



**TROPOSPHERIC OZONE CLIMATOLOGY OVER EQUATORIAL AND
SOUTHERN AFRICA USING CLIMATE CHANGE PARAMETERS**

By

JEAN-PIERRE MFUAMBA MULUMBA

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requirements for the degree of Doctor of Philosophy in the School
of Chemistry and Physics,
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Durban

SUPERVISOR: PROFESSOR VENKATARAMAN SIVAKUMAR

CO-SUPERVISOR: PROFESSOR THOMAS JOACHIM ODHIAMBO AFULLO

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ABSTRACT

Tropospheric ozone climatology over equatorial and southern Africa has been at the core of this study. SHADOZ (Southern Hemisphere ADditional OZonesondes) network data for the period 1998-2013, from Irene (South Africa) and Nairobi (Kenya), and MOZAIC (Measurement of OZone and water vapor by Airbus In service air Craft) programme data for the period 1998-2001 from Brazzaville (Congo) respectively have been used to investigate tropospheric ozone characteristics with regard to climate change parameters. These locations, which represent three different African climate zones including tropical (Brazzaville), equatorial (Nairobi) and subtropical (Irene) are poorly documented with regard to the variation and distribution of tropospheric ozone, although its levels over the region have been increasing since the last two decades of the twentieth century. With recent changes observed on climate parameters due to climate change, tropospheric ozone distribution and variability over this region have been investigated. Climate parameters including air temperature and relative humidity and ozone parameters such as partial pressure have been used to achieve the objective of this study. Results from tropospheric ozone modeling at Irene, using long term ozonesonde data from SHADOZ network, confirm the seasonal patterns of ozone, such as previously observed over southern Africa, with two maxima occurring in summer and spring respectively. However, increase on ozone concentrations from 55 to 65.6 DU in spring and from 32 to 55 DU in summer has been noted, in comparison with previous short term studies undertaken at this location. In the Congo Basin tropospheric ozone climatology investigated using short term aircraft data from MOZAIC programme collected at Brazzaville for the period 1998-2001 also presents two seasonal maxima occurring in August and February with 35.4 DU and 26.1 DU

respectively. Over equatorial eastern Africa, which presents one of the most complex meteorological system in the African continent, seasonal ozone distribution has also been noted with two peaks (43.0 DU) and (46.8 DU) occurring in July and October respectively. Analysis of case studies using HYSPLIT_4 (Hybrid Single-Particle Lagrangian Integrated Trajectory version 4) model and NCEP/NCAR (National Centers for Environmental Prediction/National Center for Atmospheric Research) reanalysis model has shown that increase on tropospheric ozone over these regions is determined by precursor from both local and long range transport based from remote sources (biomass burning, lightning and biogenic emissions). The role played by dynamic processes is defined by positive divergence values and negative flux on zonal and meridional wind patterns prevailing at upper troposphere due to a quasi-permanent low pressure system prevailing in the region which in turn implies the highest partial ozone value observed in this region.

PREFACE

The work described by this thesis was carried out at the University of KwaZulu Natal, School of Chemistry and Physics, Durban, from February 2014 until December 2015 under the supervision of Professor Venkataraman Sivakumar, and co-supervision of Professor Thomas-Joachim Odhiambo Afullo.

This thesis is entirely, unless specifically contradicted in the text, the work of the author, and has not been previously submitted, in whole or in part, to any other tertiary institution. Where use has been made of the work of others, it is duly acknowledged in the text.

Signed: _____ Jean-Pierre Mfuamba Mulumba

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DECLARATION 1- PLAGIARISM

I, Jean-Pierre Mfuamba Mulumba, declare that

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DECLARATION 2-PUBLICATIONS

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CHAPTER ONE

INTRODUCTION

1.0 Background

The focus on tropospheric ozone climatology in Africa remains based on the observed dramatic increase on its concentration levels over the tropics (Fishman *et al.* 1991), and the effects of such concentrations on human life and the environment. Ozone is present in the atmosphere in both, the stratosphere and the troposphere. In the stratosphere, ozone accounts for about 90 % (Lelieveld and Dentener, 2000) where it protects the biosphere against harmful ultraviolet radiation from sunlight (Crutzen and Lelieveld, 2001). In the range of 200 to 300nm stratospheric ozone absorbs short wave solar radiation; at this stage, it prevents harmful energy radiation reaching the earth's surface (Chameides and Walker, 1976).

In the troposphere, ozone constitutes a particular threat to human health, to forest and crops, and to the environment. With regard to human health, acute respiratory effects have been reported in children and adults, especially those suffering from asthma when ozone exceeds the standard level of 0.12 ppm, averaged over one hour (McKee *et al.* 1993). Increase in ozone concentration above the guideline value increases numerous and severe health effects, at the population level. Such effects can occur in places where concentrations are currently high due to human activities or are elevated during episodes of very hot weather (WHO, 2005). Adverse effects of ozone on vegetation were first identified in 1950s, where field experience showed that ozone can reduce agricultural yield by a variety of mechanisms

(Ashmore, 2005). Elevated ozone concentrations can cause damage to agricultural crops by obstruction of plant stomata, which allow the exchange of carbon dioxide and water vapor between the inside of the leaves, and the outside ambient atmosphere (Slanima, 2008).

In the environment, tropospheric ozone is known as a strong oxidant and a greenhouse gas (Logan and Kirchhoff, 1986; Crutzen, 1987). Despite its relatively small fraction (10%) in the atmosphere (Lelieveld and Dentener, 2000), tropospheric ozone has a negative impact on climate through global warming. It also governs oxidation processes in the earth's atmosphere through the formation of the hydroxyl (OH) radical, and contributes to the oxidation of chemical species important for the radiative budget or acidification processes in the lower atmosphere (Baldy *et al.* 1996).

Tropospheric ozone concentrations have been on the rise since the last two decades of the 20th century over tropical and southern Africa (Fishman *et al.* 1991). Photochemical ozone production from various precursor sources, including biomass burning emissions (Fishman *et al.* 1996, Randriambelo *et al.* 2003), biogenic and lightning as well as stratospheric ozone intrusion (Baray *et al.* 1998) have been identified as contributing factors, which strongly depend on prevailing meteorological parameters. Since tropical and subtropical African regions are known as major sources of photochemical ozone precursors in the globe, change on climate parameters are likely to impact on ozone characteristics and trends. To this end, ozone chemistry and budget is key for the better understanding of the role played by photochemical and dynamic factors on ozone enhancement. The section below provides insight on ozone chemistry as well as its budget in the atmosphere.

1.1. Ozone chemistry and photochemical reactions

Ozone is a secondary pollutant, which formation occurs through catalytic reaction from nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), often emitted simultaneously with hydrocarbons (RH) and carbon monoxides (CO) by natural or man-made sources (Lelieveld and Dentener, 2000), under sunlight influence as shown in the following equations:



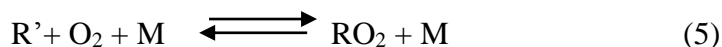
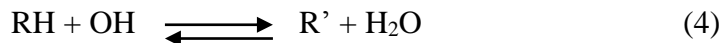
where $h\nu$ is the electromagnetic energy from the sun and M is a catalyst.

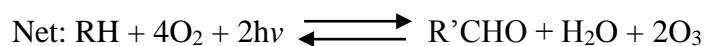
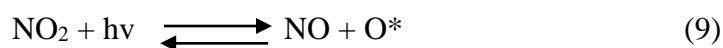
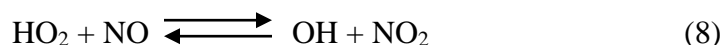
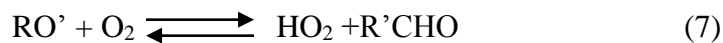
Ozone in the troposphere is important in the atmospheric chemistry as it generates OH radical from the photolysis of ozone at wavelengths $< 319 \text{ nm}$ (Demore *et al.* 1990).



The formation of OH radicals leads to a cycle of reactions that results in the photochemical degradation of organic compounds from anthropogenic and biogenic source, the enhanced formation of ozone, and the atmospheric formation of acidic compounds (WMO, 1986).

Typical of these reactions are shown below:





Adapted from Bundi (2004),

where initial reaction between a hydrocarbon (RH) and a hydroxyl radical (OH) results in the production of two ozone molecules, and an aldehyde R'CHO or a ketone. Fig. 1-1 and Table 1-1 below present the summary of tropospheric ozone chemistry, and present-day global budget of tropospheric ozone respectively.

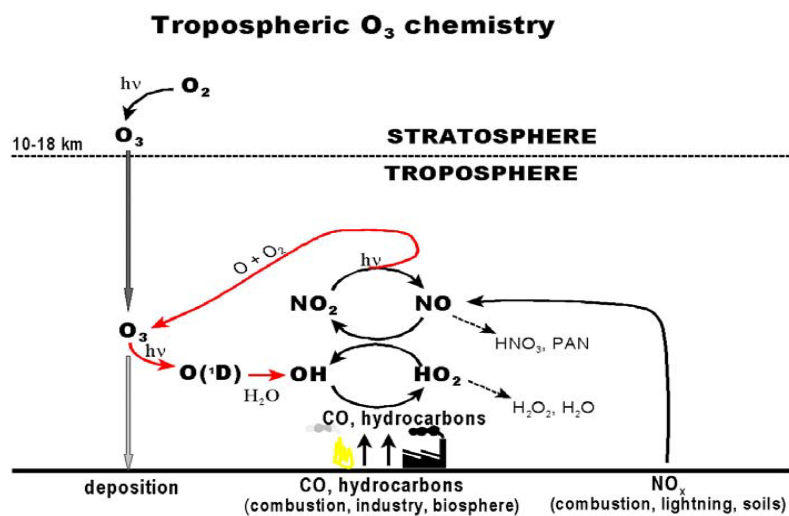


Fig. 1-1. Summary of tropospheric ozone chemistry

Source: NASA, 1999

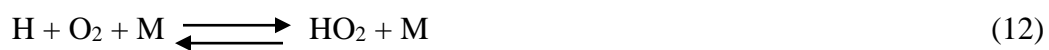
Table 1-1. Present-day global budget of tropospheric ozone expressed in teragram per year

Sources	Tg Ozone / Year
	3400-5700
Chemical Production	3000-4600
HO ₂ + NO	70%
CH ₃ O ₂ + NO	20%
RO ₂ + NO	10%
Transport from stratosphere	400-1100
Sinks	3400-5700
Chemical loss	3000-4200
O (¹ D) + H ₂ O	40%
HO ₂ + O ₃	40%
OH + O ₃	10%
Others	10%
Dry deposition	500-1500

Source: NASA, 1999

Additional ozone molecules can then be produced from the degradation of R'CHO. In addition to the oxidation of hydrocarbons, ozone can be generated from CO oxidation in reactions (11) and (12) followed by (8'), (9') and (10') as shown below.

Thus,



Hydrocarbons and carbon containing compounds provide the fuel for the production of tropospheric ozone, and are consumed in the process. In remote areas of the troposphere, carbon and methane, typically provide the fuel for ozone production (Seiler and Fishman, 1981). In urban locations, reactive hydrocarbons (often but not exclusively of anthropogenic origin) are usually the dominant fuel, while in rural areas reactive biogenic VOCs (Volatiles Organic Compounds) such as isoprene often dominate (Trainner *et al.* 1987; Chameiders *et al.* 1988). Thus increased burden of waste gases (precursors) in the atmosphere exacerbate the photochemical production of ozone (National Research Council, 1991) over the world and investigation are needed to determine the contributing sources and their dynamic.

1.2. Investigations on tropospheric ozone over tropical and southern Africa

Investigations on tropospheric ozone enhancement have been first addressed since the early second half of the 20th century, following urban episodes observed in the northern hemisphere (Haagen-Smit and Fox, 1956; Leighton, 1961). In tropical and southern Africa investigations, started toward the late end of the 20th century through several field campaigns (Sauvage *et al.* 2004). These campaigns aimed at determining the root causes of ozone enhancement observed through satellite images (Fishman *et al.* 1991) over the region. Contributing sources as well as dynamic factors were identified along with their temporal and spatial variations over the region (Fishman *et al.* 1986; Cros *et al.* 1988, Marengo *et al.* 1990; Laucaux *et al.* 1996). Traditionally, it was assumed that tropospheric ozone was controlled by Stratosphere Troposphere Exchange (STE) across extra tropical tropopause (Regener, 1957, Junge, 1962; Danielsen, 1968, Dusch, 1971). This assumption based on the observed ozone gradient with altitude was later corroborated by the work of Lelieveld and Dentener (2000), who found that 90% of the total ozone is present in the stratosphere

and only 10% is in the troposphere. Hence, the tropopause was suggested to be the source, with the sink at the surface.

Primary analysis made in the 1960's to comprehend the source of tropospheric ozone showed the photochemical formation of ozone in the troposphere as a product of the breakdown of hydrocarbons on urban environment during summer (Haagen-Smit and Fox, 1956; Leighton, 1961). According to these authors *in-situ* ozone formation is catalysed by nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) often emitted simultaneously with hydrocarbons (RH) and carbon monoxides (CO). Further photochemical studies undertaken in 1970's on ozone formation in the troposphere suggested that photochemical oxidation of all hydrocarbons, such as methane (CH_4) and carbon monoxide (CO), can cause ozone formation in large areas of the troposphere (Lelieveld and Dentener, 2000). Thus, it was predicted that tropospheric ozone in NO_x - rich air was predominant while destruction prevailed in NO_x -deficient air (Crutzen, 1973). This finding evolved two lines of thinking about the origin of tropospheric ozone: one emphasized the role of *in-situ* photochemistry (Chameides and Walker, 1976; Crutzen, 1974; Fishman *et al.* 1979), and the other emphasized ozone transport from the stratosphere (Chatfield and Harrison, 1976).

Over tropical and southern Africa, these factors have been poorly investigated, although a few studies undertaken in this region (Logan and Kirchhoff, 1986; Fishman *et al.*, 1990; Thompson *et al.*, 1996; Mauzerall *et al.* 1998) confirmed that biomass burning emissions constitute a significant and dominant source for tropospheric ozone formation during dry burning season (August—November), although Mauzerall *et al.* (1998) argued that biomass burning alone cannot fully explain these ozone enhancements during the dry season.

Further investigations undertaken by Chandra *et al.* (2002); Fishman *et al.* (1996); Thompson *et al.* (1996); Jacob *et al.* (1996), using ground-based instrument measurements as well as remote sensing satellite, confirmed seasonal variation of tropospheric ozone as a product of photochemical sources from biomass burning and stratospheric tropospheric exchange. This line of thinking concluded that ozone production in the troposphere is controlled by transport from the ozone-rich stratosphere (Olsen *et al.* 2000) and by photochemical oxidation of carbon monoxide (CO), methane (CH₄) and other volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO_x=NO+NO₂) (Crutzen, 1974; Atkinson, 2000).

Because transport from the ozone-rich stratosphere involves dynamic meteorology, three dimensional chemistry transport models (CTM) (Crutzen and Zimmermann, 1991; Müller and Brasseur 1995; Bernsten and Isaksen, 1997; Levy *et al.* 1997; Tie and Hess, 1997; Houweling *et al.* 1998; Wang *et al.* 1998; Hauglustaine *et al.* 1998; Crutzen *et al.* 1999) have been developed to understand dynamic processes contributing to ozone enhancement. Results from these models confirmed both photochemical and stratospheric as contributing sources of the tropospheric ozone; the preponderance of stratospheric intrusion compared with *in-situ* photochemical formation was also noted. A special approach was then advocated by these authors suggesting an approximate global budget contribution balance of both sources, which may be different from place to place. With this in mind, one may explain the highly variable spatial and temporal ozone distribution in various regions.

Subsequently, work done by Logan and Kirchhoff, (1986); Fishman *et al.* (1990); Thompson *et al.* (2003) suggested that the middle and upper troposphere of the tropical

Atlantic exhibits a persistent ozone maximum as part of the well-known zonal wave-one. At this altitude, ozone is critical for the global warming of the earth system, with maximum positive radiative effect (Forster and Shine, 1997). Attempts made by several authors to understand the origin of the observed ozone maximum gave evidence of various influence by the different regional sources, such as biomass burning (Pickering *et al.* 1996; Edwards *et al.* 2003; Jenkins and Ryu, 2004b; Sauvage *et al.* 2006), biogenic sources (Meyer-Arnek *et al.* 2005), lightning (Thompson *et al.* 2000; Martin *et al.* 2002) transport (Chatfield *et al.* 2004), as well as stratospheric-tropospheric exchange (Weller *et al.* 1996, Leleiveld and Dentener, 2000). At some extent, model analysis undertaken by Moxim and Levy (2000) quantified NO_x transported into that region during September, while Wang *et al.* (2006) suggested that both the Hadley and Walker circulation can contribute to the zonal wave-one pattern.

Furthermore investigation undertaken by Sauvage *et al.* (2007) suggested that despite tremendous accomplishments made on the origin of ozone maximum, much was still needed to be known of the tropical tropospheric ozone maximum, and atmospheric oxidation. The motive behind this approach was that there has been no quantitative estimation of the different sources contributing to the annual ozone maximum in this region. So far neither accurate emission inventory of ozone precursors such as NO_x, nor the contribution of each source to OH concentrations over tropical and eastern equatorial Africa troposphere was addressed to date. Findings made by these authors stipulated that determining processes that control the abundance of OH is then critical to understand how the oxidation capacity of the troposphere is changing due to OH short lifetime; this rather depends more on chemical reactions than on transport control (Bloss *et al.* 2006). To

address this pending issue, Sauvage *et al.* (2007) used a three dimensional global chemical transport model (Goddard Earth Observing System, GEOS-Chem), with emissions of nitrogen oxides (NO_x) from lightning, biomass burning, soils and volatile organic compounds (VOCs) constrained by *in-situ* and satellite observations. The model includes a detailed simulation of tropospheric ozone, nitrogen oxides, hydrocarbon chemistry as well as of aerosols and their precursors, using 41 tracers, around 90 species, and 300 reactions. The emission inventory in model simulation has been validated with *in-situ* measurements from aircraft (MOZAIC), and ozonesondes (SHADOZ) as well as GOME (Global Ozone Monitoring Experiment an instrument on board the ERS-2 satellite) measurements over the tropics. Results from this simulation provided a useful tool to fully understand the ozone maximum over the tropical Atlantic.

In the bid to provide more insight on the topic, Thompson *et al.* (2000) used satellite derived tropical data to study tropospheric ozone climatology over tropical Africa. Conclusions of their study suggested an apparent paradox existing between ozone precursors (biomass burning) and dynamic factors (inter-hemispheric transport across the intertropical convergence zone, ITCZ). These authors found that it was hard to reconcile summer biomass burning that occurs north of the ITCZ, and the maximum tropical tropospheric ozone (TTO) columns observed in the southern hemisphere (SH) tropical Atlantic, south of the ITCZ with modelling studies, which generally show high tropospheric ozone in regions of intense burning. This is the contrary of the situation observed later in the year, when the high ozone amounts, which develop in the southern Atlantic in September and October correlate reasonably well with the peak of the biomass burning activity in southern Africa and South America. These findings were drawn when tropospheric ozone studies relied on

field campaigns, regular ground-based and aircraft measurements from specific sites, and on an important contribution from chemical-transport modelling (Edwards *et al.* 2003). More recently satellite remote sensing has been used to complement previous studies by adding a larger geographical area, and seasonal context although it presents particular problems for isolating the tropospheric ozone from stratospheric total ozone column (Edwards *et al.* 2003).

According to the same authors, these challenges have been overcome thanks to new instruments that offered an exciting opportunity to extend knowledge of global tropospheric chemistry and assess whether these measurements are consistent with current understanding. This is substantially one of the key questions addressed in this thesis. At which extent change from meteorological factors can influence dynamic sources contributing to tropospheric ozone concentration in tropical and southern Africa. How likely these changes may affect the tropospheric ozone climatology in these regions given their vulnerability to climate change? These are the key research questions.

1.3 Study area

The scope of this study is limited to three climatic regions including Congo basin, equatorial eastern Africa and southern Africa (Fig. 2-1). According to the Intergovernmental Panel for Climate Change (IPCC, 2001) these regions are the most vulnerable in with regard to climate change with high population rate growth, high industrialization and urbanization and low resilience to mitigate climate change challenges. In addition, the variability of climate characteristics and the frequency of extremes climate events and the paucity of research due to lack of sufficient data in these three regions constitute the some key criteria

on which the choice of this region was made for this study. Although these stations are not representative of the regional climate characteristics of the individual region, ozone data observed in individual station may provide an indication on ozone variability due to climate change at regional scale.

