Introduction

Tropospheric ozone is a secondary pollutant and greenhouse gas [1] produced by photochemical oxidation of its precursors such as carbon monoxide (CO), methane (CH₄), and non-methane volatile organic compounds (NMVOCs) and nitrogen oxides (NOx) in presence of hydroxyl radical (OH) [2]. It is a public health concern [3,4] and an environmental issue that is poorly documented in developing countries especially in Southern Africa. For more than two decades tropospheric ozone climatology in African tropics has been under investigation following the dramatic enhancement of its levels observed through satellite imagery [5] and ground based measurements in few stations over this region. Preliminary study on tropospheric ozone climatology using short period SHADOZ data was first performed by Thompson et al. [6] who sought to establish tropical ozone climatology over the tropics. Results from this study provided the characteristics of tropospheric ozone climatology in this region as well as the contributing factors to supplement findings from SAFARI-92 and Trace-A campaigns [7-9]. Subsequently, the first study on tropospheric ozone climatology at Irene was undertaken by Diab et al. [10] who used SHADOZ data from 1990-1994 and 1998-2002. This study revealed a seasonal ozone variation characterized by a spring maximum modulated by both tropical and mid-latitude influences due to its location (25°54’S, 28°13’E) on the boundary of zonally defined meteorological regimes. Photochemical factors (biomass burning, lightning and biogenic emissions) together with dynamical and synoptic weather system prevailing in the region were identified as main contributing factors to seasonal tropospheric ozone variation and enhancement.

Long term tropospheric ozone climatology at Irene has been investigated using multi-instrumental dataset: PTU-O3 ozonesondes, DIAL LIDAR (Light Detection and Ranging) and MOZAIC (Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft) airborne instrumentation [11]. Results from this study confirmed the finding made by Diab et al. [10]. A positive linear ozone

Keywords: Tropospheric ozone; Air temperature; Relative humidity; Correlation

Abstract

The climatology of tropospheric ozone at Irene has been investigated using SHADOZ network data to assess the correlation between the observed seasonal ozone enhancement and meteorological factors. Previous studies identified photochemical sources (biomass burning, biogenic and lightning emissions) as well as dynamic factors (synoptic weather system, stratospheric intrusion) as contributing factors to ozone enhancement observed during Austral spring (October) and Austral summer (February). Recent global increase in temperature due to climate change has raised concern on the impact of such increase on seasonal ozone enhancement over this region. As tropospheric ozone is poorly documented over southern Africa, a few studies have been undertaken to understand the correlation between change in meteorological parameters and tropospheric ozone variation. The objective of this paper is to providing a comprehensive correlation between meteorological parameters and tropospheric ozone concentrations over Irene (South Africa) for the period 1998 to 2013 in order to predict possible change in the concentration of ozone and water vapor as greenhouse gases. To this end correlation analysis has been used to assess annual and seasonal TTO (Total Tropospheric Ozone) variation over different layers up to the tropical tropopause height. Seasonal TTO trends have shown identical seasonal ozone patterns with two maxima occurring in summer and spring respectively. However an increase on ozone concentrations from 55 to 65.6 DU in spring and from 32 to 55 DU in summer have noted in comparison with previous short term study at the same location. This was evidenced by seasonal ozone profiles which showed a sharp seasonal increase of 23 and 14 ppbv in the layer 10-12 km in spring and summer respectively. While autumn profile displays an increase of 12 ppbv, winter profile presents a 6 ppbv decrease at this very layer. The role played by temperature and relative humidity is depicted by the strong correlation existing between both temperature and ozone concentrations from surface; 2 km and 2-4 km and weak correlation in upper layers. In contrast relative humidity shows a weak correlation from surface to 3 km and a strong correlation from 3 km to upper layers. A multiple linear regression model was used to provide seasonal correlation between ozone and temperature and relative humidity. All seasons display strong regression coefficients (0.96<R²<1) between ozone and temperature. Similar trends are also observed for relative humidity and TTO concentrations (0.91<R²<1) in autumn, spring and summer. However a weak correlation is noted in winter, when TTO minimum values are recorded (0.58<R²<1). We suggest for future study the inclusion of atmospheric pressure, wind speed and wind direction to better understand the chemistry of tropospheric ozone due to global warming and provide a very inclusive ozone model.

