: Relative Humidity at 100mb at latitudes 5S-5N (2003-2005)