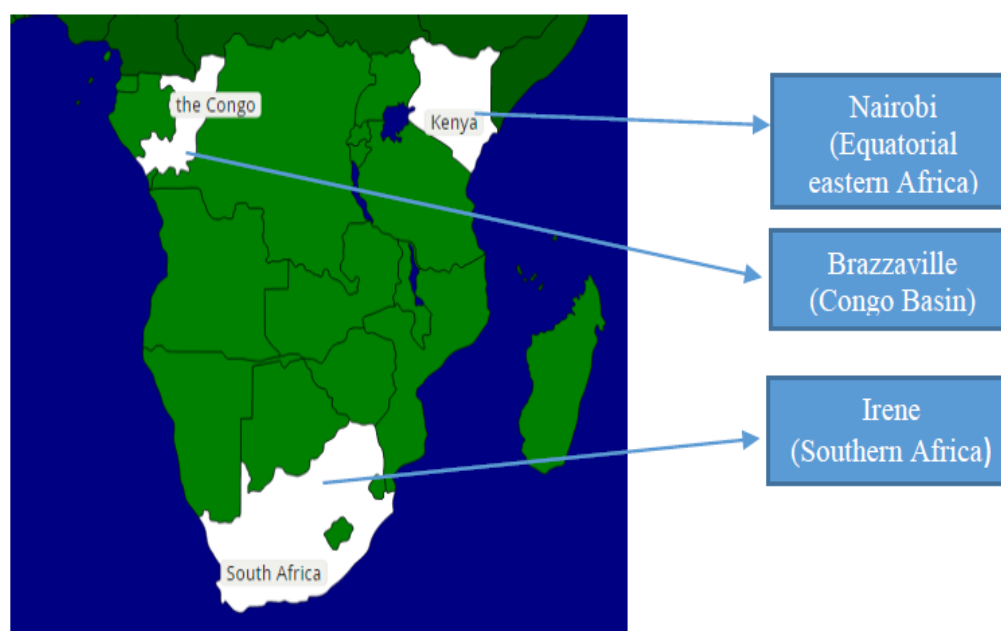


Fig.1-2. Map representing the study area (Brazzaville: the Congo Basin, Nairobi: Equatorial eastern Africa, and Irene for southern Africa)

Adapted from <http://online.seterra.net/en/vgp/3036> accessed on 19/11/2015

We investigate previous studies undertaken and the results obtained in individual region, and compare with the findings from this study in order to draw conclusion of tropospheric ozone climatology trends these three different climatic regions. Tropospheric ozone data from MOZAIC programme observed at Brazzaville and SHADOZ network data from Nairobi and Irene have constituted the basis of this study for the period 1998-2001, and

1998-2013 respectively. Details pertaining these programmes, and data acquisition and processing are duly provided in respective papers constituting the body of this thesis.

1.4 Purpose and objective of the study

The purpose of this thesis is therefore to model tropospheric ozone climatology by including climate change parameters over equatorial and southern African regions. This will be achieved through the following objectives:

- To assess tropospheric ozone characteristics and trends in the three climatic regions including southern Africa, the Congo basin and the eastern equatorial African region;
- To assess the main contributing sources of tropospheric ozone, their dynamic and occurrence in individual location
- To investigate the relationship between climatic factors and tropospheric ozone variation distribution in these regions.
- To document and fill the existing gap on tropospheric ozone climatology with regard to their relationship with climate change parameters in these regions;
- To assess ozone trends in these regions with regard to climate change parameters, and elaborate suitable solutions for a better management strategy and climate change mitigation programme.

1.5 Thesis outline

This work reports tropospheric ozone climatology by including climate change parameters in three different climatic regions including southern Africa, Congo Basin and equatorial eastern Africa. It is believed that change in meteorological parameters due to climate change

such as observed in recent years may have an impact on tropospheric ozone contributing factors. Consequently, impact on these factors may have an influence on tropospheric ozone variation and distribution at regional and global scale. This work is divided into six chapters. The first chapter provides a summary on tropospheric ozone background including its chemistry and budget, its effects on human health and the environment, and the purpose of its investigation in tropical and southern Africa. The second chapter presents sources contributing to tropospheric ozone enhancement over tropical and southern Africa and the impact of climate change on these sources. Part of this work has been presented as a conference papers at the 31st South African Society of Atmospheric Science conference at Pretoria from 21-23 September 2015, Peer review Conferences proceedings ISBN 978-0-620-67825-4. Chapter three presents the modeling of tropospheric ozone climatology at Irene (South Africa) using retrieved remote sensing and ground-based measurement data. This chapter has been published and may be cited as:

Mulumba et al. (2015). Modeling Tropospheric Ozone Climatology over Irene (South Africa) Using Retrieved Remote Sensing and Ground-Based Measurement Data. J. Geophysical Remote Sensing, 2015, 4:3 <http://dx.doi.org/10.4172/2169-0049.1000151>., pp11. Chapter four provides the modeling of tropospheric ozone climatology over the Congo basin. This chapter is to be submitted for publication. Chapter five presents the modeling of tropospheric ozone climatology over equatorial eastern Africa using climate change parameters and will also be submitted for publication. Chapter six summarizes the results of this work and provide some suggestions for the future research.

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Present-day global budget of tropospheric ozone/ Summary of tropospheric ozone chemistry

<http://online.seterra.net/en/vgp/3036> accessed on 19/11/2015: Map representing the study area: Brazzaville: the Congo Basin, Nairobi: Equatorial eastern Africa, and Irene for southern Africa.

CHAPTER TWO

CLIMATE CHANGE IMPACT ON SOURCES CONTRIBUTING TO TROPOSPHERIC OZONE OVER EQUATORIAL AND SUBTROPICAL AFRICA

Part of this chapter has been presented at 31st annual conference of South African society for atmospheric science held during 21-23 September 2015 at Hennops River Valley, Pretoria, South Africa.

CLIMATE CHANGE IMPACT ON SOURCES CONTRIBUTING TO TROPOSPHERIC OZONE OVER EQUATORIAL AND SUBTROPICAL AFRICA

2.0 Abstract

There is very less information on sources contributing to tropospheric ozone formation in Equatorial and Subtropical African regions with regard to their dynamic and occurrence. Five main contributing source emissions including stratospheric tropospheric exchange (STE), biomass burning and urban industrial, biogenic and lightning have been identified from satellite imagery and a few measurement campaigns undertaken in the region. As tropospheric ozone variability sharply depends on prevailing meteorological conditions in a given location, it is has been proven that change in these conditions may have an impact on ozone transport and chemistry, which determine the lifetime of ozone precursor's species in the atmosphere. Recent changes observed in climatic parameters at global scale, may have outstanding effect on tropospheric ozone concentration over equatorial and subtropical region, due to its geographic position, its ever growing population, and its recent urbanisation and industrialisation progress. In the absence of specific data on ozone precursors over these particular regions, we use existing sources emission inventory to assess individual source dynamic and occurrence, and ultimately predict the possible impact due to climate change. Biomass burning, which is the largest source of trace gas emission in the region (38%) can be exacerbated due to prolonged drought conditions that may prevail over subtropical region hence, providing more dry matter for fire burning. Biogenic and lightning emissions with 25% and 17% respectively are set to rise as result of severe thunderstorms, accompanied with abundant rainfall and flood which may be experienced in

equatorial region. Notwithstanding stratospheric ozone intrusion and lightning emission, which contributes to almost 52% of annual tropospheric ozone are also vulnerable change on climatic parameters as these changes may exacerbate chemical and transport process in both ways stratosphere – troposphere and vice versa, and cause more ozone enhancement in the upper and middle troposphere in these regions.

Key words: *Climate change, impact, sources, tropospheric ozone*

2.1 Background

The presence of ozone in the troposphere is driven by natural sources such as stratospheric tropospheric exchange (that control direct intrusion of stratospheric ozone into the troposphere) as well as photochemical sources including lightning, biogenic and anthropogenic emissions. In equatorial and subtropical Africa contribution of these sources has poorly been investigated and documented, with regard to their occurrence as well as their dynamic, although a few studies undertaken in the region emphasize the role of photochemical ozone at the surface, and stratospheric ozone intrusion in upper troposphere (Diab *et al.* 2004; Thompson *et al.* 2003). Ozone formation is driven by both chemical and dynamic processes. Dynamic processes are responsible for transport of trace chemical species from anthropogenic and natural emissions (Holton *et al.* 1995), while chemical effects from stratospheric tropospheric exchange (STE) can consequently influence the radiative flux balance in the troposphere and lower stratosphere in many ways (Ramaswamy *et al.* 1992; Toumi *et al.* 1994). Hence, climate change may significantly affect downward transport (Butchart and Scaife 2001), and the oxidizing capacity of the troposphere (Lelieveld and Dentener 2000). This transport not only constitutes the main removal

mechanism for many stratospheric species including those involved in ozone depletion, but also represents a significant input of ozone and other reactive species into the tropospheric chemical system (Levy *et al.* 1980). Hence, tropospheric ozone budget strongly depends on the origin and nature of ozone precursor's species that contribute to its formation. These species, as well as the majority of those emitted into the troposphere from the surface and the stratosphere, are subject to a complex series of chemical and physical transformations, which determine their life time in the troposphere (Monks, 2005). As a result, a variety of radicals that exert a substantial influence on the ultimate composition of the atmosphere is produced (Monks, 2005). Sinks contributing to the tropospheric ozone budget are dry and wet deposition, photolysis and catalytic destruction of hydroxyl radical. In this work, we assess individual source categories dynamic and interaction on tropospheric ozone enhancement, with regard to climate change impact in these regions. We also examine tropospheric ozone budget and their effect on the environment. A summary of the main ozone contributing sources as well as their respective climate change impacts discussed above will conclude this chapter.

2.1.1 Stratospheric tropospheric exchange

Stratospheric and Tropospheric Exchange (STE) is one of the key processes that influence the composition of the atmosphere at a given altitude and latitude, in a particular region. It is a two-way exchange process, which includes upward transport from the troposphere to the stratosphere, and downward transport from the stratosphere to the troposphere (Stohl *et al.* 2003). As such, STE encompasses dynamical, chemical, and radiative coupling processes that must be understood for prediction of global atmospheric change (Holton *et*

al. 1995). Dynamic processes are responsible for transport of trace chemical species from anthropogenic and natural emissions (Holton *et al.* 1995). Chemical effects consequently influence the radiative flux balance in the troposphere and lower stratosphere in many ways (Ramaswamy *et al.* 1992; Toumi *et al.* 1994). Hence, change in climate parameters may significantly affect the downward transport (Butchart and Scaife, 2001) and the oxidizing capacity of the troposphere (Lelieveld and Dentener 2000). Upward transport of anthropogenic species from the troposphere into the stratosphere, are responsible for much of the chemistry that initiate stratospheric ozone depletion (WMO, 1995), and can occur on timescales as short as a few hours via moist convection, and on timescale of days via baroclinic eddy motions in middle latitudes. Vertical transport which can take months, a year or more in the lower stratosphere, is more often accompanied by radiative heating or cooling as shown in Fig. 2-1 (Holton *et al.* 1995). These processes can be observed through by the rapid increase in ozone mixing ratio, and the rapid decrease in water vapor mixing ratio with altitude that occurs just above the tropopause. For this reason, it was then suggested that measurement of STE must be done by taking into account the following parameters: the rate at which tropospheric material is supplied to, and removed from the regions in the stratosphere; the species' photochemical sensitivities at different altitudes and latitudes; and the global-scale circulation including the spatiotemporal structure of transport within the stratosphere. In addition to these parameters, others parameters such as thermal inversion, in which temperature stable layers favour strong relative humidity decrease and ozone enhancement (Taupin *et al.* 2001) can also be considered. Such phenomena has been identified by Baray *et al.* (1998) who classified ozone enhancement due to temperature and humidity subsidence as of stratospheric origin through potential

vorticity study. They suggested a study of thermal and chemical behaviour of the tropopause in order to better understand the contribution of stratospheric ozone into the troposphere. This concept led to defining the notion of tropopause as a strong indicator for STE detection.

Conventionally, the World Meteorological Organisation (WMO) defines the tropopause as the lowest level at which the temperature lapse rate decreases to $2\text{ }^{\circ}\text{K km}^{-1}$ or less and the lapse rate averaged between this level and any level within the next 2 km does not exceed $2\text{ }^{\circ}\text{K km}^{-1}$. According to Holton *et al.* (1995) this region is characterized by an increase in the static stability in moving from the troposphere to the stratosphere.

On the basis of these notions, tropical and extra-tropical tropopause can be distinguished; the first roughly corresponding to an isentropic temperature or stratification surface (whose potential temperature varies from $0 \sim 380\text{ }^{\circ}\text{K}$ in the annual mean) and the second roughly corresponding to a surface of constant potential vorticity. Because of persistent doubt about STE contribution to tropospheric ozone, many authors (e.g. Crutzen and Zimmermann, 1991; Müller and Brasseur, 1995; Roelofs and Lelieveld, 1995; Beretsen and Isaksen, 1997; Levy *et al.* 1997; Tie and Hess, 1997; Houweling *et al.* 1998; Wang *et al.* 1998; Crutzen *et al.* 1999) used three dimensional global chemistry transport models to explicitly account for both photochemical and meteorological processes contribution to ozone formation in upper troposphere. Results from these models in many cases indicated that a large portion of global tropospheric ozone was from the stratosphere as suggested by Lelieveld and Dentener (2000).

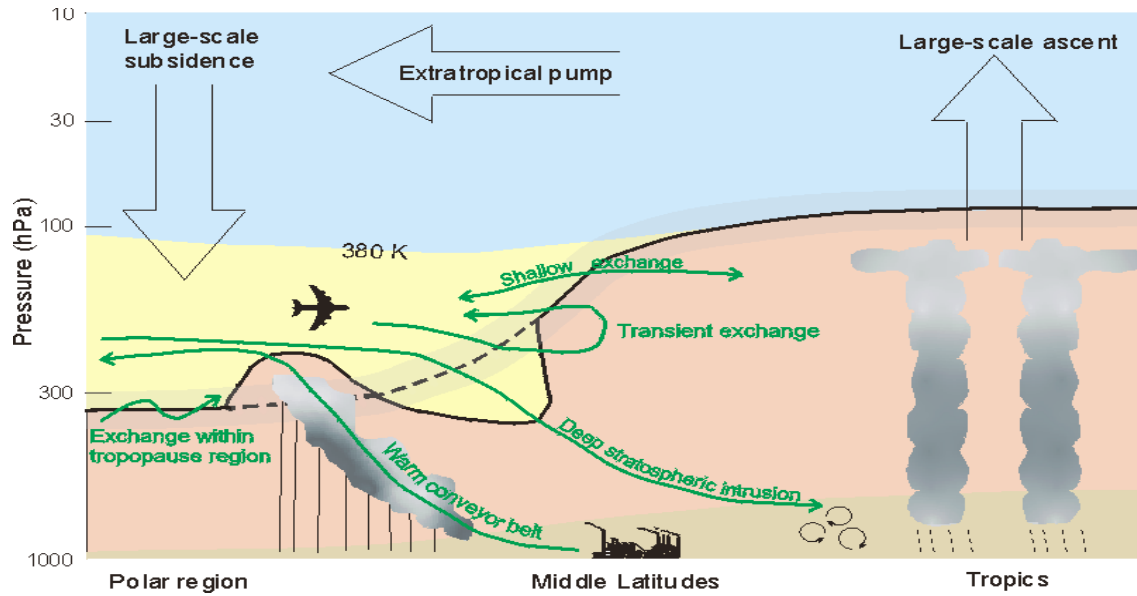


Fig 2-1. Global aspects of STE from Holton *et al.* (1995), with Lagrangian STE concept superimposed.

The average position of the tropopause is shown by the thick black line, with shaded regions on either side representing the tropopause region. The blue region is the “overworld,” in which isentropes (above the 380-K isentropic surface) lie entirely in the stratosphere, the yellow region is the lowermost stratosphere where isentropic surfaces cross the tropopause, the pink region is the free troposphere, and the brown region is the ABL. Broad arrows show transport by the global-scale circulation. Green trajectories illustrate our new concept. Pink and yellow bulges near the warm conveyor belt and the deep stratospheric intrusion indicate strong perturbation of the tropopause from its average position (dashed). Note that the pressure is not to scale.

Source: Stohl *et al.* (2003)

Subsequently results from a global chemistry transport model that used European Centre for Medium-Range Weather Forecasts (ECMWF) meteorological reanalysis data to drive tracer transport and removal, suggested that STE is relatively strongest in mid-latitudes and high-latitudes in the Northern Hemisphere winter. In addition, seasonal changes in the mass of the lower-most stratosphere, as well as the tropopause altitude change (e.g in spring) entrain stratospheric air into the troposphere (Reiter, 1975; Appenzeller *et al.* 1996).

It was then assumed that these processes combined are responsible for downward ozone transport that reaches a maximum in winter and early spring in mid-latitude northern

hemisphere. However observations made in several stations in the northern hemisphere by Lelieveld and Dentener (2000) stipulated that spring maximum was due to photochemistry rather than to STE. The above findings were on line with those made by Holton *et al.* (1995) who suggested that the lowermost stratosphere and upper troposphere are more important for global chemical processes than it was formerly thought. For example, some of the heterogeneous chemistry responsible for observed ozone depletion occurs in the lowermost stratosphere, and much of the tropospheric non-urban photochemical ozone production occurs in the upper troposphere (WMO, 1995).

Hence understanding and modelling the chemistry of these regions requires that temporal and spatial distribution of trace chemical transport in the upper troposphere and lowermost stratosphere shall be known, both along and across isentropic surfaces (Holton *et al.* 1995). To illustrate this concept, Collins *et al.* (2003) found discrepancy between estimate inputs from the stratosphere considered as a significant source of ozone in the troposphere from a range of 340 to 930 Tg/year⁻¹ in comparison with Collins *et al.* (2000) estimate photochemical production of 2820–4190 Tg yr⁻¹. This shows the importance of this particular source where ozone is most effective as a greenhouse gas. Thus prediction of future radiative forcing from ozone depends on accurate simulation of the upper tropospheric ozone concentration, hence, on the simulation of the cross tropopause transport of ozone (Collins *et al.* 2003).

However, according to Zanis *et al.* (2003), downward transport of ozone from the stratosphere to the lower troposphere can only occur under certain circumstances such as suggested by Haynes *et al.* (1991) who stipulated that the bulk of air downward through the

extra tropical tropopause is determined by the Brewer Dobson circulation. This circulation is primarily driven by wave disturbance that originates in the troposphere (Charney and Drazin, 1961; Haynes *et al.* 1991) through air flow from mountains, synoptic weather systems and deep convection. Given future climate change, this circulation, which is driven by Rossby wave action in the extratropical middle atmosphere (Collins *et al.* 2003), may also change the rate of exchange between the stratosphere and the troposphere as predicted by Lelieveld and Dentener (2001); Butchart and Scaife (2001).

Accordingly, while finding made by Butchart and Scaife (2001) suggested an increase in the mass exchange between the stratosphere and troposphere in a changed climate, Stohl *et al.* (2003) confirm that on a local scale, synoptic scale disturbances in the tropopause regions, as well as frontal circulation and convective systems are responsible for the cross-tropopause transport of ozone. Previous studies using model predictions of future tropospheric ozone changes and radiative forcing have initially focused on projection of precursors emissions (Stevenson *et al.* 1998a; IPCC, 1996). However more recently three dimensional models used by Johnson *et al.* (1999), Grewe *et al.* (1999), and Stevenson *et al.* (2000) have shown that climate change reduces ozone concentrations. According to these authors, increase in specific humidity leading to a greater flux through the reaction of $O(^1D)$ with water vapour is responsible for this reduction. This is one of the key questions, which the impact of climate change parameters on tropospheric ozone distribution and variations is based upon. Because change in specific humidity implies change in temperature and other meteorological factors, a correlation influence of these parameters may possibly provide more insight on the topic.

2.1.2 Photochemical ozone emission sources and their dynamic over equatorial and southern Africa

2.1.2.1 Biomass burning

Contribution of biomass burning to atmospheric chemistry presented less interest until the first papers pioneering its impact on the atmosphere were published in the 1970s and early 1980s (e.g., Eagan *et al.* 1974; Radke *et al.* 1978). Despite its least social and economic importance in the developed world, biomass burning remains a traditional energy source, and a secular cultural practice for agriculture and pastoral activities as a response to socio-economic pressure of the ever growing population in developing world particularly in African continent (Anderson *et al.* 1996; Guild *et al.* 1998). For almost two decades, a large body of research (Crutzen *et al.* 1985; Crutzen and Andreae, 1990; Watson *et al.* 1990; Fishman *et al.* 1991; Andreae *et al.* 1994; Cahoon *et al.* 1994; Folkins *et al.* 1995; Browell *et al.* 1996; Connors *et al.* 1996; Talbot *et al.* 1996; Thompson *et al.* 1996; Jonquie`res *et al.* 1998; Novelli *et al.* 1998; Blake *et al.* 1999; Gregory *et al.* 1999; Singh *et al.* 2000) widely recognized biomass burning as a significant source of radiative species including aerosols, carbon dioxide (CO₂), nitrogen oxides (NO_x = NO + NO₂), carbon monoxide (CO), which play an important role in the chemistry and the radiative budget of the troposphere. In addition, it also contributes to the greenhouse effect directly through the emission of CH₄ and nitrous oxide (N₂O), methyl bromide (CH₃Br), ammonia (NH₃), non-methane hydrocarbons (NMHCs), and other species, and indirectly through the production of tropospheric ozone (Lindesay, 1992; Mano and Andreae, 1994). With regard to the above mentioned reasons, Hao and Liu (1994) consider Africa to be a leading source of air pollution from biomass burning. This statement seems to be in good agreement with the

findings made by Andreae, (1997); van der Werf *et al.* (2003); van der Werf *et al.* (2006), who stipulated that African fires are responsible for an average of perhaps 30 to 50% of the total amount of vegetation burned globally each year, making Africa, on average, the single largest biomass burning emissions source. Illustration of trace gas emissions from various sources for Africa is provided in Table 2-1. Moreover a study undertaken by Delmas *et al.* (1991) suggests that annual burned dry matter biomass over Africa is estimated at 1.3×10^6 tons year⁻¹. This is due primarily to human activities, such as biomass burning through cleaning of forest and bush land for agricultural use, conversion of forests to agricultural and pastoral lands, energy production for cooking, heating and fuel, control of pests, insects and weeds, nutrient mobilization, and removal of bush and litter (Crutzen and Andreae, 1990).