*Corresponding author: Jean-Pierre Mulumba, College of Agriculture, Engineering and Science. School of Chemistry and Physics and School of Electrical and Electronic Engineering University of KwaZulu Natal, South Africa


Copyright: © 2015 Mulumba JP, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
trends that maximizes in austral spring (SON), summer (DJF) and minimize in Autumn (MAM) and winter (JJA) has been observed. Furthermore, increase in tropospheric ozone over Irene occurred mainly in the lower layers due photochemical mechanism although stratospheric intrusion has also been noted. This finding was in good agreement with observations based on a global network made by Oltmans et al. [12] with some stations located in the tropical and subtropical regions.

Understanding the climatological characteristics of tropospheric ozone production and fluxes in subtropical regions is important for assessing ozone’s direct effect on climate [13,14] and its role in atmospheric chemistry on both regional and global scales. Although tropospheric ozone accounts for only 10% of all atmospheric ozone, its role in the maintenance of the chemical composition of the atmosphere is crucial. Change in meteorological factors due to climate change is likely to influence ozone photochemistry as well as its vertical and spatial distribution over a given region. This would consequently have an impact on radiative forcing, and therefore worsening climate change impact on the region. Hence, air temperature and relative humidity as elements of atmospheric thermodynamic can serve as tools to synthesize the complex effect of meteorological and chemical factors influencing ozone concentration in the troposphere. In recent years there have been increasing concerns on air temperature and ozone concentration due to climate change. Studies undertaken by Jacob, Ryan and Camalier et al. [15-17]. Ascertain that temperature constitutes a meteorological factor influencing surface ozone formation amongst other conditions. According to International Panel for Climate Change [18] surface ozone is expected to rise, all else being equal, with an increase in temperature. Consequently areas with rising temperature and precursor emissions are projected to suffer the consequences of worsening air pollution including increase in mortality and morbidity [19,20] along with significant damage to crops [21]. Moreover rising temperature is directly correlated with increasing relative humidity which implies higher percent of water vapor in the atmosphere. Because water vapor is the most abundant greenhouse house in the atmosphere, change in its concentration which is considered as climate feedback resulting from warming of the atmosphere, rather than a direct result of industrialization is critically important for future climate change projection (http://www.sjsu.edu/faculty/watkins/watervapor01.html) [22]. Increase in water vapor in the atmosphere will then contribute to more cloud formation which may play a significant role on incoming energy balance (reflection of incoming solar radiation and cooling of the earth) and the transport of latent heat.

Although chemical and dynamic factors contributing to ozone enhancement over southern African tropic are known, investigation on the relationship between meteorological factors and ozone trends has not been undertaken in this region. The present work aims at assessing the tropospheric ozone response to inter-annual variation in air temperature and relative humidity for the period 1998-2013 at Irene. Data and method used to achieve the objective of this study are presented in section two. The next two sections present the monthly and seasonal TTO, air temperature and relative humidity variation as well as the seasonal regression models for both investigated parameters and ozone concentrations. A discussion of the results followed by a conclusion and suggestions for future research constitute the last part of this paper.

Data and Method

Tropospheric ozone concentration at Irene has been retrieved from ozonesondes data for the period 1998 to 2013 since this meteorological station became part of SHADOZ programme in 1998 [23] Ozone profiles are collected using ozonesonde balloons launched on weekly basis. The SHADOZ network which involves 15 stations distributed in the tropical and subtropical southern hemisphere was originally intended to complete the sparse amount of tropospheric and stratospheric ozone data and consequently remedy data discrepancy in this region. The aim of this programme was therefore to provide a consistent data set of tropospheric ozone that can be used for assessing the trends and variability of this greenhouse gas. A total number of 253 profiles over 16–year period ranging from 4 to 30 profiles per month have been used to compute total tropospheric ozone climatology at Irene. This data set was downloaded from SHADOZ archive website http://croc.gsfc.nasa.gov/shadoz/ [24].