Further investigations undertaken on emissions from biomass burning done by Cauten *et al.* (1999) suggested that emissions of radiative species depend on biomass type, meteorology and combustion stage. Depending on the above mentioned parameters, these species can alter the radiation budget of the earth, either by contributing to global warming through the production of aerosols. Moreover, chemical species such as methane (CH₄) and Nitrogen oxides (NO_x) play a major role in local downwind concentrations of the major atmospheric oxidants namely O₃ and OH radical (Prasad *et al.* 2000).

Because there are no adequate data on the regional occurrence, size distributions, or trends in fire numbers or areas burned annually, it is assumed that southern Africa has the most extensive biomass burning in the world (Dwyer *et al.* 2000). This was suggested due to ozone enhancement observed through satellite and ground based measurement over this region (Seiler and Cruzen, 1980; Cruzen and Andrea, 1990). These findings were in

agreement with those made by Andrea and Merlet, (2001) who confirmed biomass burning as a major source of tropospheric ozone formation over southern Africa and the adjacent Indian Ocean, although quantification of the effect of emissions on atmospheric chemistry and radiative budget is inaccurate due to uncertainties in knowledge of the magnitude, spatial and temporal location of emissions (IPCC, 2001).

Table 2-1. Annual trace gas emissions from various sources for Africa (inTeragram)

Source	Emissions, yr ⁻¹				
	CO ₂ , Tg C	CO, Tg C	CH ₄ , Tg C	NMHC, Tg C	NO _x , Tg N
Biofuel*	181	16.3	0.8	1.3	0.4
Other biomass burning†	156	79.6	5.4	11.8	2.7
Industry‡	228.9	4.0	2.3	4.7	1.0
Biogenic§	...	11.9	9.6	105.2	1.8
Lightning	1.2
Total	565.9	112	18.1	123	7.1
Other estimates (biofuels) <i>Olivier et al. [1996]</i>	262	19.2	2.8	6.2	0.3

*Own inventory (see text).
†Includes savanna burning, agricultural waste burning, and deforestation fires. For CO₂ only deforestation fires have been considered.
‡Includes fossil fuel burning and industrial processes.
§Includes soil and vegetation emissions.

Sources Marufu *et al.* (2000)

Thus, although biomass burning does not generate large amounts of ozone in a global sense, the burning yields larger upsurges in other important trace gases. Therefore tropospheric ozone produced from biomass burning is primarily a regional effect within, and near the burning with most generated ozone lying in the low troposphere (Ziemke *et al.* 2009). Growing scientific interests on this topic suggested that some atmospheric pollutants from biomass burning could rival fossil fuel use as a source of atmospheric pollution (Seiler and Crutzen, 1980; Crutzen and Andreae, 1990). Evidence that these emissions could affect large areas of the world, as a consequence of long-range transport has been provided with the studies undertaken by Andreae, (1983); Kirchhoff and Nobre, (1986); Reichle *et al.*

(1986); Fishman *et al.* (1990). With this in mind, emissions of ozone precursors from biomass burning and their consequent photochemistry have been observed at different scales (Andreae *et al.* 1988, 1992; Marenco *et al.* 1990; Fishman *et al.* 1990; Jonquieres *et al.* 1998). Conclusion of these studies generally recognized that emissions from biomass burning produced by forest and savannah fires in southern Africa, and Brazil are a significant source of ozone precursor gases, which may produce 10-15 DU increase in tropospheric column ozone (TCO) in the South Atlantic region during austral spring (e.g. Fishman *et al.* 1996, Thompson *et al.* 1996, Jacob *et al.* 1996), and several related papers in the special issue (e.g. STARE, TRACE-A and SAFARI 2000).

In contradiction with the above findings, studies based on three-dimensional (3-D) atmospheric chemistry and transport models suggested that the photochemical O₃ formation from biomass burning may be less important than indicated in previous studies (e.g., Lelieveld and Dentener, 2000; Marufu *et al.* 2000; Moxim and Levy, 2000). In support with these findings, Martin *et al.* (2007) argue that more than 40% of the tropospheric ozone, throughout much of the tropics, is generated from lightning while Sauvage *et al.* (2007) emphasised that lightning is 4-6 times more efficient in producing ozone than the combined effects of biomass burning, soils, and fossil fuels. These findings have been corroborated by Ziemke *et al.* (2009) who confirmed that biomass contribution to ozone formation is smaller when compared to the effects from lightning and transport in the troposphere. Therefore in order to complement existing information on biomass burning contribution to ozone formation, temporal as well as spatial distribution of fire over a region was needed.

The importance of temporal and spatial distribution of biomass burning as global phenomenon can be understood by the fact that it can modify land surface properties, influence atmospheric chemistry and air quality, and perturb the radiation budget (IPCC, 2001). Therefore information pertaining temporal and spatial distribution of biomass burning is useful to provide a better understanding of the dynamic evolving emission of ozone precursors in a given region. In the bid to get hold on this information, a great deal of research was carried out a couple of decades ago to monitor the spatial and temporal distribution of African biomass burning (e.g. Giglio *et al.* 2006b; Cooke *et al.* 1996; Dwyer *et al.* 2000; van der Werf *et al.* 2004). Finding of these studies stipulated that over tropical south Atlantic, biomass occurs during dry season extending from August to November (Logan and Kirchhoff, 1986; Fishman *et al.* 1990; Thompson *et al.* 1996 and Mauzerall *et al.* 1998). According to these authors biomass burning is suggested to be a significant source of ozone precursors in this particular region during this period of the year. Unfortunately, field campaigns for this research were based on short time periods (usually less than a year) and could not detect inter-annual variability in biomass burning emission and atmospheric transport over the region (Allen *et al.* 1996; Barbosa *et al.* 1999; van der Werf, *et al.* 2006). Hence, to better understand temporal and spatial biomass burning distribution inter-annual variation as well as long term trends, more investigations were absolutely required (Wai *et al.* 2013). These investigations have the advantage of providing necessary information for forecasting future potential impacts of global change on atmospheric composition and air quality. Unfortunately most of these studies were mainly focused on the northern mid-latitudes, in particular the developed regions (e.g., Liao *et al.*, 2006; Unger *et al.* 2006; Hedegaard *et al.* 2008; Wu *et al.*, 2008a, b) and none was

undertaken on the Southern Hemisphere (Wai *et al.* 2013). Hence, by virtue of filling up the existing gap these authors recently studied the impact of biomass burning on tropospheric composition in the tropics and Southern Hemisphere. The aim of this study was to examining seasonal variation and long-term trends by combining *in-situ* measurement data and model simulations, and to assessing the potential impacts on tropospheric composition, in this particular region. Accordingly, IPCC voice that this region is driven by 2000–2050 changes in emissions and climate, and suggest that all future socioeconomic scenarios developed will have significant changes in global emissions of ozone precursors (NO_x, VOC and CO), including emissions from biomass burning over the 21st century (Nakicenovic and Stewart, 2000). The findings of this study revealed that in southern Africa, the wide-spread burning events occur mainly in Angola, Zambia and Democratic Republic of the Congo and Zambia where an estimate 40–150 Tg were burned during July to September. According to these authors, fire event is exacerbated by persistent low-level easterlies/south-easterlies winds which facilitate the westward transport of CO plumes from Southern Africa. They associated the existence of three synoptic-scale high pressure systems which are persistently located over Southern Africa, Latin America/adjacent Atlantic Ocean and Indian Ocean. In addition, subsiding air and relatively low wind speeds which limit the dispersion of the biomass burning were also featured under the influence of the high pressure system prevailing over Southern Africa, causing the recirculation of CO plumes over the continent (Wai *et al.* 2013) and consequently enhancing much pollution over this region.

Furthermore, work done by Giglio *et al.* (2006b) voiced a strong variability of fire in Africa, which is characterized by diurnal and seasonal variation. This variation is linked to land cover type as it determines the amount of biofuel burned and (Roberts *et al.* 2008) carbon emission rate into the atmosphere. To illustrate this concept, (Korontzi, 2005) provided an example of earlier dry season fires which is characterized by incomplete combustion due to the higher fuel moisture contents, and consequently emit a greater proportion of less oxidized trace gas products such as CO than do later dry season events (Korontzi, 2005). According to recent research, southern Africa is dominated by 46% woodland, 25% grassland, 15% shrubland, and 9% cropland by area; the rest are dessert and water. Most fires occur primarily between June and October, generally moving from the northeast to southwest of this region. Fires are much less common in the equatorial areas of the “woodland” land cover class, which is generally dominated by moist tropical forest that is resistant to burning when in an undisturbed state (Bucini and Lambin, 2002). Accordingly Roberts *et al.* (2008), southern African woodland burning dominates the first half of the dry season (May–June), but becomes less dominant later on (July–October) when burning in shrubland and grassland becomes more significant. This corresponds to the southward movement of fire activity from the south-central African woodlands into the shrublands and grasslands of South Africa which also displays a longer fire season than most other areas, with some burning occurring throughout the year. Fire seasonality over southern Africa has been questioned given the discrepancy observed between various data sources. Subsequently, Edwards *et al.* (2006) who used atmospheric chemical transport model demonstrated that three quarters of fire-emitted CO would be transported out of the region within 8 days, which is too short to explain the seasonality differences observed. However

Justice *et al.* (2002) confirm that although active fire locations have been derived systematically by hotspot detection algorithms applied to orbital satellite data, these data do not provide reliable information on the spatial extent and timing of burning, as clouds may preclude hotspot detection and because the satellite may not overpass when burning occurs.

In contrast to Equatorial region, most fires in southern Africa occur in the dry season, from approximately May to October, when herbaceous vegetation is either dead (annual grasslands) or dormant, and when deciduous trees have shed their leaves, thereby contributing to an accumulation of dry and fine fuels that are easily combustible (Scholes 1997, Frost 1999). The availability of fuel is primarily controlled by annual precipitation and soil fertility, and is reduced by livestock (e.g. cattle grazing) and by people (e.g. fuel collected for domestic energy) (van Wigen and Scholes 1997, Frost 1999). This is the reason why fire is less common in arid regions in the west and south western interior where there is often insufficient biomass fuel (the part of the biomass that normally burns, i.e. dead wood, grass, shrubs and litter).

2.1 2.2. Anthropogenic emissions

Anthropogenic emissions refer to human activities including energy-use in industry, transportation, mining, construction, and in the household (Aghedo *et al.* 2007). These activities constitute a source of trace gases (NO_x , SO_x and SO_4 , CH_4), that result on tropospheric ozone formation. A study done by Lelieveld and Dentener, (2000) shows that in the tropics and extra-tropical Southern Hemisphere, these emissions contribute 10 to 20% to the total column ozone. While southern African region is known as one of the fastest

growing region with regard to human population and urbanisation, it is likely that anthropogenic emissions in this region may increase as the needs of energy for household, transportation and industrialisation use is also set to increase (UNEP, 1999). Recent study performed by Lelieveld *et al.* (2004) on the topic confirms that tropospheric ozone enhancement observed over Atlantic Ocean is attributed to increase in anthropogenic NO_x emissions in Africa. This increase may be due to the fact that most countries in southern Africa either lack or have inadequate air quality standards (UNEP, 1999) and capacity to control anthropogenic emissions from mobile and stationary sources. This is one of the reasons why this region remains a poorly documented in terms of air quality as *in-situ* measurements on urban and industrial pollutants are still scarcely undertaken (Sauvage *et al.* 2006).

However, South Africa as well and Reunions Island are the only countries in the region where anthropogenic emissions from urban and industrial activities have been studied with regard to tropospheric ozone (Diab *et al.* 2004, Clain *et al.* 2009). For instance, results from *in-situ* measurements conducted at Irene (South Africa) shows that much of tropospheric ozone observed in this station was due to urban and industrial pollution from Gauteng province which accounts eleven large coal power plants with a generating capacity of 34 Giga Watts (Diab *et al.* 2004).

2.1.2.3. Biogenic emissions

Biogenic emissions sometimes referred to as BVOCs, are volatile organic compounds (VOCs), which encompass many gases resulting from biological metabolic processes on land and in the Oceans (USEPA, 2005). Their emissions are principally found in forests

and savannas (Scholes and Andreae, 2000) where important quantities are most observed in the month of October corresponding to the rainy season in the Southern Hemisphere. During this period of the year, microbial activity processes (nitrification/denitrification) that were slowed down in dry soil conditions in winter (June, July and August) resume (USEPA, 2005), and lead to the production of NO, which is quickly oxidized in NO₂ (Delon *et al.* 2008; Delon and Reeves, 2007). Oxidation of VOCs from biological sources (soils and vegetation) in presence of NO_x (NO+NO₂), and sunlight leads to the formation of ozone in the troposphere (Delon *et al.* 2008). According to these authors, NO emissions from soils amongst other sources directly influence NO_x concentrations due to the oxidation of NO₂. Therefore change in NO sources is said to consequently modify the rate of ozone production. This confirms the findings made by Harris *et al.* (1996) who suggested that biogenic emissions lead to ozone enhancement.

In essence, it is well known that biogenic emissions significantly contribute to atmospheric chemistry both at a global and regional scale (Otter and Scholes, 2005). However, emissions strength of biogenic species depend on ecological factors such as temperature, soil type (Ludwig *et al.* 2001; Delon *et al.* 2009) light intensity and moisture (Otter and Scholes, 2005). These conditions, which prevail in tropical regions for several months, even the entire year, are responsible for higher emission rate observed (Otter and Scholes, 2005) therein. However, emissions are insignificant in semi-arid ecosystems where high temperatures, periodic droughts, and low to no vegetation cover with less microbial activities are recorded.

Despite the scarcity of data, and large uncertainties on emission rate (Nyamadzawo *et al.* 2012) the most important factor in determining biogenic emissions is the response to environmental changes occurring during the year (Delon *et al.* 2008). Accordingly Otter and Scholes (2005) argue that the long dry season often leads to a build-up of nutrients in the system, particularly in the soil, and rain acts as a switch for microbial activity to begin immediately and release ozone precursor gases. The most commonly known biogenic species present in the atmosphere include NO, N₂O, VOCs, and CH₄. However, nitric oxide (NO), and carbon monoxide (CO) are both chemically active, and impact on the chemistry of the troposphere (Houghton *et al.* 1990).

With regard to ozone formation and reactivity with OH (Royal Society, 2008) isoprene is the most dominant biogenic species (Guenther *et al.* 2006), although recent field measurements have shown that a diverse range of Biogenic Volatile Organic Compounds (BVOCs) are released at lower rates from a range of vegetation types (e.g. Villanueva-Fierro *et al.* 2004). According to Williams *et al.* (2009), nitric oxide from recently wetted soils is also important in tropospheric ozone formation. However, Otter and Scholes (2005) suggest that the pulsing of nitric oxide after rain is insignificant at the global scale although numerous regional studies emphasise that these pulsing events are extremely important for regional atmospheric chemistry. This confirms the finding made by Yienger and Levy (1995) who stipulate that nitric oxide is widely recognized as an important natural source of reactive nitrogen at remote locations in the tropics.

In southern Africa, it has been suggested that biogenic emissions during spring time, both the NO from pulsing and VOCs from increased leaf density, could have an important

contribution towards the annual austral spring mid-tropospheric ozone maxima over the tropical south Atlantic (Otter and Scholes, 2005). Although the rate of deforestation of virgin rainforest in Africa is about 0.43% per year (this represents 8500 square-km/year), the results of global biogenic emissions from vegetation calculated with the Model of Emissions of Gases and Aerosols from Nature (MEGAN) by Guenther *et al.* 2006, which is incorporated into the general circulation model ECHAM5 (the 'EC' being short for 'ECMWF' (European Centre for Medium-Range Weather Forecasts) and the place of development of its parameterisation package, Hamburg, version 5) (Roeckner *et al.* 2003) show that Africa contributes about 24% (i.e. 120 Tg(C)/year) of isoprene and 18% (i.e. 30 Tg(C)/year) of total terpenoids emitted globally (Aghedo, 2007). With regard to NO_x emissions from soil, present in the atmosphere Lelieveld and Dentener (2000) estimate ~5 to 12 Tg N per year which encounters air mass already enriched with biomass burning to enhance ozone production. Accordingly, surface soil temperature and moisture, associated with nitrogen deposition and nitrogen content in the soil are the main controlling factors in tropical regions (Ludwig *et al.* 2001; Pilegard *et al.* 2006). This is consistent with findings made by Davidson *et al.* (1993) who stipulated that biogenic emissions are strongly regulated by both soil moisture and soil nitrogen content.

While African savannahs soil moisture content is determined by both soil type and fire regime (Huntley and Walker, 1982), biogenic emissions of NO_x from a range of ecosystems may be of the same order of magnitude as those from anthropogenic sources (Levy *et al.* 1997). Therefore, savannas in the tropics and subtropics constitute one of the key source regions of global soil biogenic NO_x, owing to high temperatures and their wide geographic

coverage. Since Africa is covered by 65% of tropical savannas (Huntley and Walker, 1982), they are regarded as an important contributor to such emissions (Levine *et al.* 1996; Scholes and Andreae, 2000). CO production resulting from chemical oxidation of soil organic matter (Conrad and Seiler, 1985) and biological oxidation of CO by soil micro-organisms also constitutes an important biogenic source. Due to its slow photochemistry, CO is known as an important contributing factor to ozone formation, mainly at a large scale in the free atmosphere (Coll *et al.* 2006). In African savannas, this biogenic source emission is mainly active during daylight hours and has potential to reach very high levels (Scholes and Andreae, 2000). These emissions are produced close to the surface, and hence their effect on tropospheric ozone production has been found to be most prominent in the boundary layer (Diab *et al.* 1996a).

With regards to climate change research done by Royal Society (2008) stipulates that biogenic emissions are likely to increase. For instance, soil NO_x emissions, are expected to change in the future as they are closely associated with land-use change and human activities (Granier *et al.* 2003; Hauglustaine *et al.* 2005; Liao *et al.* 2006; Wu *et al.* 2007b). Moreover many studies show that natural emissions of CH₄ from wetlands are sensitive to temperature. As temperature is set to substantially increase with climate change, typical responses from peat wetlands show an increase in CH₄ emission of a factor of two for an increase in temperature of 4°C (Hargreaves and Fowler 1998). Temperature changes will change global hydrological cycle, which in the case of CH₄ emissions, regulates the water table and therefore controls whether soils are a sink or a source of CH₄ (Pyle *et al.* 2007).

2.1.2.4 Lightning

Traditionally, photochemical ozone was known to be only a product of oxidation reactions between carbon monoxide (CO), hydrocarbons, and nitrogen oxides (NO_x) from anthropogenic emissions in lower troposphere and from stratospheric intrusion in the upper stratosphere. Although biogenic and soils were known as sole sources of NO_x contributing to tropospheric ozone formation less was known on NO_x generated from lightning. However, findings made by (Pickering *et al.* 1998; Otto *et al.* 2010) showed that NO_x from lightning was crucial for the formation of upper tropospheric ozone as greenhouse gas. Yet lightning formation in the atmosphere is still not well understood as radiative forcing for tropospheric ozone formation and a greenhouse gas is still uncertain (Yuan *et al.* 2012). Subsequently early findings made by Wang and Jacob, (1998); Hauglustaine and Brasseur, (2001); Lamarque *et al.* (2005); Gauss *et al.*(2006); Horowitz, (2006); Stevenson *et al.* (2006); Wild, (2007) assumed that natural background O₃ concentration was a key source of uncertainties along with other factors for assessing radiation forcing.

Hence, in the bid to comprehend the radiative forcing differentiating current and background ozone levels Yuan *et al.* (2012) used Chemical Transport Models to remove known ozone concentration from anthropogenic emissions and infer natural ozone background. However, prior to the radiative forcing differentiation Lamarque *et al.* (1996); Hauglustaine *et al.* (2001); Tie *et al.* (2001); Martin *et al.* (2007); Otto *et al.*(2010) stated that upper tropospheric ozone formation is particularly sensitive to lightning NO_x because of a combination of the low background concentration and long lifetime of NO_x in the upper troposphere especially in the tropics where anthropogenic sources are sparse (Schumann

and Huntrieser, 2007; Labrador *et al.* 2005; Sauvage *et al.* 2007; Lamarque *et al.* 2010). In addition to these findings Thompson *et al.* (2000); Martin *et al.* (2002b); Edwards *et al.* (2003); and Sauvage *et al.* (2007) suggested that lightning generated NO_x, here after referred as (LNO_x), was instrumental on understanding of the dominant features in tropical tropospheric ozone distribution, and even over downwind of mid-latitude continents where anthropogenic sources are strongest. In fact, lightning can generate NO₂ indirectly by releasing NO that is quickly oxidized into NO₂, which can be observed using satellite and/or *in situ* measurements (Morris *et al.* 2010; Beirle *et al.* 2010; Bucsela *et al.* 2010). Figure 2.2 below shows lightning densities over southern Africa and adjacent Indian Ocean Islands as function of flash per km² per year. High density lightning are located at low latitude central equatorial region and low to medium density near and below 20° south latitude. While Altshuller (1987) noted that the role of NO_x in the tropospheric ozone formation is especially critical, Yuan *et al.* (2012) confirm that lightning NO_x accounts amongst natural sources of ozone precursors.

Although accurate source strength of LNO_x and its variability is poorly documented since preindustrial time, Mickley *et al.* (2001); Schumann and Huntrieser, (2007) mostly assumed that source strength of LNO_x regardless of its uncertainty has been constant with time because lightning is considered as a natural process with no clear mechanisms that link its frequency to human activities at large scales. Furthermore studies undertaken by Lyons *et al.* (1998); Mickley *et al.* (2001); Altaraz *et al.* (2010); Yuan *et al.* (2011); Sherwood *et al.* (2006) assume that aerosols can change lightning activity. However, a debate on this topic (Williams *et al.* 2002, Williams 2005) concluded that a causal aerosol–lightning link was difficult to be proven due to the strong coupling between meteorology, deep convection

lightning and aerosols. They assumed for example that if meteorology is responsible for both the aerosol and lightning anomaly, the correlation between aerosol and lightning could not be attributed to a physical cause. Figure 4 illustrates southern Africa and the Adjacent Indian Ocean Islands lightning map showing lightning intensity expressed in flash per km² per year. Consequently in order to elucidate the relationship between aerosols and lightning and avoid the convolution, strong evidence of aerosols enhancing lightning activities of tropical oceanic clouds have been provided (Yuan *et al.* 2012). These authors stipulate that physically more aerosols may delay or suppress the warm rain by increasing number of cloud droplets, decreasing droplet size, enhance cloud mixed-phase activity, invigorate convection and increase lightning frequency of pristine maritime cumulonimbus clouds. Similar effects have been noted over land by Lyons *et al.* (1998); Altaratz *et al.* (2010); Albrecht *et al.* (2011) who suggested that lightning activity and LNO_x, can no longer be assumed to be constant in the face of anthropogenic changes given the physical link between aerosols and lightning.

To comply with the objective of this work, these notions need to be deeply investigated in order to determine the relationship between lightning frequency and intensity, and aerosols concentration on the formation of tropospheric ozone over the southern African region where mesoscale convective systems play a considerable role.

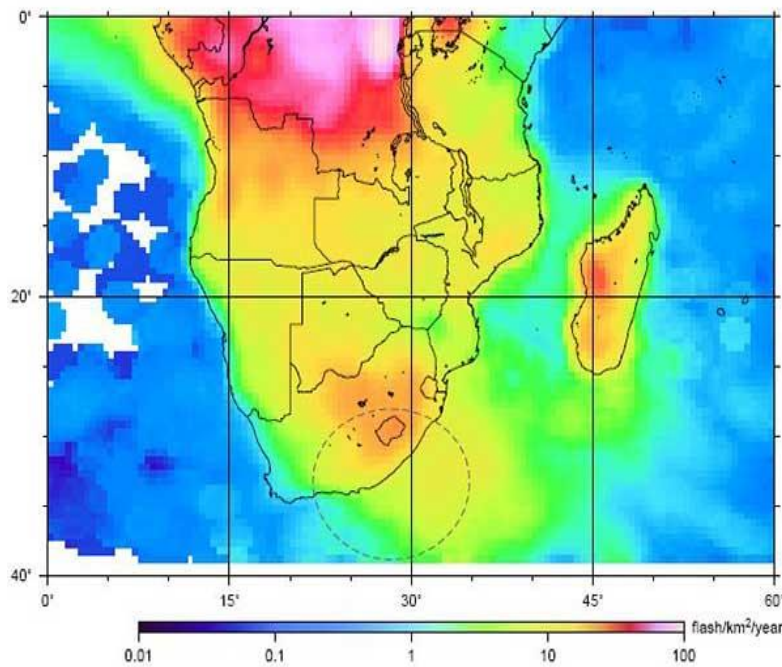


Fig. 2-2. Map of Southern Africa Indicating Lightning Densities
Sources: <http://www.sme.co.za/index.php/useful-info/lightning-map>

Mesoscale convective systems (MCSs) as a characteristic of tropical weather patterns are major contributors to global rainfall and therefore a key component in the maintenance of the global atmospheric circulation via latent heating and are responsible for lightning occurrence at global scale as shown by (Toracinta and Zipser, 2001). Given that lightning occurrence fluctuates between land and the ocean (Orville and Henderson 1986; Goodman and Christian 1993; Christian *et al.* 1999) a study undertaken by Toracinta and Zipser (2001) who used satellite data, suggests that lightning is more preponderant over land than the ocean. This confirms results from previous regional studies undertaken by Williams *et al.* (1992); Rutledge *et al.* (1992); Zipser (1994); Petersen and Rutledge (1998) who found that tropical continental MCSs are much more prolific lightning producers than their oceanic counterparts. A comparison study undertaken by Toracinta and Zipser (2001),

suggested seasonal variability of MCS and lightning intensity and frequency over land and ocean, in which a decrease in the occurrence of mesoscale and lightning clusters distributions occurred under convective system in the Northern Hemisphere during *September–October–November (SON)* and an increase in the Southern Hemisphere during the same period. The same trend was also noticed for the period *December–January–February (DJF)* distributions. According to Boccippio *et al.* (2000b) and Williams *et al.* (2000) generally the significant seasonal changes during this period tend to occur in MCS or cluster frequency rather than intensity. Conclusions of this study may be useful to understand the role played by lightning towards ozone formation during spring and summer maximum observed in the upper troposphere in southern Africa and Indian Ocean.

2.2. Sinks contributing to the tropospheric ozone budget

Tropospheric ozone budget strongly depends on the origin and nature of ozone precursor's species that contribute to its formation. These species as well as the majority of those emitted into the troposphere from the surface and the stratosphere are subject to a complex series of chemical and physical transformations which determine their life time in the troposphere (Monks, 2005). Reactions of variety of radicals that exert a substantial influence on the ultimate composition of the atmosphere is produced are presented in Fig.2-3 and Fig. 2-4.

As stated above, it was traditionally believed that tropospheric ozone was controlled by a balance between stratosphere-troposphere exchange (STE) processes at the tropopause (Holton *et al.* 1995). Yet, although early studies undertaken by Crutzen (1973) and

Chameides and Walker (1976) suggested the photochemical source of ozone at the surface, subsequent analysis based on observed ozone gradient with altitude advocated the source to the tropopause and sink at the surface (Lelieveld and Dentener, 2000). Numerous studies carried out on *in-situ* ozone photochemistry in different regions found that photochemistry can result in either, a net photochemical loss, or gain of ozone depending on the environment (O'Connor *et al.* 2004). Photochemical loss or gain originates from photo dissociation of trace species and photo production of ozone respectively with other molecules which lead to the production of the highly reactive atoms and /or radicals (Monks, 2005; Hasekamp, 2002). According to these authors, the hydroxyl radical OH is the most important due to its reactivity and initiation of radical-chain oxidation. This reaction mainly involves the oxidation of both CH₄ and CO, which are abundant trace gas species with relatively long lifetimes (Williams *et al.* 2009) in the atmosphere. Oxidation process that leads to the removal of these species is principally governed by the resident concentration of the OH radical formed via the photolysis of O₃ in the presence of H₂O, where O₃ is efficiently regenerated in the presence of NO_x and sunlight. Figures 2-5 and 2-6 illustrate the sources production and destruction sinks of ozone in the atmosphere.

A chemical budget analysis from a typical three-dimensional (3-D) chemical transport model (CTM) simulation ran by Williams *et al.* (2012) reveals that CO and CH₄ scavenge ~40% and ~16% of the available global OH in the troposphere, respectively, with a large fraction of the oxidation occurring in the tropics (30°S–30°N). Because radical OH reacts with almost all gases (hydrocarbons, carbon monoxide, and Nitrogen dioxide) that are emitted into the atmosphere by natural processes and anthropogenic activities, it is therefore called detergent of the atmosphere as it removes atmospheric pollution (Hasekamp, 2002).

Atmospheric pollutants removal occurs through dry deposition of VOCs and NO_y (reactive, odd nitrogen produced from the oxidation of NO_x) to vegetation, land and water surfaces.

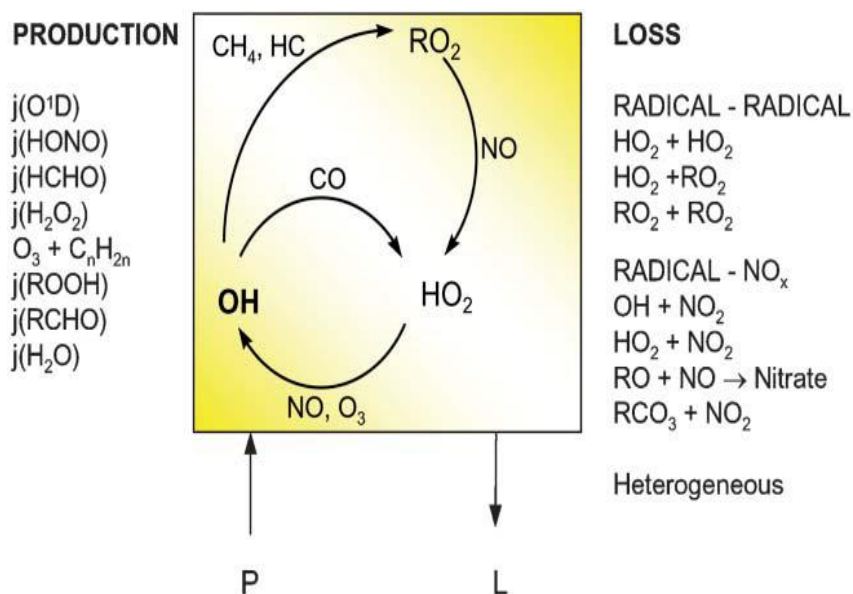


Fig. 2-3. The sources, interconversions and sinks for HO_x (and RO_x) in the troposphere
Sources: Monks (2005)

The resulting products can re-enter the gas phase as cloud droplets evaporate, or can be deposited to the ground as precipitation (National Research Council, 1991). The removal process of tropospheric ozone occurs through photolysis, destruction of OH/OH₂ catalysed and surface deposition processes, which are examined in the section below.

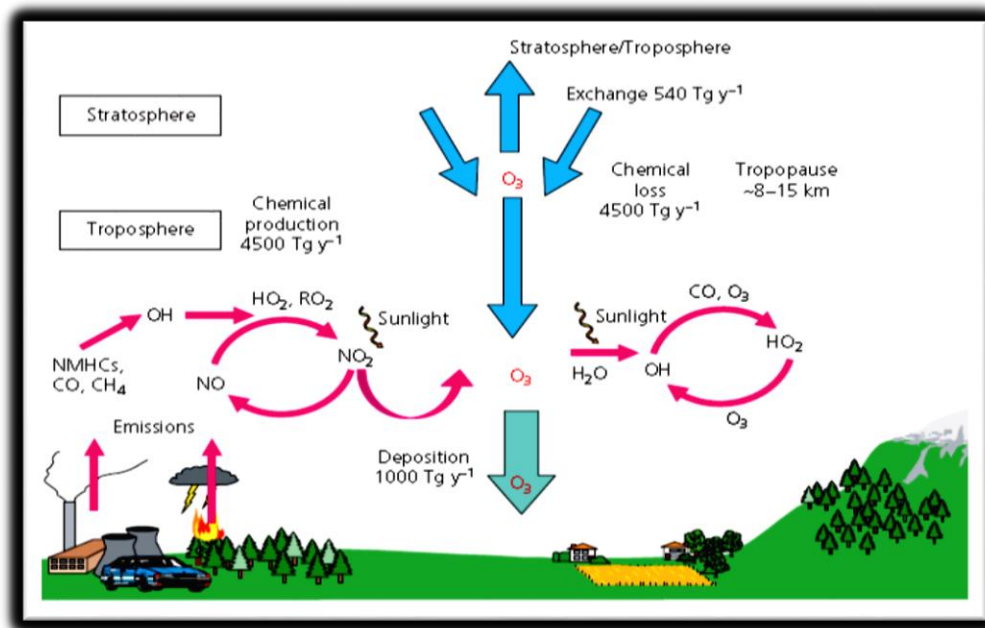
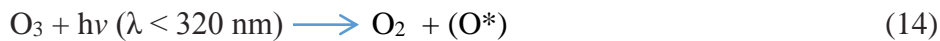


Fig 2-4. Ozone production and destruction in the atmosphere
Sources: Royal Society 2008.

2.2.1 Photolysis

The photolysis of ozone is summarized as a destruction process that occurs through the photodissociation of ozone by short wave radiation ($<320\text{nm}$) into (O^*) in the presence of water vapour as expressed in the reaction (14) and (15).



(Adapted from Yienger *et al.* 1999)

Electronically excited (O^*) atoms that form OH are dependent on the concentration of H_2O (Zachariasse *et al.* 2000, Monks, 2005). This reaction determines the oxidizing capacity of the atmosphere, and thus the lifetime of many tropospheric gases (Balis *et al.* 2002). This implies that the lifespan of ozone is limited by the concentration of water

vapour present and the amount of solar radiation (Zachariasse *et al.* 2000). Typically in a lower layer of the atmosphere over the oceans, about 10% of the O* generates OH. This reaction explains why tropospheric ozone has a very short lifetime (2-5 days) in the continental or marine boundary layer in presence of high levels of water vapour and about 3 months in the middle and upper troposphere when drier conditions prevail (Fisher *et al.* 1991).

2.2.2. HO₂/OH catalyzed destruction

Since the discovery of OH radical in the 1970's (IPCC, 1995) there are still some uncertainties on the role played by perhydroxyl HO₂/OH radicals in the destruction of tropospheric ozone. Though there is relatively little knowledge about atmospheric chemistry in the tropics and subtropics (Crutzen and Lelieveld, 2001), it is assumed that ozone is destroyed in the reaction with OH and HO₂ (Yienger *et al.* 1999; Lelieveld and Dentener, 2000) as shown in equations (16) and (17) below:



However, recent work on the chemistry of OH and HO₂ radicals in the boundary layer over the tropical Atlantic Ocean done by Whalley, *et al.* (2010) shows that HO₂/OH radical control of ozone loss rate depends on their concentrations which increase with the height. Due to surface loss they contribute to a larger fraction of the ozone destruction than at the surface. Fig. 2.5 shows HO distribution in the troposphere as function of pressure (hPa) and

latitude. Thus, determining processes controlling the abundance of OH are then critical to understand how the oxidation capacity of the troposphere is changing.

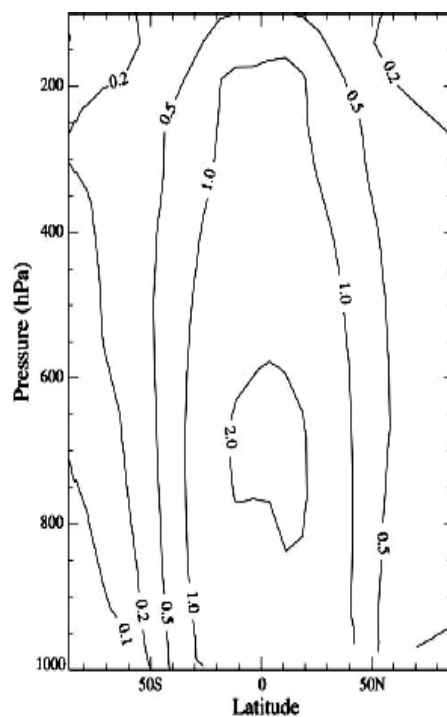


Fig 2.5. Model-calculated zonal and annual OH distribution in the troposphere in millions of molecules/cm
Source: Lelieveld and Dentener (2000)

2.2.3 Surface deposition

Deposition of ozone occurs in most surfaces including soil, vegetation and building materials by wet or dry process (Royal Society, 2008). Wet deposition is often associated to rain fall due to the solubility of ozone in water, and dry deposition occurs when ozone is not associated with rainfall and depends on their chemical, physical and biological properties (Kley *et al.* 1996). The rate of ozone dry deposition is determined by the removal rate and depends largely on the nature of the surface itself (Wesely *et al.* 2000). It tends to be largest for soils whose exposed surface has high levels of organic matter and a low to moderate moisture content (Wesely *et al.* 2000). Likewise, observations made by Royal

Society (2008) suggest that although the rates of dry deposition to terrestrial surfaces are larger than those to ocean surfaces, it is assumed that dry deposition is important in the global budget as sea waters occupy approximately 70% of earth's surface (Royal Society, 2008). Increased surface deposition of pollutants is responsible for human exposure and environmental damages including agricultural crops, forests and ecosystems as well as materials such as rubber, paints and dyes. This is one of the reasons why the USA's National Acid Precipitation Assessment Program (NAPAP) has ranked ozone as the most dangerous air pollutant in terms of potential to negative growth (yield and quality of agricultural crops) compared to SO₂, Acid and NO₂ deposition respectively (Shriner *et al.* 1990). This is fundamentally important with regard to region of high tropospheric ozone concentrations such as equatorial and southern Africa where damages due to ozone deposition are likely to cause significant impact in the environment.

2.4 Conclusion

Five main sources including stratospheric tropospheric exchange, Biomass burning (BB), anthropogenic emissions (AE), biogenic emissions (BE) and lightning emissions (LE), contributing to ozone enhancement over equatorial and subtropical region have been scrutinized, with regard to their dynamic as well as the occurrence which strongly depend on prevailing meteorological factors. With the recent changes observed on climate factors due to climate change, it is assumed that the characteristics of these sources over the region may be affected, which can impact ozone concentrations and therefore the regional and global climate.

Stratospheric and Tropospheric Exchange is responsible for the chemistry, transport and radiative flux balance in the troposphere at the lower stratosphere at a given altitude and latitude. These processes also are responsible for the removal mechanism for many stratospheric species including those involved in ozone depletion, and a significant input of ozone and other reactive species into the tropospheric chemical system. Change in climate parameters may significantly affect the downward transport and the oxidizing capacity of the troposphere. Conversely, upward transport of anthropogenic species from the troposphere into the stratosphere are responsible for much of the chemistry that initiate stratospheric ozone depletion.

Biomass burning constitutes the second contributing source to tropospheric ozone formation over tropical and southern Africa. It is a significant source of radiative species, which play an important role in the chemistry and radiative budget of the troposphere. Nonetheless it remains a traditional energy source and secular cultural practice for agriculture and pastoral activities as a response to socio-politic and economic pressure of the ever increasing population in developing world, particularly in African continent. Biomass burning does not generate large amounts of ozone in a global sense, but it is primarily a regional effect within and near the burning area, with most generated ozone lying in the low troposphere. Although emission inventory data present some uncertainties, it is somehow assumed that Africa is the single largest biomass burning emissions source in the world. Fire events in this region are exacerbated by persistent local synoptic weather which limits the dispersion of the pollutant and causing the recirculation of CO plumes over the continent. Since fire seasonality and trend depend on land cover and fuel availability

less occurrence is observed in the equatorial areas whereas they are dominant in shrubland, and grassland towards the south west of the regions. For the purpose of future study the analysis of parameters including fire seasonality, annual precipitation, soil fertility and fuel availability combined with emissions inventory data may provide good understanding of biomass burning contribution to tropospheric ozone enhancement.

Anthropogenic emissions refer to human activities including energy-use in industry, transportation, mining, construction, and in the household. These activities constitute a source of trace gases (NO_x , SO_x and SO_4 , CH_4) that result on tropospheric ozone formation. Contribution of anthropogenic emissions is set to increase in the equatorial and southern African region given socio economic pressure due to rapid growing population, urbanization and industrialization. This increase may be due to the fact that most countries in southern Africa either lack or have inadequate air quality standards and capacity to control anthropogenic emissions from mobile and stationary sources. This is one of the reasons why this region remains a poorly documented in terms of air quality as *in-situ* measurements on urban and industrial pollutants are still scarcely undertaken.

Emissions of biogenic gases such as NO , N_2O , VOCs, and CH_4 from soils and vegetation contribute to ozone formation in the troposphere. In the southern hemisphere, biogenic emissions are principally found in forests and savannas where important quantities are most observed in the month of October corresponding to the rainy season. The rate of emission depends on the nature of chemical specie, on meteorological factors (such high temperature), soils type, moisture content, and vegetation cover. More emissions are observed in wetted soils, which correspond to intensive microbial activities. These

conditions which prevail in tropical regions for several months, even the entire year, are responsible for higher emission rate observed therein. Biogenic source emissions are mainly active during daylight hours and have the potential to reach very high levels. This is the reason why these emissions which are produced close to the surface have an effect on tropospheric ozone production which has most prominently been found to be in the boundary layer. With climate change effects, it is suggested that biogenic emissions may increase leading to more tropospheric ozone formation.