Ozone data is recorded through and electrochemical concentration cell which is integrated in a radiosonde attached to a free flying balloon with Vaisala RS80 radiosondes for measuring temperature, pressure and humidity. Wind speed and direction are determined using GPS navigation satellites. The system also provides synoptic upper-air messages for numerical weather prediction models and weather forecast. As the balloon carrying the instrument moves high through the atmosphere it sends the measurements to the receiving station [25]. The vertical extension of profiles range from ground level of 1524 m up to gust altitude reaching 30 to 35 km in most cases is covered [11]. It uses the latest technology to ensure accuracy. According to Smit et al. [26]. The precision and the accuracy of ECC-sonde is estimated at 3-5% and 5-10% below 30 km altitude respectively in comparison with SPC-6 A and ENSCI-Z ozonesondes. More details on ozonesonde description can be found in SHADOZ website as mentioned above. Data consists of ozone expressed in ppmv (per million per volume), DU (Dobson Unit), ozone partial pressure (mPa), relative humidity (%) and temperature (°C), recorded at 5 second interval. The methodology used to retrieve ozone data from SHADOZ programme in this work is similar to that used by Diab et al. [10] Data quality check was performed to discard instrument anomalies before averaging it in 100 m interval. A measure of total tropospheric ozone (TTO) was obtained by integrating the ozone concentration from the surface to 16 km which corresponds to the height of the tropopause. A threshold of 16 km was found to be appropriate for estimating TTO [8,27] although it is not corresponding exactly with the height of the meteorological or chemical tropopause. For the objective of this work, DU (Dobson Unit) was considered for vertical ozone concentration for the computation of Total Tropospheric Ozone. Air temperature as well as relative humidity are expressed in degree Celsius (°C) and percent (%) respectively Annual and seasonal TTO variations were computed using monthly data grouped in 8 layers ranging from Surface to 2 km, 2 to 4 km, 4 to 6 km, 6 to 8 km, 8 to 10 km, 10 to 12 km, 12 to 14 km and 14 to 16 km for the total period of investigation. Air temperature and relative humidity were computed to provide annual and seasonal variation in comparison with TTO variation. Seasonal tropospheric ozone profiles where also computed and compared with both air temperature and relative humidity. In order to establish the relationship between TTO and meteorological factors (air temperature and relative humidity) a statistical model was performed as suggested by Akdemira et al. [28]. For the objective of this work, we use graphical analysis and regression model which is one of the most widely used method for predicting the effect of meteorological data on ozone levels. The general regression model used is shown in Equation (1):

\[ Y = a_0 + a_1x_1 + ... + a_mx_m + \varepsilon \]  

(1)
where Y is an objective variable (ozone concentrations);

m is the number of independent variables (meteorological variables);

xj are independent variables (Temperature, Relative humidity);

aj are regression coefficients (estimated using the least squares procedure);

ε is an error term associated with the regression analysis.

**Mean monthly total tropospheric O_3 variation**

Monthly variation of Total Tropospheric Ozone (TTO) at Irene for the period 1998-2013 is presented in Figure 1. Two ozone peaks occurring in October (65.6 DU) and February (55.1 DU) corresponding to austral spring (SON) and austral summer (DJF) are noted respectively. Low TTO concentrations of 32.3 DU were recorded in June corresponding to winter (JJA) season. Spring ozone peak is in good agreement with previous finding made by Diab et al. [10] which is widely attributed to photochemical sources (biomass burning, biogenic emissions and lightning) and stratospheric ozone injection of ozone rich air into the troposphere. The second peak which occurs by the end of austral summer is attributed mid-latitude westerly wave transporting ozone precursors as well as from urban-industrial zone of Johannesburg and neighbouring cities. This period of the year corresponds to biomass burning period in central region of Africa including Congo Brazzaville, Angola, DRCongo and Zambia where agriculture activities are taking place. Ozone precursors can be uplifted through convection movement and transported by long range jet stream from the region of low pressure to high pressure system. These sources contribution to tropospheric ozone in southern African region have been specifically addressed by many authors including Diab, Thompson, Zunckel, Cros and Dentener and Leleiveld et al. [5-7,10,29-31]. A review of sources contributing to tropospheric ozone in southern African will be published in South African Atmospheric Science Society proceedings. According to this review an estimated of 16% contribution from biomass burning was found in comparison with 26% from stratospheric input. Urban-industrial, biogenic and lightning contribution accounted for 9%, 12% and 27 respectively [32].