Lightning contribution to ozone formation and enhancement was poorly documented since knowledge on radiative forcing for tropospheric ozone formation as a greenhouse gas was still poorly understood. One of the major difficulties to fulfil this task was uncertainties for the differentiation of natural background O_3 concentration along with other factors for assessing radiation forcing. Although lightning generated NO_x is poorly documented since pre-industrial era, research has concluded that it remains a natural process with no clear mechanisms that link its frequency to human activities at large scales. However, a causal relationship between the lightning and aerosol has been highlighted, yet it is difficult to be proven due to the strong coupling between meteorology, deep convection lightning and aerosols. To comply with the objective of this work, deep analysis of these factors is needed in order to investigate and determine the relationship between lightning frequency and intensity, and aerosols concentration on the formation of tropospheric ozone over tropical and southern African region where mesoscale convective systems play a considerable role. Because lightning occurrence fluctuates between and land tropical continental MCSs are much more prolific lightning producers than their oceanic counterparts. Tropospheric ozone budget strongly depends on the origin and nature of ozone precursor's species that

contribute to its formation. Depending on these factors, these species are subject to a complex series of chemical and physical transformations which determine their life time in the troposphere.

These transformations lead to photochemical loss, or gain of ozone depending on the environment. Loss or gain which originate from photo dissociation of trace species and photo production of ozone respectively with other molecules leads to the production of the highly reactive atoms and /or radicals which the most important radical is hydroxyl radical OH. The removal process of tropospheric ozone occurs through photolysis, destruction of OH/OH₂ catalysed and surface deposition. The rate of ozone dry deposition is determined by the removal rate and depends largely on the nature of the surface itself and also widely as function of their chemical, physical and biological properties. Removal rates tend to be largest for soils whose exposed surface has high levels of organic matter and a low to moderate moisture content. Increased surface deposition of pollutants is responsible for human exposure and environmental damages including agricultural crops, forests and ecosystems as well as materials such as rubber, paints and dyes. Because of its negative effects on human and vegetation, in the USA, ozone is ranked as the most dangerous air pollutant in terms of potential to negative growth (yield and quality of agricultural crops) compared to SO₂, Acid and NO₂ deposition respectively. This is fundamentally important to other regions of the world particularly southern Africa and adjacent Indian oceans where tropospheric ozone enhancement constitutes a matter of concern since more than 3 decades.

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CHAPTER THREE

MODELING TROPOSPHERIC OZONE CLIMATOLOGY OVER IRENE (SOUTH AFRICA) USING RETRIEVED REMOTE SENSING AND GROUND BASED MEASUREMENT DATA

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Modeling Tropospheric ozone climatology over Irene (South Africa) using retrieved remote sensing and ground-based measurement data.

Jean-Pierre Mulumba, Venkataraman Sivakumar¹ and Thomas Joachim Odhiambo Afullo²

¹.College of Agriculture, Engineering and Science. School of Chemistry and Physics and School of Electrical and Electronical Engineering

University of KwaZulu Natal/ South Africa

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3.0 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 ($0.96 < R^2 < 1$) between ozone and temperature. Similar trends are also observed for relative humidity and TTO concentrations ($0.91 < R^2 < 1$) in autumn, spring and summer. However a weak correlation is noted in winter, when TTO minimum values are recorded ($0.58 < R^2 < 1$). 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.

Key words: *Tropospheric Ozone, Air Temperature, Relative Humidity, Correlation.*

3.1 Introduction

Tropospheric ozone is a secondary pollutant and greenhouse gas (Lacis *et al.* 1990) produced by photochemical oxidation of its precursors such as carbon monoxide (CO), methane (CH₄), and non-methane

volatile organic compounds (NMVOCs) and nitrogen oxides (NO_x) in presence of hydroxyl radical (OH) (Rasmussen *et al.* 2012). It is a public health concern (Bernard *et al.*, 2001; Levy *et al.* 2010) 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 (Fishman *et al.* 1991) 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.* (2003) 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 (Zunckel *et al.* 1992, Diab *et al.* 1996a, Thompson *et al.* 1996). Subsequently, the first study on tropospheric ozone climatology at Irene was undertaken by Diab *et al.* (2004) 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 (Clain *et al.* 2009). Results from this study confirmed the finding made by (Diab *et al.* 2004). A positive linear ozone 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.* (2006) 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 (Watson *et al.* 2001; Pachauri and Reisinger, 2007) 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 luckily 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 *et al.*, (1993); Ryan *et al.*, (1998); Camalier *et al.*, (2007), ascertain that temperature constitutes a meteorological factor influencing surface ozone formation amongst other conditions. According to International Panel for Climate Change (IPCC, 2007), 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 [(Bell *et al.* 2005; Levy *et al.* 2001, National Research Council (NRC, 2008)] along with significant damage to crops [Ellingsen *et al.* 2008]. 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.ht>). 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 modeling 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.

3.2 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 (Thompson *et al.* 2003). 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/>.

Ozone data is recorded through an 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 (Ogunniyi, 2014).

The vertical extension of profiles range from ground level of 1524m up to gust altitude reaching 30 to 35 km in most cases is covered (Clain *et al.* 2009). It uses the latest technology to ensure accuracy. According to Smit *et al.* (2007) 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.* (2004). Data quality check was performed to discard instrument anomalies before averaging it in 100m 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 (Diab *et al.* 1996a, Siva *et al.* 2011) 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 were 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.* (2013). 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):

$$Y = a_0 + a_1x_1 + \dots + a_mx_m + \varepsilon \quad (1)$$

where Y is an objective variable (ozone concentrations);

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

x_j are independent variables (Temperature, Relative humidity);

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

ε is an error term associated with the regression analysis.

3.3 Mean monthly Total Tropospheric O₃ variation

Monthly variation of Total Tropospheric Ozone (TTO) at Irene for the period 1998-2013 from surface to 16 km is presented in Fig. 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.* (2004) 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, DR Congo 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 *et al.* 2004, Thompson *et al.* 2003, Zunckel *et al.* 1992, Cros *et al.* (1988), Dentener and Leleiveld (2000). 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 (Marufu *et al.* 2000). 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 anticyclonic winds drive off pollutants from inland to the Indian Ocean. The same trend is observed in all layers from surface to 16km. Correlation between monthly TTO trends as well as air temperature and relative humidity is fully discussed in the sections below.

3.4 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 Figure 2a and 2b. Mean monthly air temperature variation in the layer “Surface to 2km” 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 2-4km 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 3-1.

3.5 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 late summer (February). This maximum value does not correspond with the maximum TTO value which occurs in the middle of spring (October).

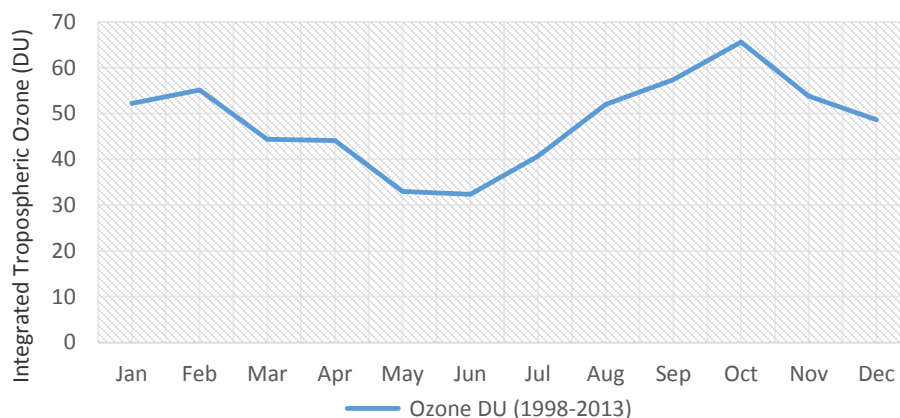
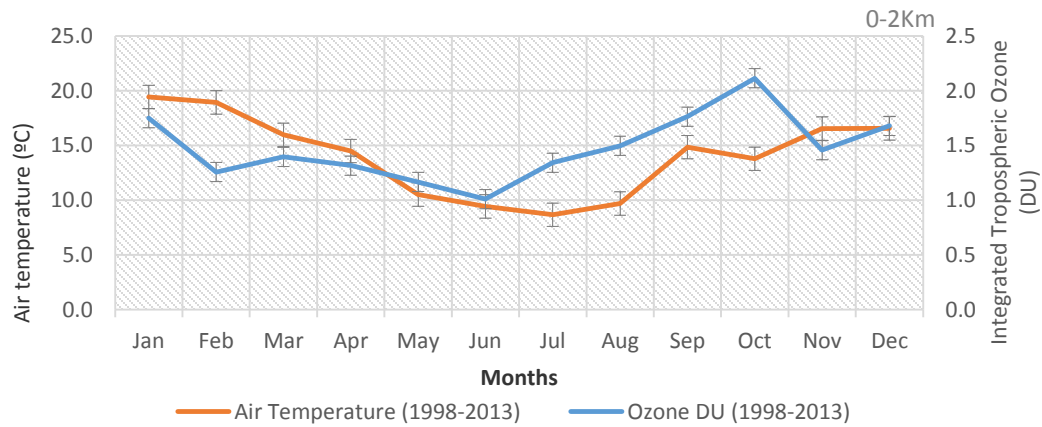
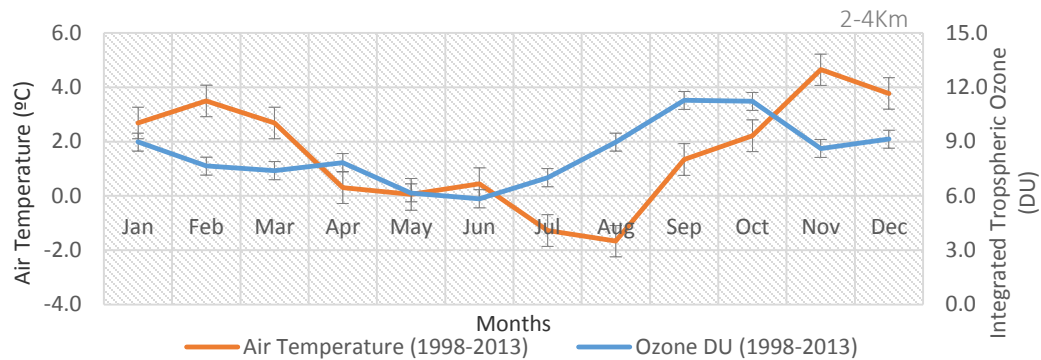


Fig. 3-1. Monthly TTO variations at Irene for the period 1998-2013



a)

Fig. 3-2a. Mean Monthly TTO and Air Temperature variations at Irene for the period 1998-2013 (layer surface to 2km) with standard errors



b)

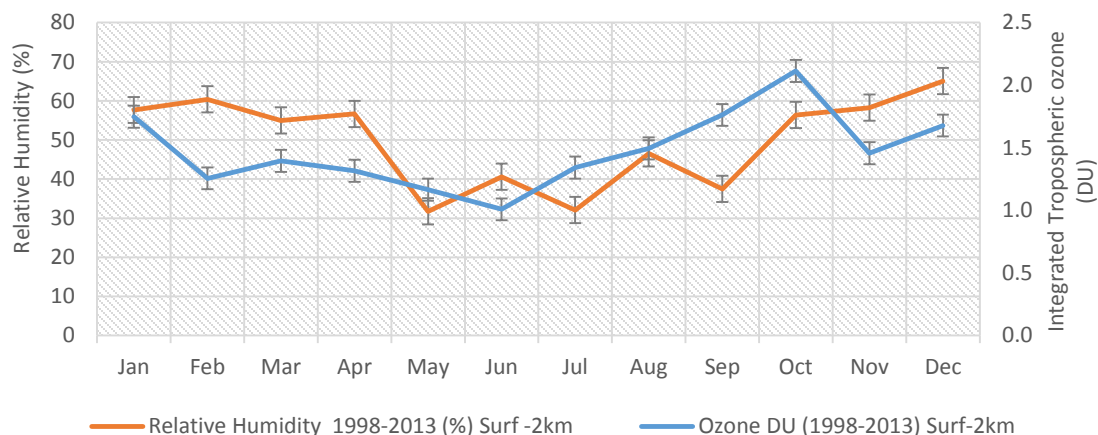
Fig. 3-2b. Mean Monthly TTO and Air Temperature variations at Irene for the period 1998-2013 (layer 2-4 km) with Standard errors bars

Table 3-1: Polynomial coefficient for TTO (DU), Air temperature (°C) and Relative Humidity (%) per layer

Layer (Km)	TTO (DU)	Air Temperature (°C)	Relative Humidity (%)
Surface -2	0.8979	0.9502	0.7074
2-4 km	0.9790	0.9179	0.9063
4-6 km	0.9609	0.6614	0.9698
6-8 km	0.9675	0.5657	0.9657
8-10 km	0.9668	0.6155	0.8890
10-12 km	0.9656	0.6670	0.8545
12-14	0.9590	0.7720	0.9026
14-16 km	0.9442	0.8297	0.7747

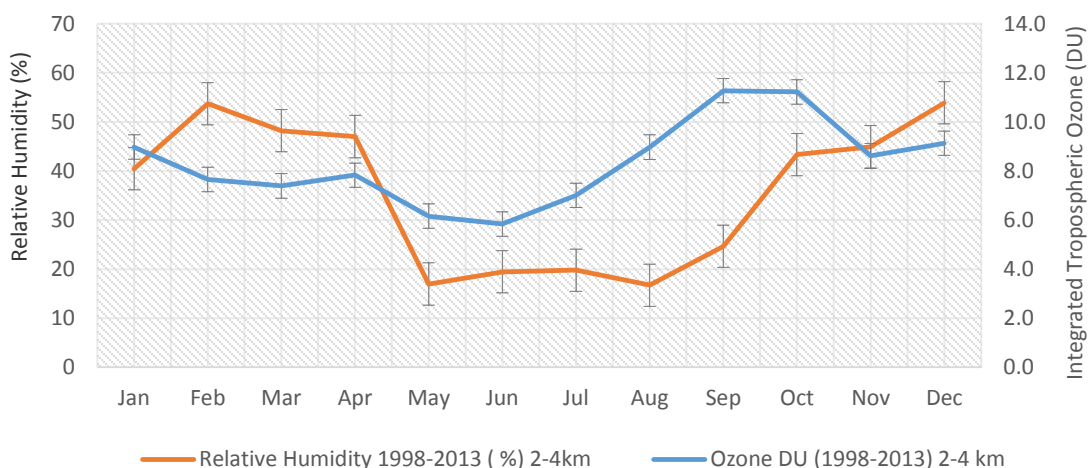
Minimum relative humidity of 32% which occurs in late autumn (May) and middle winter (July)

corresponds to minimum TTO concentration of 1 DU observed during winter (June).



a)

Fig. 3-3a: Mean Monthly TTO and Relative humidity variations at Irene for the period 1998-2013 (layer 2-4 km) with standard errors bars



b)

Fig. 3-3b. Mean Monthly TTO and relative humidity variations at Irene for the period 1998-2013 (layer 2-4 km) with standard errors bars

The upper layer 2 to 4km 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 favour ozone production or destruction.

3-6 Comparison of ozone profile and relative humidity

Comparison between seasonal ozone and relative humidity profiles shows that summer profiles displays 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 intercepts ozone profile at 4 km in summer (Fig 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.

3-7 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 (Mulumba, 2007). 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 Fig. 5 (a, b, c,d,e). 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 2km with 43 and 42 ppbv, respectively followed by autumn (MAM) with 39 ppbv (Fig.5b and 5c). Winter (JJA) presents the lower surface ozone concentration with 35 ppbv (Fig 5a). Mean annual profile presents surface ozone concentration of 38 ppbv (Fig 5e). The highest seasonal ozone enhancement of 94 and 85 ppbv were recorded in the upper troposphere (14 to 16 km) 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 (Fig 5a and 5c) with 62 and 80 respectively.

These concentrations are also lower than those observed by Diab *et al.* (2004) with 150-175 ppbv and 125-150 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 Fig. 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.

3-8 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)

$$y = a_0 + a_1x_1 + \dots + a_2x_2 + \varepsilon, (2)$$

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 humid

ε is an error term which can be associated with the regression analysis or data measurement.

Therefore seasonal prediction models can be expressed in equations (3), (4), (5) and (6) below as follows:

$$Y_s = -8.47 - 0.79 X_1 + 0.41 X_2 + \varepsilon \quad (3)$$

$$Y_a = -16.4 - 0.82 X_1 + 0.62 X_2 + \varepsilon \quad (4)$$

$$Y_w = 4.5 - 0.53X_1 + 0.04 X_2 + \varepsilon \quad (5)$$

$$Y_{sp} = 7.02 - 0.68 X_1 + 0.08 X_2 + \varepsilon \quad (6)$$

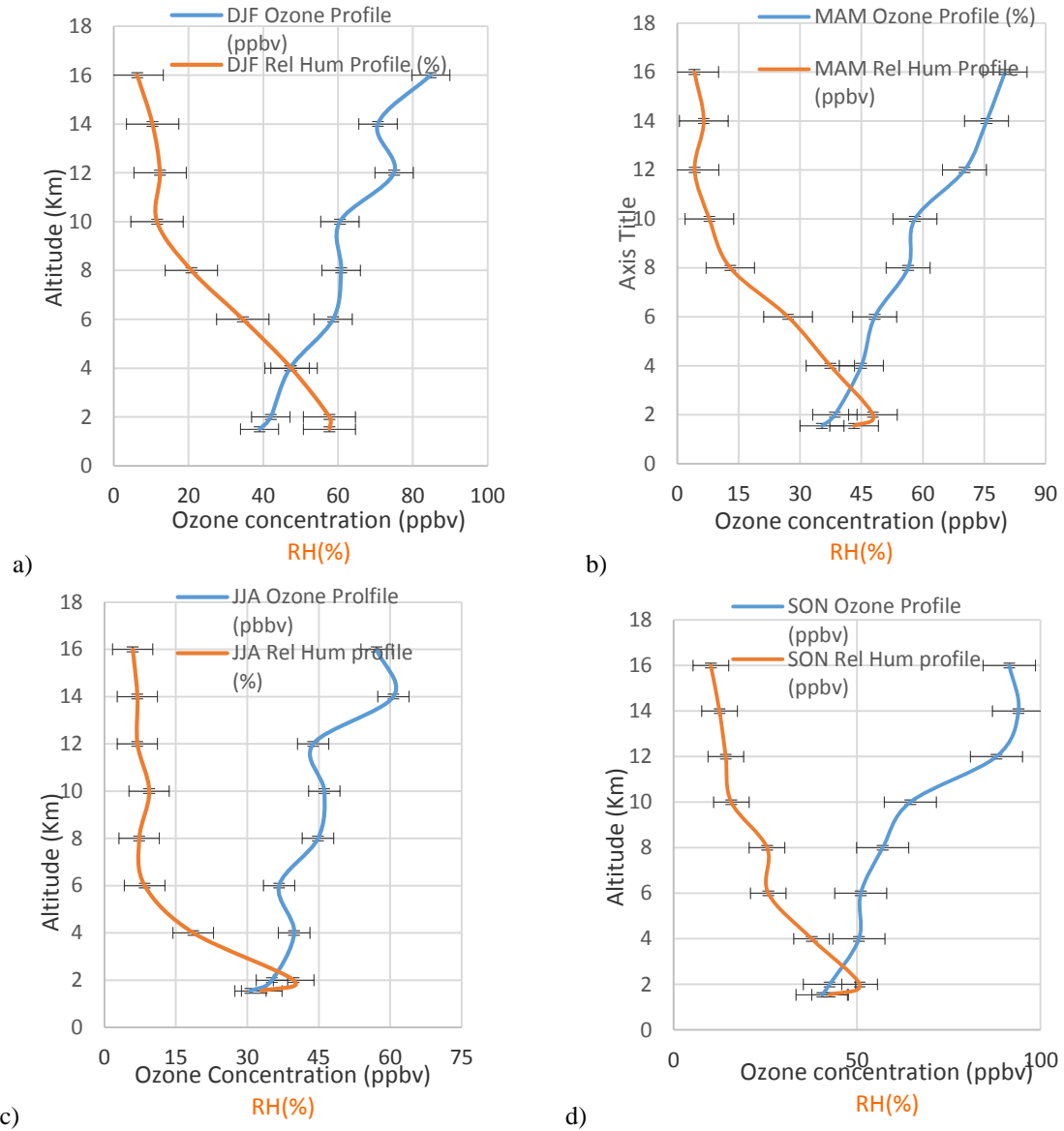


Fig. 3-4. Seasonal Relative humidity (%) profiles variation in comparison with tropospheric ozone profiles variation at Irene for the period 1998-2013

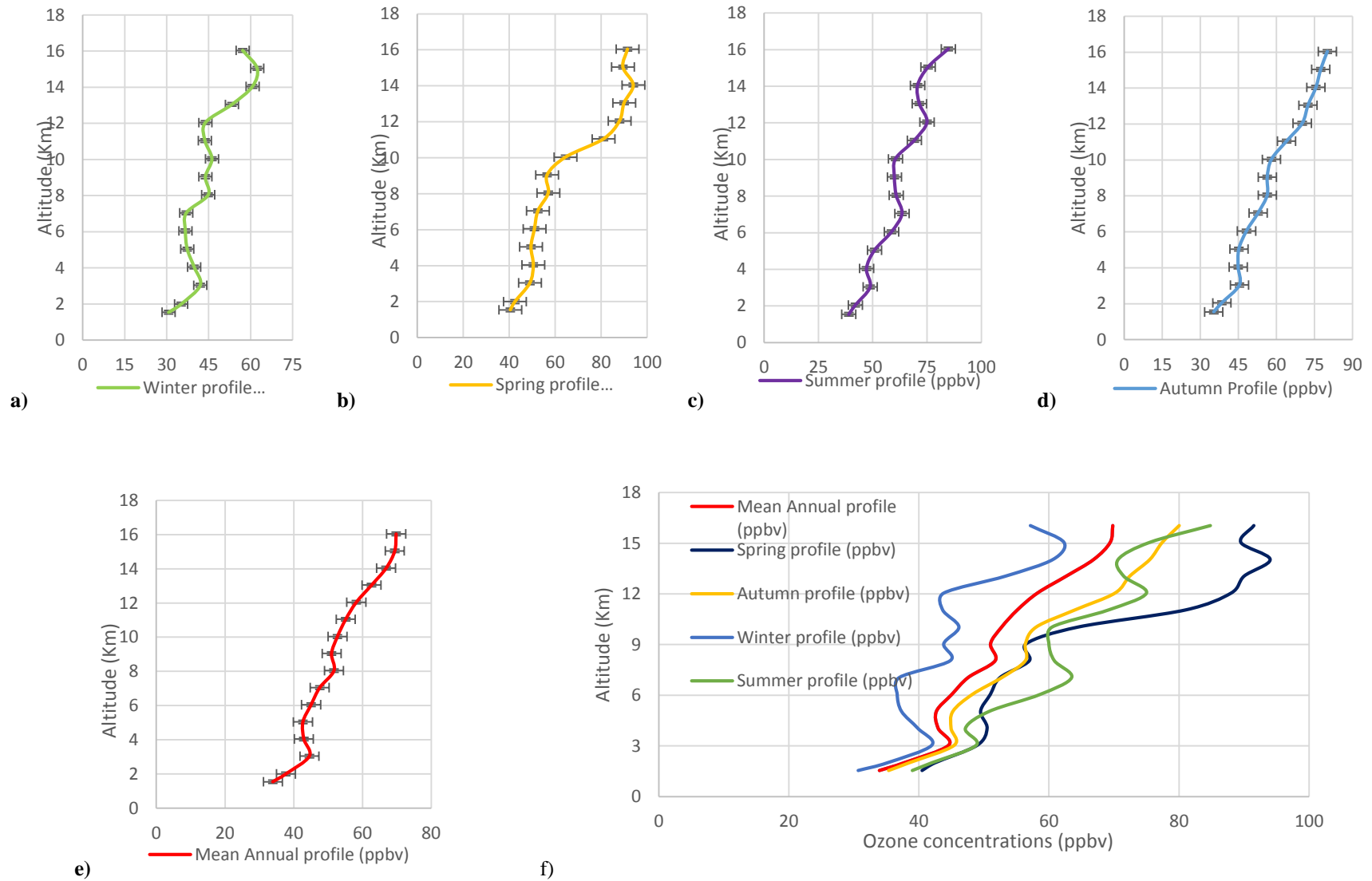


Fig.3-5. Seasonal and annual tropospheric ozone profiles for the period 1998-2013 at Irene (a= winter profile, b= spring profile, c=summer profile, d= autumn profile and e= mean annual profile and f= mean seasonal and annual profiles

Seasonal linear regression models line fit plots are presented in Fig 6(a, b), 7 (a, b), 8(a, b) and 9 (a,b) for

ozone concentration as function of temperature and relative humidity respectively.

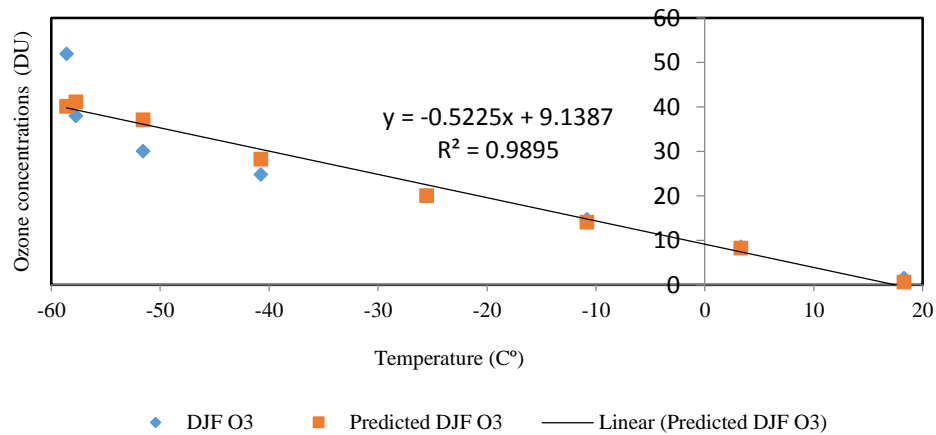


Fig. 3-6a. Linear regression model for summer ozone-temperature

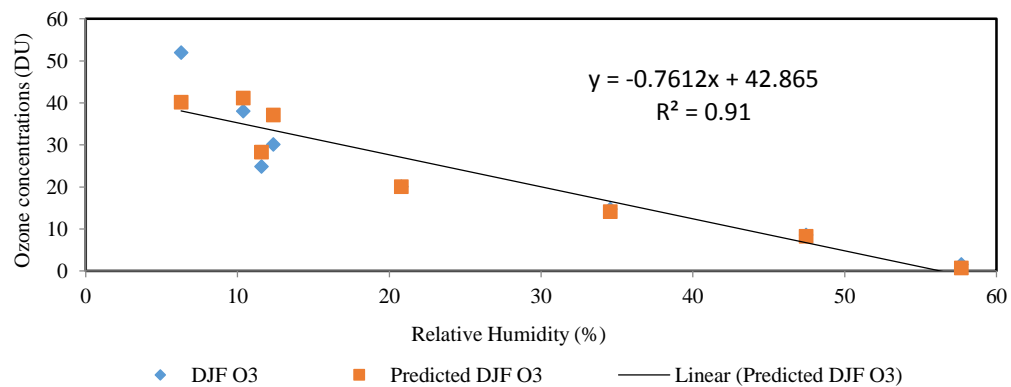


Fig. 3-6b. Linear regression model for summer Ozone- Relative humidity

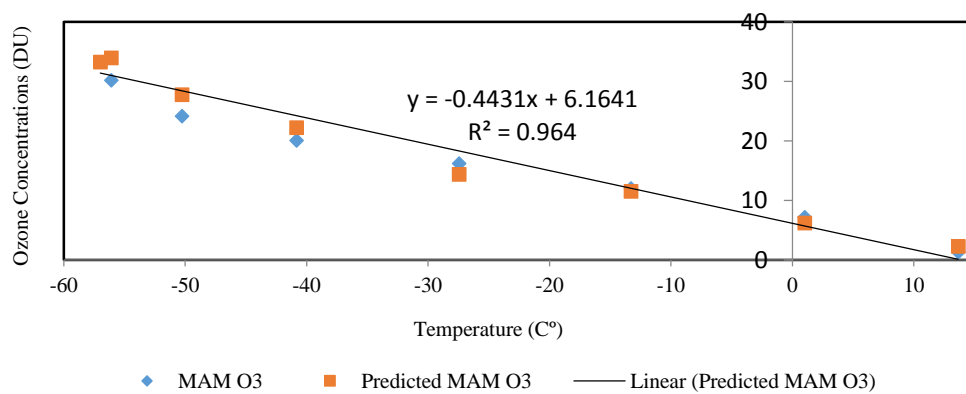


Fig. 3-7a. Linear regression model for autumn Ozone-Temperature

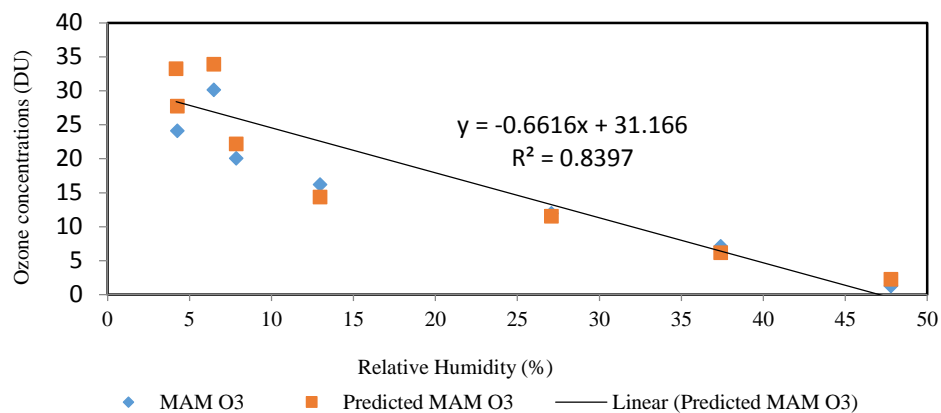


Fig. 3-7b. Linear regression model for autumn Ozone- Relative Humidity

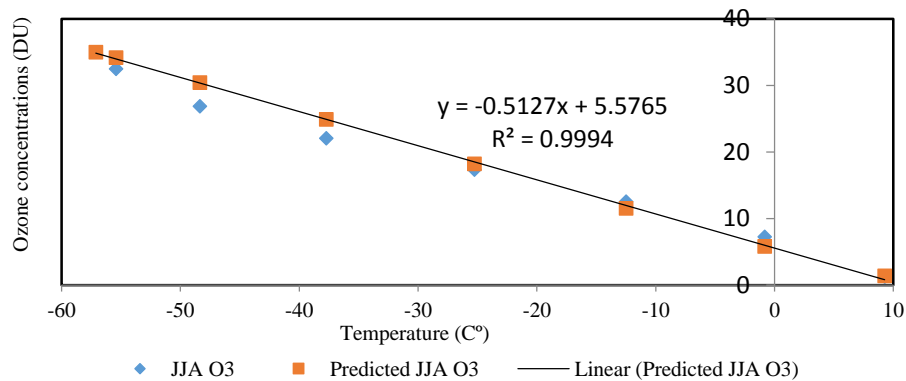


Fig. 3-8a. Linear regression model for winter Ozone- Temperature

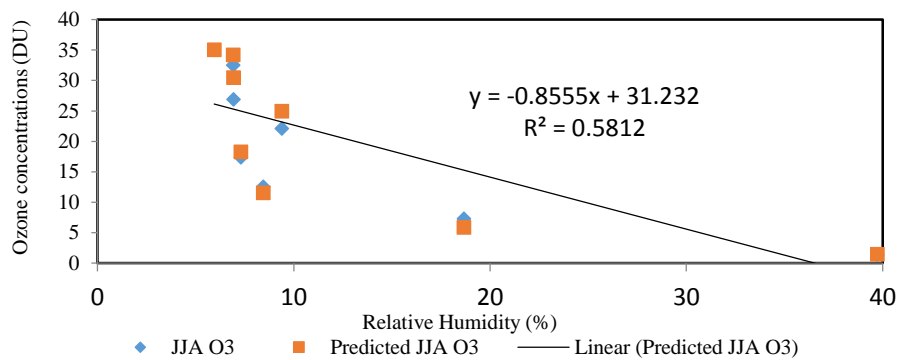


Fig. 3-8b. Linear regression model for winter Ozone- Relative humidity

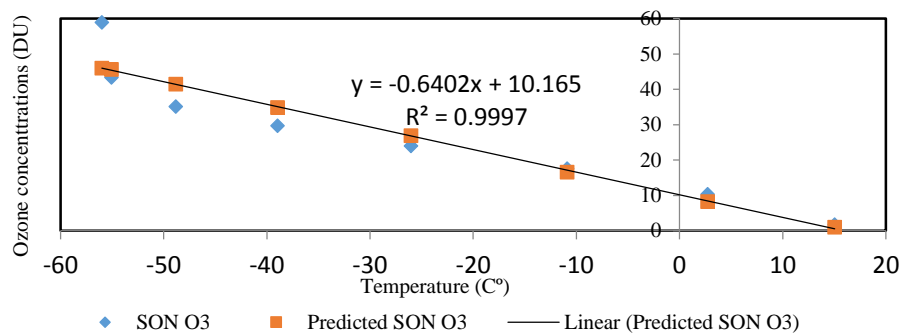


Fig.3-9a. Linear regression model for spring Ozone- Relative humidity

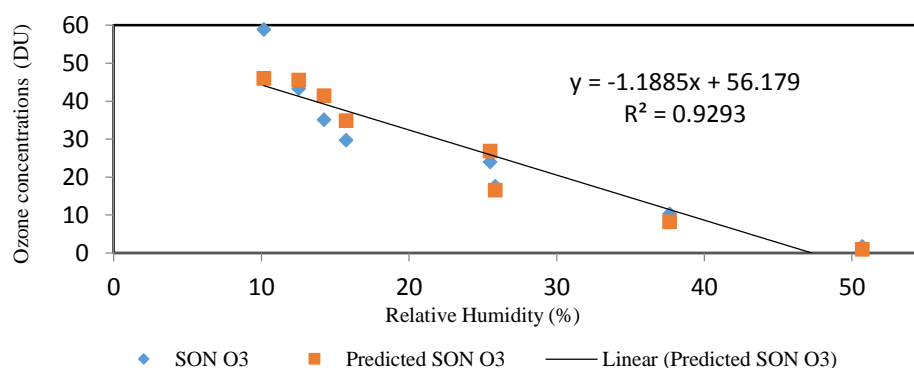


Fig. 3-9b. Linear regression model for spring Ozone-Relative Humidity

Table 3-2. Linear Regression coefficients for TTO and meteorological factors

Seasons	Regression coefficient (R ²)	
	Ozone vs Temperature	Ozone vs Relative Humidity
Winter	0.99	0.58
Autumn	0.96	0.94
Spring	0.99	0.92
Summer	0.99	0.91

3-9. 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 (Diab *et al.* 2004, Clain *et al.* 2009).

Two maxima occurring in austral spring (65.6 DU) and austral summer (55.1 DU) were observed. Spring ozone maximum corresponds with the peak of the biomass burning activity in southern Africa and South America (Thompson *et al.* 2000). It is also during this season that biogenic emission (CH₄) and NO_x emission from lightning have been observed (Zunckel *et al.* 1992, Diab *et al.* 1996a, Thompson *et al.* 1996) 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.* (2004) for the period 1990-1994, 1998-2002. This is inconsistent with seasonal ozone profiles values found by Diab *et al.* (2004). The reason for the discrepancy are unknown and may be attributed to ozone anomalies observed by Lightner *et al.* (2009). 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 4km) although maximum temperature is not congruent with maximum TTO concentrations. 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.

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.* 1995). The correlation between TTO and water vapour have shown a slightly stronger correlation in the Surface to 2km layer which becomes stronger in the layers from 2km 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 nonseasonal 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.

In order to predict seasonal TTO concentration due to change in meteorological factors a multiple linear regression model was used. Results from graphical line fit plots provide seasonal linear regression model with strong correlation with $0.96 < R^2 < 1$ for air temperature in all seasons of the year. However relative humidity and TTO concentration display strong correlation in winter and autumn and summer only with regression $0.58 < R^2 < 1$. A weak correlation is noted in spring when TTO maximum values are recorded.

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.

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CHAPTER FOUR

TROPOSPHERIC OZONE CLIMATOLOGY IN THE CONGO BASIN

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Tropospheric ozone climatology in the Congo Basin

Jean-Pierre Mulumba¹, Venkataraman Sivakumar² and Thomas Joachim Odhiambo Afullo³
College of Agriculture, Engineering and Science. School of Chemistry and Physics and School of Electrical
and Electronical Engineering
University of KwaZulu Natal/ Durban South Africa

¹ Jean-Pierre M. Mulumba: jpfuamba62@yahoo.fr; ²Sivakumar Venkataraman: ventakaramans@ukzn.ac.za
³ Thomas Joachim Odhiambo Afullo: afullot@ukzn.ac.za

4.0 Abstract

Tropospheric ozone climatology in the Congo Basin has been investigated using short term aircraft data from MOZAIC programme collected at Brazzaville for the period 1998-2001, on weekly basis depending on the flight frequency to this destination. Seasonal as well as vertical tropospheric ozone variation have been at the core of this study. Results from Total tropospheric ozone (TTO) columns at Brazzaville show a maximum of 35.4 DU in August and 26.1 DU in February. Vertical ozone profiles variation shows two peaks occurring in summer (February) and spring (September-October) respectively. These results confirm the role played by ozone precursor's gas from biomass burning emission in the lower troposphere where ozone peaked at about 100 ppbv at an altitude ~2 km. The spring ozone peak noted corresponds well with the seasonal biomass burning peak in this region. The summer peak with ~65 ppbv at an altitude of ~4 km, corresponds to onshore transport of ozone precursors from neighbouring coastal Atlantic countries where biomass burning is also noted during the same period. Further investigation on ozone in the Congo Basin in the mid-troposphere shows the role played by dynamical processes following its position near the Inter Tropical Convergence Zone (ITCZ) on the movement of air mass from the North Hemisphere to the South Hemisphere. Two case studies on ozone enhancement events occurring in both summer and spring confirm the photochemical sources and dynamical processes affecting ozone concentration at lower layer and mid-altitude respectively. The origin of these sources has been determined using five days back trajectory modeling (HYSPLIT_4 model) and NCEP/NCAR reanalysis model to provide further insight into the circulation pattern on the selected days for case study. Results from these models ascertain the photochemical origin of ozone at 850 hPa, as well as the transport of ozone precursor's gas from neighbouring and remote African countries at 500 hPa

Keywords: climatology, enhancement, seasonality, tropospheric ozone

4-1 Background

Ozone is present in both the troposphere and stratosphere. While stratospheric ozone shields us from ultraviolet radiation in the troposphere, tropospheric ozone constitutes a particular threat to human health, forest and crops, and the environment. With regard to human aspect, acute respiratory effects have been reported in children and adults, especially those suffering from asthma when ozone exceeds the standard level of 0.12 ppm, averaged over one hour (McKee *et al.* 1993). Adverse effects of ozone on vegetation were first identified in 1950s (Ashmore, 2005) where field experience showed that ozone can reduce agricultural yield by a variety of mechanisms. Elevated ozone concentrations can cause damage to agricultural crops by obstruction of plant stomata, which allow the exchange of carbon dioxide and water vapor between the inside of the leaves and the outside ambient atmosphere 4.0(Slanima, 2008). In the environment, tropospheric ozone is known as a strong oxidant and a greenhouse gas (Logan and Kirchhoff, 1986; Crutzen, 1987). Despite its

relatively small fraction (10%) in the atmosphere (Lelieveld and Dentener, 2000) tropospheric ozone as greenhouse gas, has a negative impact on climate through global warming. It also governs oxidation processes in the earth's atmosphere through the formation of the hydroxyl (OH) radical, and contributes to the oxidation of chemical species important for the radiative budget or acidification processes in the lower atmosphere (Baldy *et al.* 1996).

Tropospheric ozone has been a topic of much concern during the two last decades of the twentieth century, since its levels have been acknowledged to be increasing over much of the world. Over the southern tropical Atlantic Ocean between South America and Equatorial Africa dramatic enhancement of tropospheric ozone has been observed in September and October each year (Fishman *et al.* 1991). Measurements undertaken in the African tropics through remote sensing and *in-situ* observations (Fishman *et al.* 1986; Cros *et al.* 1988; Marengo *et al.* 1990; Laucaux *et al.* 1996) have shown that seasonal enhancement of tropospheric ozone is largely due to widespread biomass burning occurring in

this particular region. In order to investigate this finding, many studies including ground-based and satellite measurements (Andreae *et al.* 1996b, Lindesay *et al.* 1996; Thompson *et al.* 2002) were undertaken to provide accurate understanding on the role played by photochemical and dynamic factors on the observed high levels of ozone in this region. These studies essentially confirmed the role played by dynamic factors and photochemical sources (biomass burning, urban-industrial, biogenic emissions and lightning) in the enhancement of tropospheric ozone in the central Equatorial and southern African region.