A decrease in ozone concentrations noted from March to June ranging from 44.1 DU and 32.3 DU respectively corresponds to autumn and winter where anti cyclonic winds drive off pollutants from inland to the Indian Ocean. The same trend is observed in all layers from surface to 16 km. Correlation between monthly TTO trends as well as air temperature and relative humidity is fully discussed in the sections below.

**Total tropospheric ozone and air temperature correlation**

Monthly integrated TTO concentrations and air temperature variation within the lower tropospheric layers, viz surface to 2 km and 2-4 km are displayed with their standard errors bars in Figures 2a and 2b. Mean monthly air temperature variation in the layer “Surface to 2 km” shows a maximum value occurring in later summer (February) with 19.4°C. This maximum value does not correspond with the maximum TTO value of 2.1 DU which occurs in the middle of spring (October). Minimum temperature of 8.7°C occurs in winter (July) while minimum TTO concentration is observed a month earlier during the same season in June. Similar temperature trend is observed in the layer 2-4 km with a sole difference that maximum temperature of 4.6°C is observed in spring (November) while maximum TTO value of 11.3 DU is observed in spring (September). The minimum temperature of -1.7°C is observed in late winter (August) which corresponds to a critical period of TTO enhancement within the layer. These sequential variations are indicative of the relationship existing between the two parameters as shown in the correlation coefficient in Table 1.

**Total tropospheric ozone and relative humidity correlation**

Monthly integrated TTO concentrations and relative humidity variation within the lower tropospheric layers viz Surface to 2 km and 2-4 km are displayed with their standard errors in Figures 3a and 3b. Mean monthly relative humidity variation in the layer Surface to 2 km displays a late summer maximum of 60% occurring in midsummer (February). This maximum value does not correspond with the maximum TTO value which occurs in the middle of spring (October). Minimum relative humidity of 32% which occurs in late autumn (May) and middle winter (July) corresponds to minimum TTO concentration of 1 DU observed during winter (June).

![Figure 1: Monthly TTO variations at Irene for the period 1998-2013.](image-url)
The upper layer 2-4 km displays the same trend as the lower layer with a maximum relative humidity of 54% occurring in late summer (February) and does not correspond with TTO maximum value of 11.3 DU recorded in early spring.

The minimum relative humidity values of 17% observed in late autumn (May) and late winter (August) corresponds with the minimum TTO value of 5.8 DU observed during early winter (June). This implies that TTO and relative humidity are inversely proportional and their relation which may be dependent on other factors such as the presence or absence of ozone precursors (NOx) may favor ozone production or destruction.

Comparison of ozone profile and relative humidity

Comparison between seasonal ozone and relative humidity profiles shows that summer profiles display high relative humidity (58%) from Surface to 4 km in contrast with the lowest ozone value of 39 ppbv which is higher than the value recorded in winter (31 ppbv) and autumn (35 ppbv) but lower than spring value (43 ppbv). Relative humidity which decreases with the altitude intersects ozone profile at 4 km in summer (Figure 4a) while it does below this height in autumn, spring and winter. This indicates the chain chemical reaction influence...
played by high relative humidity in presence of ozone as it shortens its lifespan and cause the surface deposition by photolysis. The role played water vapor in ozone enhancement is noted in all seasons above 4 km as decrease on relative humidity with the altitude favors ozone formation and its long lifespan. This is critical as both ozone and relative humidity have an influence in radiative budget (Table 2).

Vertical tropospheric ozone distribution of at Irene

Seasonal and annual profiles are useful tools for determining the vertical variability of tropospheric ozone at a particular location [33]. They indeed enable to identify possible contribution factors such as photochemical and dynamical processes that may be responsible for ozone enhancement. In this section, we assess seasonal and annual distribution of tropospheric ozone at Irene for the period 1998-2013 as showed in Figure 5a-5e. Seasonal and annual profiles which are expressed in parts per billion per volume (ppbv). These profiles were computed with error standards expressing vertical variability of ozone at different layers partitioned in 1 km interval, except the first layers where standard error starts from 1.5 km which is the sampling height point for ozonesonde balloons. Spring (SON) and summer (DJF) profiles present the highest ozone concentrations at surface to 2 km with 43 and 42 ppbv, respectively followed by autumn (MAM) with 39 ppbv (Figure 5b and 5c). Winter (JJA) presents the lower surface ozone concentration with 35 ppbv (Figure 5a). Mean annual profile presents surface ozone concentration of 38 ppbv (Figure 5e). The highest seasonal ozone enhancement of 94 and 85 ppbv were recorded in the upper troposphere (14 to 16 km) $\epsilon$ is an error term which can be associated with the regression analysis or data measurement.