In the Congo Basin a few studies have been undertaken using satellite (Fishman and Brackett, 1997; Kim *et al.* 2001) aircraft, ships and ground based ozonesonde data from Brazzaville (Republic of Congo), (Cros *et al.* 1987b; Cros *et al.* 1992a; Diab *et al.* 1996b; Nganga *et al.* 1996). Results from these studies confirmed the role played by biomass burning and in the lower troposphere where ozone peaked at about 100 ppbv at an altitude ~2 km. As much of these results were drawn from short term and irregular campaigns, uncertainties on the validation of global models and satellite findings restricted the assessment of seasonal and vertical ozone distribution (Sauvage *et al.* 2004). In the bid to bridge this gap, these authors used the MOZAIC data to establish ozone climatology over Equatorial Africa from the first regular *in situ* measurement recorded in multiple cities over equatorial Africa. Although this study provided a broader view of the tropospheric ozone characteristics of the region, individual ozone variation in terms of seasonal and vertical distribution were still lacking.

A comprehensive tropospheric ozone climatology for the Congo Basin does not exist, and it is to this end that this paper is addressed. Data from MOZAIC programme have been used to compare findings from previous studies and provide a comprehensive ozone climatology in the Congo Basin. The advantage of aircraft measurements over satellite observations is that the data are specific to a location and not averaged over a large geographical area. They are often available at more frequent time intervals than ozonesondes, which are generally released once every week or two weeks. As such they provide useful insight into short-term variation in ozone. A tropospheric ozone climatology is aimed at defining temporal variations (inter-annual, seasonal and day to day), including long-term trends in tropospheric ozone. It further examines vertical variations in terms of dynamic and photochemical influences on tropospheric ozone. The purpose of this study is thus to determine the tropospheric ozone climatology in the Congo Basin using MOZAIC data from Brazzaville in order to assess the relationship between ozone precursors and its short-

term spatial and temporal variability and establish a comparison between previous results from satellite and ozonesonde data over the region. Three specific objectives set to achieve the goal of this paper aim to summarize the mean seasonal and annual total tropospheric ozone (TTO) characteristics; to summarize the mean seasonal and annual vertical distribution of tropospheric ozone, and to investigate the role of dynamic and photochemical factors in the short-term and seasonal variability of the tropospheric ozone, and its distribution with height.

4-2 Data and methods

Ozone data used to study the climatology of ozone in the Congo Basin extending (5° E -32° E and 15° N - 17° S) were provided by the MOZAIC (Measurement of OZone and water vapor by Airbus In service air Craft) programme for the period 1998-2001 at Brazzaville (Republic of Congo). MOZAIC programme was launched in order to collect ozone data using aircraft for a better understanding of the atmosphere and its change under human activity (Thouret *et al.* 1998). Data consisted of vertical profiles of ozone and meteorological parameters (water vapour, pressure, and temperature). These are collected with a monitoring instrument in board at cruise altitude (9-12km), while the remaining corresponds to ascent and descents in vicinity of the city visited by the aircraft. The raw observations for each flight are portioned into three sets of data namely ascent, cruise and descent. The raw data of ascent and descent profiles are averaged on a fixed grid of 68 layers each 150 m thick. MOZAIC vertical profiles data recorded over Brazzaville from September 1998 to March 2001 constitute the basis of this study. Of the 83 profiles available over the period, a total of 68 profiles were selected for the computation of total tropospheric ozone (TTO) and the analysis of vertical ozone distribution. The remaining profiles were unsuitable due to continuous missing data over a distance greater than 1050 m data, i.e. 7 layers of 150 m each, which was selected as the threshold. If the height interval over the missing data was less than 1050 m, data were interloped from the mean profile. The final data set included 68 profiles over the period 1998 and 2001. In total, only 54 profiles displayed no missing ozone readings between the altitudes 1575 to 10125 m. The remaining 14 profiles in which data were missing in the ozone column were completed using the mean profile value. Meteorological data from NCEP/NCAR reanalysis website were used to provide further insight into the circulation pattern on the day selected for case study. (<http://www.cdc.noaa.gov/cdc/reanalysis/reanalysis.shtml>). Days with elevated ozone concentration were used to provide further insight into the circulation pattern on the days selected for the case studies. Zonal (U

component) and meridional (V component) winds at the 850, 700, 500 and 300 hPa geopotential surfaces were extracted for the domain 20° N to 20° S and 20° W 60° E. TTO which represents integrated amount of ozone in a vertical column of air in the troposphere, extending from the earth's surface to the tropopause, were determined using the method described by Diab *et al.* (1992) and Zunckel *et al.* (1992). It is expressed as the thickness of ozone reduced to standard temperature (STP) in Dobson unit (DU) where 1 DU is equivalent to 0.01mm of ozone (Diab *et al.* 1992; Zunckel *et al.* 1992; Combrink 1995). Monthly mean maps (GIFimages) from Earth Probe, the Total Ozone Mapping Spectrometer (TOMS) satellite measurement, presenting mean monthly tropical tropospheric column ozone concentration over three years (1999, 2000, 2001) were used to compare MOZAIC TTO data obtained at Brazzaville for the months of February 1999 and 2000 as well as August 2001.

TTO profiles which record ozone concentration in parts per billion by volume (ppbv) at 150 m intervals were integrated from the earth's surface to 10 km above sea level. Previous studies using MOZAIC data considered 12 km as maximum height reached by MOZAIC aircraft. In this study the height of 10 km was retained, in view of the large amount of missing data above this level. The method used to integrate column ozone amount in the troposphere is based on that used by Zunckel *et al.* (1992). Five TTO layers of 2 km each were obtained as from surface to 10 km (0-2 km; 2-4 km; 4-6 km; 6-8 km; 8-10 km) in order to gain greater insight into factors controlling the vertical distribution of ozone. The breakdown into layers enhances the seasonal cycle, particularly in the lower troposphere. A daily TTO value of 30 DU is taken as a threshold above which, the day is considered to be representative of an elevated ozone event. In order to obtain further insight into seasonal tropospheric ozone enhancement, analysis of days with highest TTO was undertaken. Many authors have suggested the threshold values indicative of ozone enhancement. For example, Diab *et al.* (1996b) referred to events with TTO less than 30 DU as representative of unpolluted air, while Thompson *et al.* (1996b) used a value of 35 DU. To this end, back trajectory modeling was used to assess the origin of air mass arriving at a selected level for each ozone profile chosen as case study.

4-3 Synoptic weather in the Congo Basin

Congo Basin refers to the basin of Congo River, lying astride the Equator in west-central Africa. It is the world's largest second largest river basin (next to that of the Amazon) comprising an area of more than 1.3 million square miles (3.4 million square km). The vast

drainage area of the Congo River includes almost the whole of the Republic of the Congo, the Democratic Republic of the Congo, the Central African Republic, western Zambia, northern Angola, and parts of Cameroon and Tanzania as shows in Fig.4-1. Atmospheric circulation over central equatorial Africa is poorly documented due to poor meteorological observations. However, a useful study is that of van Heerden and Taljaard (1997) which summarizes the circulation over Africa south of the Equator. The Congo River, which the Basin dominates the region and provides a path for moist oceanic air to penetrate inland (van Heerden and Taljaard, 1997).

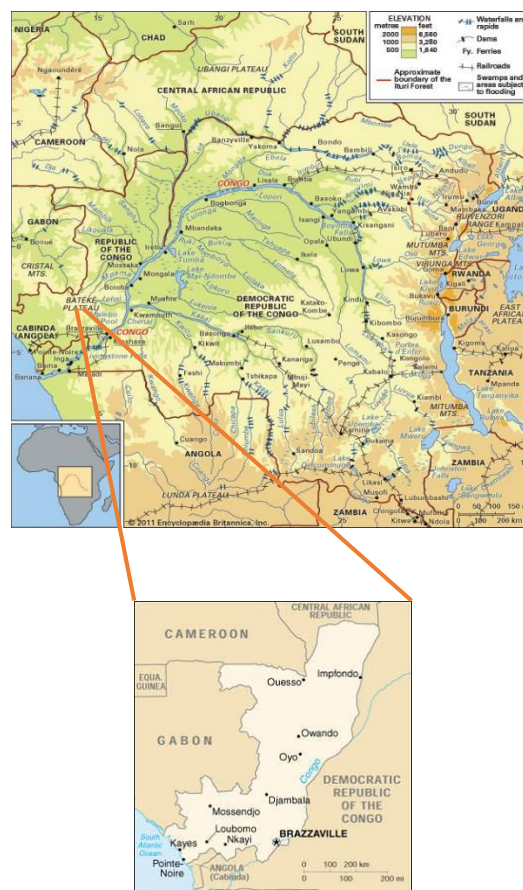


Fig.4-1. Map representing Congo Basin and the study area Brazzaville (Republic of Congo)

Source: <http://global.britannica.com/place/Congo-Basin> and <http://www.worldatlas.com/webimage/country/africa/cg.htm>

Brazzaville is located in the low pressure belt known as doldrums, which is characterized by light and variable winds (Blair and Fite, 1965). It is a region of intense solar heating and strong convection located between the IOCZ (Intertropical Oceanic Convergence Zone) and ITCZ (Inter Tropical Convergence Zone) which varies considerably by season. Over the Congo, sea level wind

flow is south-westerly in both summer and winter (van Heerden and Taljaard, 1997). It is part of the West African monsoon flow, which is driven by the thermal gradient between continent and ocean (Jury and Mpeta, 2005). The depth of the south westerly monsoon is about 1500 m at 850 hPa, although by 700 hPa, the wind dominantly remains easterly due to African Easterly Jet (AEJ) circulation and tropical Easterly Jet (TEJ) towards 150 hPa (Fontaine *et al.* 1995). The unstable baroclinical and barotropical jet stream is responsible for the transport of water vapor from the Atlantic Ocean near the surface between Saharan air mass and cooler Guinean and Atlantic ones (Monteny 1985; Cadet and Mnoli, 1987).

4-4 Tropospheric ozone climatology in the Congo Basin

TTO is a key parameter used for the comparison of tropospheric ozone at different geographic locations. Its computation enables the detection of temporal (daily, seasonal and annual) variations in ozone at a given geographical area. Many authors (Badly *et al.* 1996; Browell *et al.* 1996; Cros *et al.* 1987, 1988, 1992; Diab *et al.* 1996a, 1996b, 2003; Fishman *et al.* 1991, 1996; Krisnamurthi *et al.* 1993; Logan, 1985; Olson *et al.* (1996); Thompson *et al.* 1996a, 1996b, 2002; Thompson and Hudson, 1999) have used TTO to determine ozone concentration and variation at surface, and in the lower troposphere. Mean monthly and short-term variations in (TTO) at Brazzaville, for the period 1998-2001 is presented in Fig.4-2.

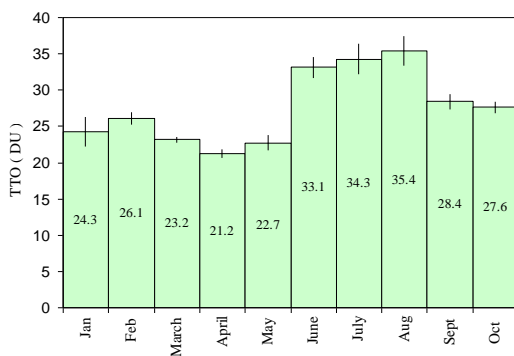


Fig.4-2. Mean monthly Total Tropospheric Ozone (TTO) in Dobson Units (DU) above Brazzaville for the period 1998-2001 based on MOZAIC aircraft data. Vertical bars represent one standard deviation.

The vertical ozone distribution, which encompasses mean seasonal and annual variations, provides a more detailed tropospheric ozone climatology, which facilitates a better understanding of mechanisms contributing to ozone enhancement. Results from Fig.4-2 show that highest TTO values are recorded

during June, July and August, which correspond to the winter season; with 33.1 DU, 34.3 DU, and 35.4 DU, respectively. Lowest values are observed in April with 21.2 DU. There is evidence of a slight secondary maximum in February when a TTO value of 26.1 DU is observed. After the August maximum ozone values decrease quite markedly to 28.4 DU in September and 27.6 DU in October. The vertical bars indicate one standard deviation and show that variability is greater in winter than the rest of the year. These results clearly establish the period June to August as the period of tropospheric ozone enhancement at Brazzaville. They however differ slightly from early findings obtained from satellite (Fishman *et al.* 1991) and ozonesonde data (Cros *et al.* 1992) and subsequently confirmed by Nganga *et al.* (1996) and Diab *et al.* (1996b) when ozone enhancement started in June to peak in September. The findings in this work conform well to the seasonal pattern observed by Sauvage *et al.* (2004) who also used MOZAIC aircraft data to study ozone characteristics over African equatorial region. The secondary maximum in late summer was also noted by Cros *et al.* (1992), Diab *et al.* (1996b) and Sauvage *et al.* (2004).

4-5 Integrated Total Tropospheric Ozone by layers

TTO variations integrated in five vertical layers i.e. surface-2 km, 2-4 km, 4-6 km, 6-8 km and 8-10 km are presented in Fig.4-3. In the surface to 2 km layer, the range is from 2.1 DU (in January) to 7.0 DU in both June and July, representative of a 3.3 fold increase. In late summer (February, March) secondary maximum is more pronounced as a result of the low January value in this layer.

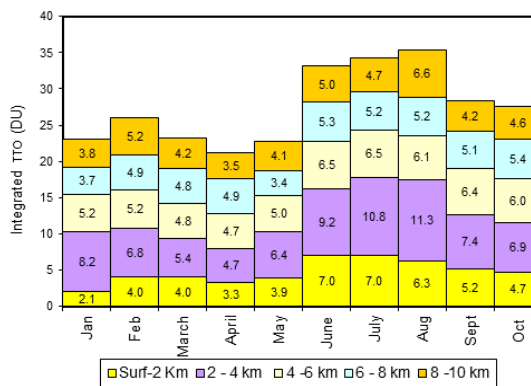


Fig.4-3. Monthly TTO integrated in layers over the period 1998-2001 showing the coincidence of the ozone maximum with the dry season (June - August).

In the remaining layers the seasonal cycle showing a minimum in autumn (April to May) and a maximum in

winter (June to August) is clearly established. The winter maximum is particularly well developed in the 2-4 km layer and comprises 32% of the TTO value in the lowest 10 km of the troposphere.

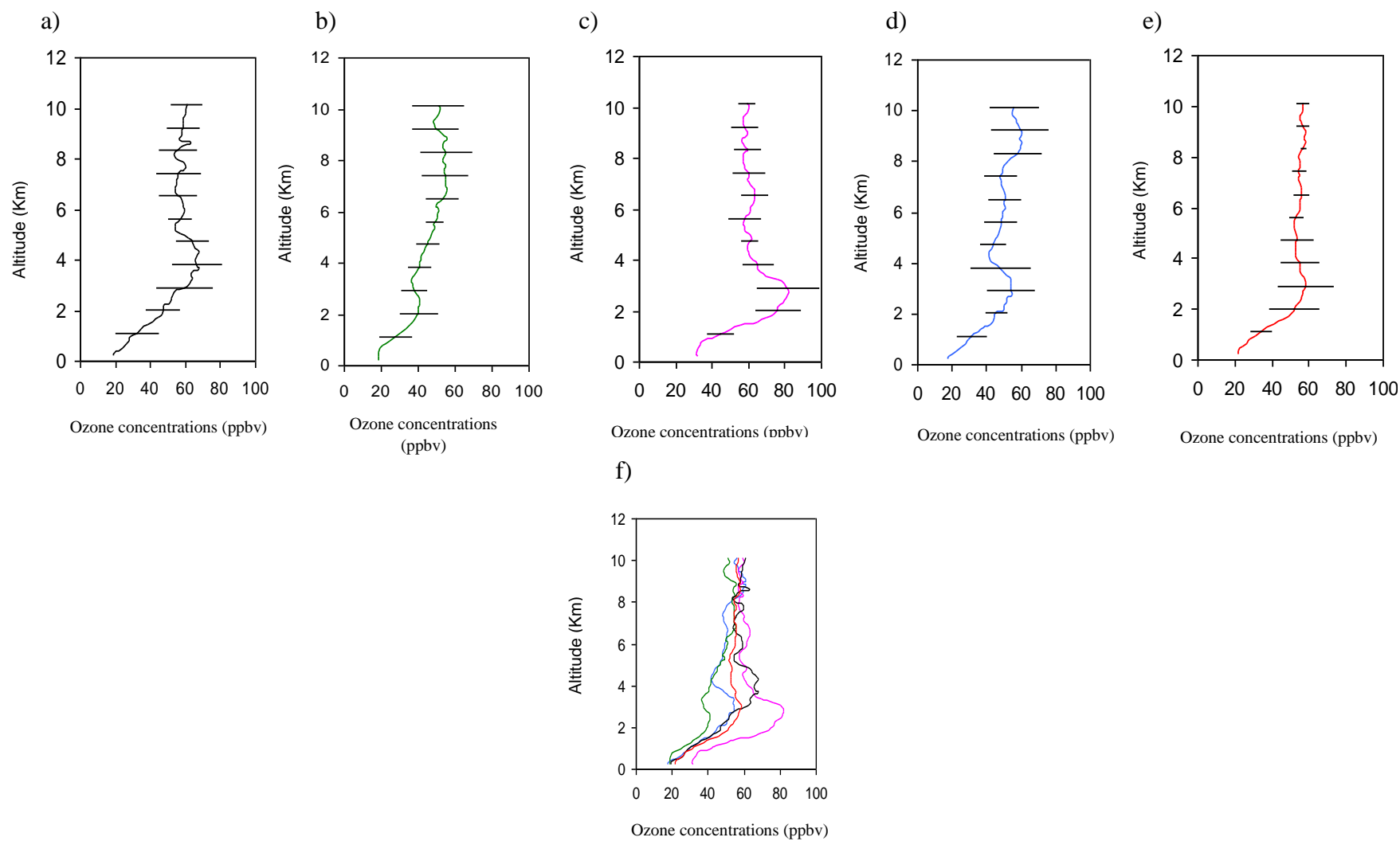


Fig. 4-4. Mean seasonal vertical of ozone (ppbv) for: a) summer, b) autumn c) winter, d) spring and e) mean annual vertical of ozone (ppbv) over the period 1998-2001, f) Mean seasonal vertical of ozone profiles (ppbv) compared to annual profile for the same period, standard deviation bars plotted at interval of 500 m show ozone variation at different layers.

In January, the corresponding figure is 34%. These results clearly evidence the lower troposphere (surface to 4 km) as bulk of the ozone enhancement is taking place, and suggest a surface-based source, when biomass burning peaks in central Africa, and the findings of previous studies (Cros *et al.* 1992; Diab *et al.* 1996b; Nganga *et al.* 1996) strengthen the cause–effect link between biomass burning and ozone enhancement.

The secondary maximum in late summer, which also occurs in the lower troposphere, is most luckily linked to cross-equatorial transport from biomass burning source in the Northern Hemisphere at this time of the year. Nganga *et al.* (1996), have previously noted this, and recently Sauvage *et al.* (2003) have provided evidence of north easterly air mass movement towards the Inter Tropical Convergence Zone (ITZC), which is situated at its southern most point at this time of year.

4-6 Vertical ozone distribution

Vertical distribution of ozone is useful for determining the variability of ozone at a particular location, and permits the identification of possible mechanisms such as photochemical and dynamical processes, that may be responsible for ozone enhancement. In this section, we provide details on the mean seasonal and mean annual tropospheric ozone distribution in the Congo basin such as observed at Brazzaville. Elevated ozone events depicted in the lower and upper troposphere will serve for cases study analysis in subsequent section. Over 68 ozone profiles from MOZAIC data recorded at Brazzaville, mean seasonal as well as mean annual tropospheric profiles (ppbv) are provided in Fig. 4-4. Standard deviation bars are given a 500 m as an indication of seasonal ozone variability. Ozone value less than 30 ppbv has been recorded in three seasons (i.e summer, autumn and spring) in contrast with the winter profile, in which surface values are above 30 ppbv (Fig. 4-4a, b and d).

These trends explain the absence of major local pollution sources at Brazzaville for most of the year, with exception of winter. The lower tropospheric peak situated ~3 km is most pronounced in winter (June to August), although it is evident in summer and autumn to a lesser extent. The winter mean profile ozone displays a sharp gradient between the surface and 3 km reaching a peak of 82 ppbv at 3 km, and then decreasing to a value of ~60 ppbv through the rest of the troposphere (Fig 4-4 c). Examination of ozone profiles shows that at an altitude of 3 km ozone concentrations vary considerably and peak at 114 ppbv on 28 June 1999. In summer the 3 km mean peak is only 54 ppbv, and in autumn it is ~ 40 ppbv (Fig.4-3 b). Upper tropospheric

~9 km mean ozone values are relatively higher than the lower tropospheric values; and thus, more prominent in summer and autumn as shown in Fig. 4-4a and 4-4b. In springtime, the ozone enhancement occurs at a higher level (i.e. 4 km), although the peak mean value of 70 ppbv is less than in winter (Fig 4.4d). Ozone variability is higher in the upper troposphere in the 8-10 km layer, particularly in autumn. The mean annual profile at Brazzaville is shown in Fig. 4-4.e, where it is depicted together with the mean seasonal profiles in Fig.4-4 f. The lower tropospheric 3 km peak is clearly evident in the mean as well as the uniformity in ozone values above this layer. The composite Fig. 4-4f shows the higher source concentration in winter, the dominance of the 3 km winter peak, the high seasonal variability of ozone in the lower troposphere and the relative uniform values above 6 km.