Therefore seasonal prediction models can be expressed in Equation 3, Equation 4, Equation 5 below as follows:in spring and summer respectively. These values are lower than those obtained for short term study by Diab et al. (2004), which presented the values varying between 175 and 200 ppbv and 100-125 ppbv for spring and summer respectively. High vertical ozone variability was observed in spring and autumn as showed by standard error bars in Figure 5b and 5d. Winter and autumn display low vertical ozone variability (Figure 5a and 5c) with 62 and 80 respectively. These concentrations are also lower than those observed by Diab et al. [10] with 150-175 ppbv and 125-150
Figure 4: Seasonal Relative humidity (%) profiles variation in comparison with tropospheric ozone profiles variation at Irene for the period 1998-2013.

<table>
<thead>
<tr>
<th>Seasons</th>
<th>Regression coefficient ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ozone vs. Temperature</td>
</tr>
<tr>
<td>Winter</td>
<td>0.99</td>
</tr>
<tr>
<td>Autumn</td>
<td>0.96</td>
</tr>
<tr>
<td>Spring</td>
<td>0.99</td>
</tr>
<tr>
<td>Summer</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Table 2: Linear Regression coefficients for TTO and meteorological factors.

ppbv respectively. Comparison between seasonal and annual profiles shows that the lowest ozone concentrations in surface to 2 km layer are recorded in winter (31 ppbv) and the highest in spring (41 ppbv) as showed in Figure 5f. Mean ozone concentration of 34 ppbv was recorded in the surface to 2 km layer for the period of investigation. The highest annual ozone enhancement of 70 ppbv was recorded in the layer 14-16 km.

Modeling prediction of seasonal tropospheric ozone with meteorological factors

Multiple linear regression was used to predict seasonal ozone concentration over different layers as function of meteorological factors (air temperature and relative humidity). Regression coefficients of both meteorological factors and ozone concentrations in DU in different layers were computed to assess the influence of each variable. The general equation for the model is expressed in Equation 2.

\[ Y = a_0 + a_1x_1 + ... + a_2x_2 + \varepsilon, \]

Where \( Y_s \) is summer ozone concentrations

\( Y_a \) is autumn ozone concentration

\( Y_p \) is spring ozone concentration

\( Y_w \) is winter ozone concentration

\( X_1 \) is air temperature; \( X_2 \) is relative humidity and

\[ Y_s = -8.40X_1 + 0.42X_2 + \varepsilon \]  

\[ Y_a = -16.4 - 0.82X_1 + 0.62X_2 + \varepsilon \]  

\[ Y_p = 4.5 - 0.53X_1 + 0.04X_2 + \varepsilon \]  

\[ Y_w = 0.79X_1 - 0.42X_2 + \varepsilon \]  

Seasonal linear regression models line fit plots are presented in Figures 6a, 6b, 7a, 7b, 8a, 8b, 9a and 9b for ozone concentration as function of temperature and relative humidity respectively.

Discussion and Conclusion

Total Tropospheric Ozone computation as well as analysis of meteorological factors including air temperature and relative humidity have provided a clear understanding of the long term climatological characteristics of tropospheric ozone production and fluxes at Irene for the period 1998-2013. Seasonal ozone variation observed are mostly due to is similar to that observed by previous studies conducted at Irene using ozonesonde data, air craft and LIDAR R data [10,11]. Two maxima occurring in austral spring (65.6 DU) and austral summer (55.1 DU) were observed. Spring ozone maximum corresponds
Figure 5: Seasonal and annual tropospheric ozone profiles for the period 1998-2013 at Irene (a: winter profile, b: spring profile, c: summer profile, d: autumn profile and e: mean annual profile and f: mean seasonal and annual profiles.

Figure 6a: Linear regression model for summer ozone-temperature.

Figure 6b: Linear regression model for summer Ozone-Relative humidity.
with the peak of the biomass burning activity in southern Africa and South America [34]. It is also during this season that biogenic emission (CH4) and NOx emission from lightning have been observed [7-9] together with the influence of dynamic processes as resultant of tropical and mid tropical position of this station. A secondary ozone maximum which occurs in austral summer (February) is also showed a characteristic of African stations in the tropics. This ozone peak is chiefly attributed to prevailing synoptic weather from mid-latitude westerly wave transporting ozone precursors as well as from urban-industrial zone of Johannesburg and neighbouring cities and from in central region of Africa where agriculture activities are taking place for the second agricultural season of the year. Tropospheric ozone values observed during the period 1998-2013 are higher than those observed by Diab et al. [10] for the period 1990-1994, 1998-2002. This is inconsistent with seasonal ozone profiles values found by Diab et al. [10] The reason for the discrepancy are unknown and may be attributed to ozone anomalies observed by Lightner et al. [35]. However TTO values for the period of study are consistent with progressive ozone enhancement timeline observed in the region since air pollution abatement measures are not implemented to tackle ozone precursor from urban industrial sources, although tremendous efforts.
have been noted in South Africa in terms of air quality management at all spheres of the country’s administration.

To better understand the relationship between TTO and meteorological factors, correlation analysis of temperature as well as relative humidity variation for the same period of study in different layers were computed. A strong correlation between temperature and TTO in the lower layers (Surface to 4 km) although maximum temperature is not congruent with maximum TTO concentrations. The no congruence of temperature and ozone concentration at these layers can be attributed to the no seasonality of ozone precursors at Irene also the prevailing weather system that allow the transport of ozone rich air from Indian ocean into the country inland. However a weak correlation was observed between the two parameters in the upper layers (4-6 km to 10-12 km). The top layers (12-14 and 14-16 km) display a lesser strong correlation between the two parameters than the lower layers. This no congruence between ozone and temperature is due to mixing ratio mechanism that occurs above the tropopause when lower temperature influence rapid increase in ozone mixing ratio with altitude due to rapid decrease in water such as explained.
by Holton et al. [36]. The correlation between TTO and water vapour have shown a slightly stronger correlation in the Surface to 2 km layer which becomes stronger in the layers from 2 km and above. The role played water vapor in ozone enhancement is noted in all seasons above 4 km as decrease on relative humidity with the altitude favors ozone formation and its long lifespan. This is critical as both ozone and relative humidity have an influence in radiative budget. Decrease in water vapor with altitude and increase in vertical ozone distribution suggests the contribution of stratospheric intrusion or change in tropospheric ozone chemistry exacerbated by ozone precursor emissions through lightning. Although TTO seasonality at Irene is suggested to be strongly influenced by non seasonal fluctuating source contribution, this finding may sustain its seasonality given correlation between meteorological factors and ozone formation. Although change in temperature and relative humidity are set to a lower path on yearly basis it is worth nothing that seasonal anomalies noted may have stronger impact on cloud formation and therefore on precipitation regime.

This work constitutes the first attempt to model the correlation between tropospheric ozone and meteorological factors (temperature and relative humidity) using SHADOZ data. The results obtained suggest that more parameters need to be included into the model to better understand the change on atmospheric chemistry due to global warming. We therefore suggest for the future study the inclusion of atmospheric pressure and ozone partial pressure to better understand the chemistry of tropospheric ozone in a changing atmosphere. Similar study using other ozone measurement data such as Lidar may also be used to ascertain the conclusion of this study.

Acknowledgement

We are thankful to SHADOZ network for the ozone data provided in there website for public use that has allowed us to conduct the study. We are grateful the University of KwaZulu Natal especially to the College of Agriculture, Engineering and Science through the School of Chemistry and Physics, and School of Electrical and Electronic Engineering for the financial support toward the achievement of this paper.

References


14. Mai Khiem, Ryozo Ooka, Hong Huang, Hiroshi Hayami, Hiroshi Yoshikado (2009) Analysis of relationship between change of meteorological conditions and the variation of ozone levels in the summer over the central Kanto area. The seventh International Conference on Urban Climate, 29 June - 3 July 2009, Yokohama, Japan.