4-7 Elevated ozone events

As described above, high ozone enhancement analysis of days with high TTO was undertaken. Of the initial 68 profiles, only 24 representing TTO values higher than 30 DU have been analyzed. Fig. 4-4 illustrates the breakdown of TTO into layers for these individual days. Most of elevated TTO events occurred almost exclusively in winter, with June experiencing 5, July 12, and August 3. The total number of events expressed above is less than 24, as there are two profiles on some days.

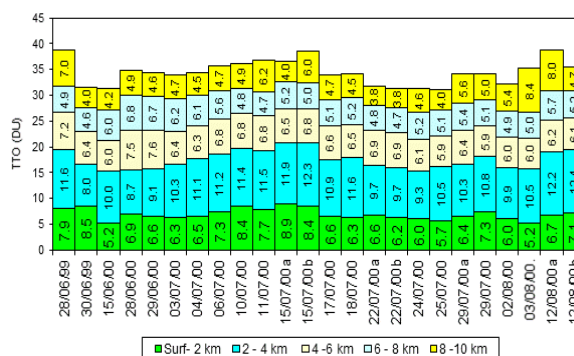


Fig. 4-5. Ozone events with TTO exceeding 30 DU. Suffixes a, b after the dates indicate that there are two profiles for a day at different time.

In order to assess the contribution of each layer to the TTO amount, the percentage contribution of each layer in an individual profile has been computed, and the results are presented in Fig.4-5. Further analysis in different layers has been undertaken in order to assess ozone enhancement in individual layer. Assuming that each individual ozone column represents a mean ozone

distribution in five layers extending from surface to 10 km in the troposphere, a percentage contribution superior or equal to mean monthly percentage in each layer has been considered as threshold above which a layer shows an ozone enhancement. The layer 2-4 km has the highest contributing percent to TTO, in which the contribution ranges between 25 and 35 % (Fig.4-6).

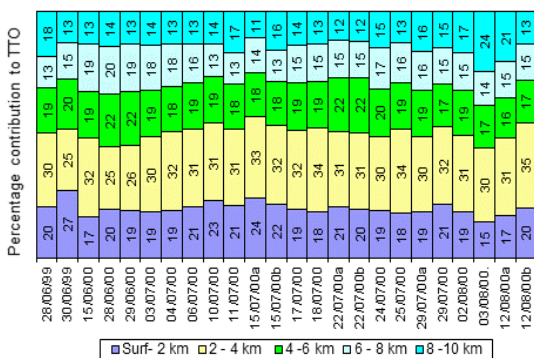


Fig.4-6: Percentage contribution of each layer to daily TTO for high ozone in events which, TTO exceeds 30 DU.

The highest percent contribution (35 %) is noted in August 12b. The lower layer as well as the layers above 4 km display a percentage contribution lesser than the minimum recorded in September for the considered events. Six events including 15 July (a) and (b) (36.5 DU; 38.58 DU); 17 and 18 July 2000 (33.9 DU; 34.1 DU) and 12 August 2000 (38.9 DU; 35.5 DU) have been under scrutiny analysis. Discussion and interpretation of these particular events are fully given in section below as case study. However, it is noted that two profiles including 10/07/2000 and 12/08/2000 present the highest contribution on the 8-10 km layer, viz. 34.1% and 34.8 %.

4-8 Analysis of case study

Four case studies have been selected for detailed analysis. Two individual dates from winter period (10 July 2000 and 12 August 2000) and two from the summer period (8 February 1999 and 26 February 2001) have been examined.

4-8-1 Winter profiles

Figure 4-7 below shows plots of individual profiles for 10 July 2000 and 12 August 2000 compared together mean winter profile at Brazzaville for the investigation period. The lower tropospheric ozone peak of 102 ppbv observed on 10 July is situated at 2 km, slightly below the altitude of the mean peak. However the peak of 109

ppbv on 12 August is noted at 3 km. These individual winter profiles display ozone enhancement in the layer 2-4 km with values higher than the seasonal maximum for both cases. However, a slight ozone enhancement in the 8-10 km layer is noted for 10 July 2000 (~75 ppbv) whereas a slight ozone decrease is noted in the same layer for 12 August 2000 (~30 ppbv). These differences can be attributed the variability of air mass flow on a daily basis in the local environment. To assess the origin of air mass contributing to ozone enhancement in these events, five day back trajectory modeling have been computed and results for the two case studies are shown in Fig. 4-7 and Fig. 4-8 below.

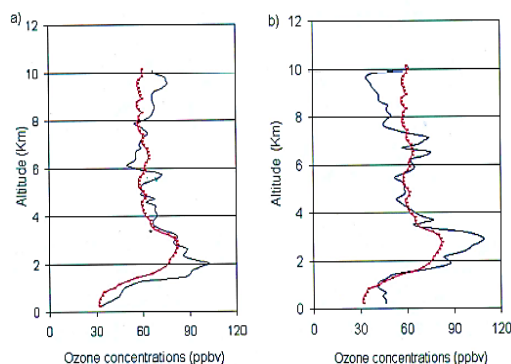


Fig. 4-7 Comparison of mean winter ozone profile (red) with individual ozone profiles blue on 10 July 2000 (a) and 12 August 2000 (b)

Both cases show onshore south westerly flow at 1 km. At 2 km level, south easterly flow from the Democratic Republic of Congo and Zambia, both regions of biomass burning at this time of the year, is evident on 10 July 2000 (Fig.4-8).

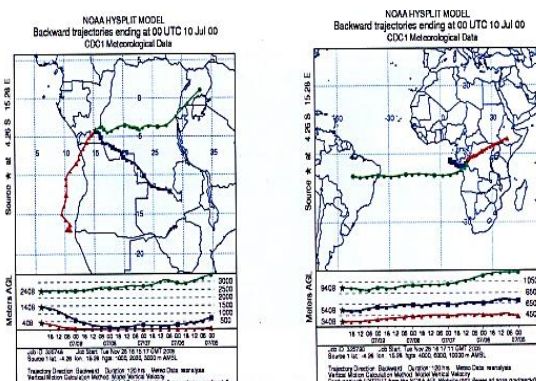


Fig.4-8. Composite plot of five-day back trajectory HYSPLIT model results for 10 July 2000 showing lower trajectories (left) originating from 1 km (red), 2 km (green) and 3 km (green) and mid troposphere trajectories right at 4 km (red) 6 km (blue) and 8 km (green)

On 12 August however the 2 km flow is still from the south west, producing a relatively deeper layer of clean maritime air. This difference is reflected in the ozone profiles for the two days (Fig.4-7) where the ozone maximum on 10 July is situated at the lower altitude (2 km). The ozone peak at 3 km on 12 August is a product of north easterly but switches to westerly at 6 km on 10 July 2000 (Fig.4-9). The onshore or west to east flow is the zonal wind flow at the 850 hPa height for the period 12 August (Fig.10), and is shown to extend from about 15° N to about 3° S. South of this, there is evidence of east to west flow associated with the northern limit of the anticyclone. The regional pattern of elevated total tropospheric ozone derived from TOMS/V8 satellite data is shown in Fig. 4-11.

The mean monthly images of TCO (Tropical Column Ozone) for the year 2000 show that between July and October, Brazzaville (S 4° 17 E 15° 16) is located within a much larger regional enhancement of ozone.

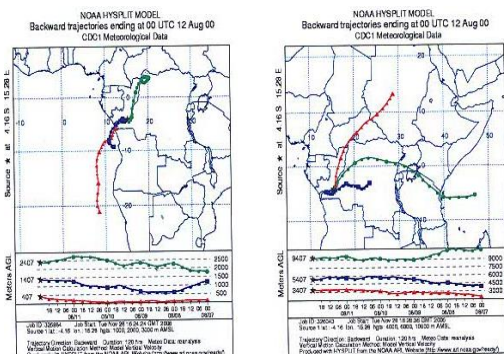


Fig. 4-9. Composite plot of five-day back trajectory HYSPLIT model results for 12 August showing lower trajectory at 1 km (red) 2 km (blue) and 3 km (green) and mid troposphere trajectories right at 4 km red 5 km blue and 6 km (green)

It is well known that the Democratic Republic of the Congo and Zambia are region of biomass burning at this time of the year, but the probability of increased BOVC emission from the spring rains could also be a possibility.

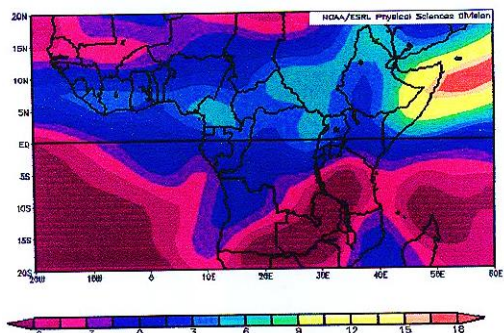


Fig. 4-10. Zonal winds (ms^{-1}) plotted at 850 hPa for the period 7-12 August 2000.

Sources: <http://www.cdc.noaa.gov/cdc/reanalysis.shtml>

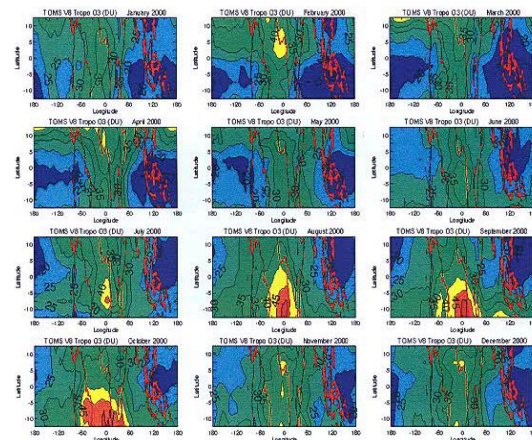


Fig. 4-11. Mean monthly maps of tropical column ozone (in Dobson units) derived from the TOMS/V8 satellite: January to December 2000. Sources: http://hyperion.gsfc.nasa.gov/Data_services/cloud_slice/gif

4-8-2 Summer profiles

The individual profiles for 8 February 1999 and 26 February 2001 are plotted together with the mean summer profiles at Brazzaville for the period (1998-2001). In both case there is an enhancement in the 8-10 km layer. Ozone value is a further enhancement at 6-7 km (Fig.4-12). Five day back trajectory modelling results for the two case studies are shown in Fig. 13 and 14. Both cases show low level (1 km) south- westerly monsoonal flow from the Atlantic Ocean. The maritime origin explains the low ozone concentration (<30 ppbv) at this level. This onshore monsoonal flow is very shallow and is replaced at 2 km by easterly flow as shown by the 2 km back trajectory in both panels (Fig.4-13). This is well illustrated in Fig. 4-13 and 4-14, as near surface air originating from Ethiopia is lifted vertically as it approaches Brazzaville reflecting convective activities that are present over the Congo Basin during summer.

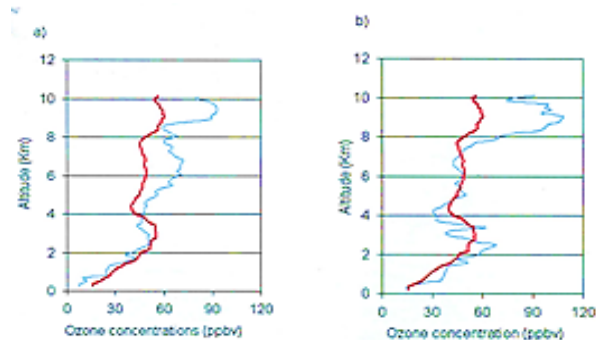


Fig. 4-12. Comparison of mean summer profile (red) with individual ozone profiles (blue) on 8 February 1999 (a) and 26 February 2001 (b).

Easterly flow is shown to dominate from 12° N to the south of the domain. At this time of the year the ITCZ is at its most southernmost position and the north-easterly trades, which originate in the Northern Hemisphere, over Sudan and Ethiopia, where Northern Hemisphere biomass burning is active in February are able to transport polluted air mass to Brazzaville and account for the ozone enhancement at upper levels (Fig. 4-12).

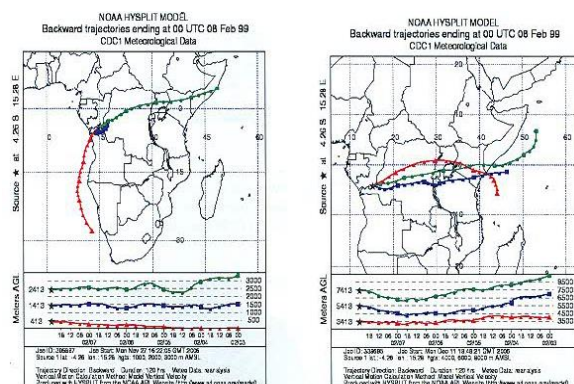


Fig. 4-13: Composite plot of five-day back trajectory HYSPLIT model results for 8 February 1999 showing lower trajectories (left) at 1 km (red) 2 km (blue) and 3 km (green) and mid troposphere trajectories (right) at 4 km (red) 6 km blue and 8 km (green)

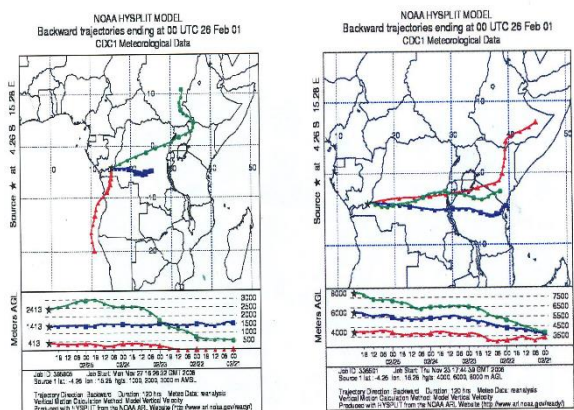


Fig. 4-14: Composite plot of five-day back trajectory HYSPLIT model results for 26 February 2001 showing lower trajectory left at 1 km (red) 2 km (blue) and 3 km (green) and mid troposphere trajectories (right) at 4 km (red) 6 km blue and 8 km (green)

Fig. 4-15, 4-16 and 4-17 below show the zonal wind plotted at 850 hPa, 500 hPa, and 300 hPa, for the period 21-26 February 2001, which confirm a zonal wind flow around 12° N from east to west of the continent and reaching Brazzaville. The 500 hPa zonal wind is luckily to have contributed to ozone enhancement at this period of the year.

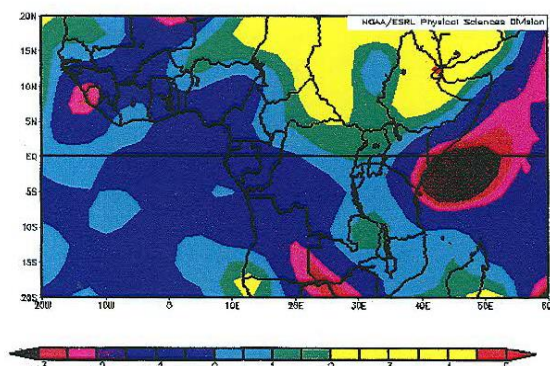


Fig.4-15. Zonal wind winds (ms^{-1}) plotted at 850 hPa for the period 21-26 February 2001.

Sources: <http://www.cdc.noaa.gov/cdc/reanalysis.shtml>

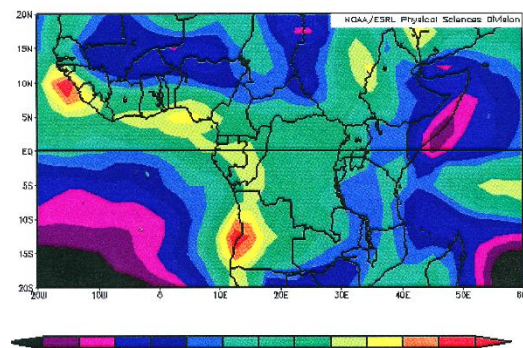


Fig.4-16. Zonal winds (ms^{-1}) plotted at 500 hPa for the period 21-26 February 2001.

Sources: <http://www.cdc.noaa.gov/cdc/reanalysis.shtml>

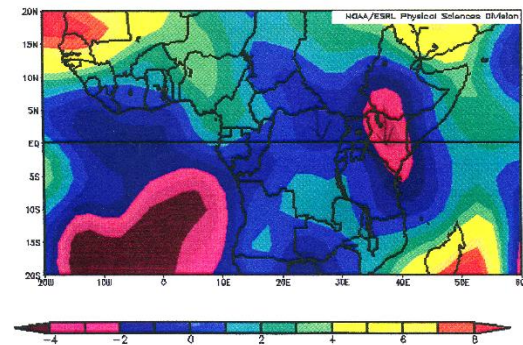


Fig.4-17: Meridional winds (ms^{-1}) plotted at 300 hPa for the period 21-26 February 2001.

Sources: <http://www.cdc.noaa.gov/cdc/reanalysis.shtml>

4-9 Conclusion and suggestions

Tropospheric ozone climatology in the Congo Basin has been the focus of this study. Previous satellite and ozone studies over the last two decades of the 20th century have

shown a dramatic enhancement of tropospheric ozone over tropical Africa. A detailed study based on MOZAIC aircraft data at Brazzaville, which is situated in the Congo basin recognised as a region of high ozone concentration, constituted a challenge that warranted investigation. Results from previous research on tropospheric ozone undertaken as part of SAFARI-92 and TRACE-A concluded an ozone enhancement in the dry season (June, July, August) when biomass burning takes place in the central African region, and a secondary ozone maximum in the summer period, December to February due to Northern hemisphere biomass burning and transport across the Equator. In this study, TTO and vertical ozone profiles at in the Congo Basin for the four year period 1998-2001 based on MOZAIC, aircraft data from Brazzaville were used to investigate short term and seasonal variability. Given the advantage provided by Mozaic data over data derived from satellites and ozonesondes, details information on the vertical ozone distribution of ozone have been provided in this work. Results from the computation of TTO have shown the seasonal variation in the tropospheric ozone namely a winter maximum in August (34.8 DU) and a well-defined summer secondary maximum in February (3.41 DU). An analysis of ozone integrated in the five layers showed the bulk of the ozone enhancement was taking place in the surface to 4 km, suggesting a surface based source. The coincidence of peak biomass burning in the dry season (June to August) over the Congo Basin was noted. Elevated ozone events showing a TTO greater than 30 DU were further computed. A well-developed lower tropospheric ozone peak situated at 3 km was noted in winter with the mean value of 82 ppbv, although individual profiles peaked at 114 ppbv. In summer, it appeared that the upper tropospheric (8-10 km) ozone values were relatively higher than in other seasons. An investigation of the origin of tropospheric ozone enhancement in 2-3 layer in the winter is associated with –easterly to south easterly flow from regions which are known to have high incidence of biomass burning at this time of the year. In summer there is evidence of a Northern Hemisphere origin of air in the upper troposphere. Northern hemisphere biomass and lighting from the convective activities present in the region, which is a source of ozone enhancement. The impact of the BOVCs emission in the region which was noted by Diab *et al.* (1996b) during early spring cannot be discarded as a possible factor contributing to ozone enhancement in the region. The methodology used to compute TTO from MOZAIC data have provided the first ozone climatology in Congo Basin, for the period 1998-2001. Results on mean seasonal patterns and short term variability of tropospheric ozone supported the results of the previous findings. More details on vertical temperature and moisture profiles at the study area would have helped to

understand the vertical transport of ozone and precursor gases. Further information based on the trade wind inversion, and its role would have been interesting to enhance these findings. This study is limited to an isolated location, a combination of detailed profile data at Brazzaville with corresponding satellite data over a larger geographic area would have helped to provide a broader perspective if ozone data could be available for two or more locations in the Congo basin. A classification approach to analysing ozone profiles would have helped further understanding the nature sources of tropospheric ozone enhancement. It would be desirable if water vapour and NO_y and CO profiles provided, by the MOZAIC programme since 2000 could also have investigated for further evidence but unfortunately these parameters were not available for Brazzaville. Given that tropospheric ozone is poorly documented, the MOZAIC programme remains a highly useful in a data spare region such as Africa and should be continued in the the future.

4-10 References

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CHAPTER FIVE

TROPOSPHERIC OZONE CLIMATOLOGY IN EASTERN EQUATORIAL AFRICA

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Tropospheric ozone climatology in Eastern Equatorial Africa

Jean-Pierre Mulumba¹, Sivakumar Venkataraman² and Thomas Joachim Odhiambo Afullo³
College of Agriculture, Engineering and Science. School of Chemistry and Physics and School of
Electrical and Electronical Engineering

University of KwaZulu Natal/ Durban South Africa

Contact details: ¹ Jean-Pierre M. Mulumba: 204517461@stu.ukzn.ac.za; ² Sivakumar Venkataraman: ventakaramans@ukzn.ac.za; ³ Thomas Joachim Odhiambo: Afullo: afullo@ukzn.ac.za

5.0 Abstract

Tropospheric ozone climatology in eastern Equatorial Africa has been at the core of this study. Seasonal and annual tropospheric ozone distribution and variation have been investigated using SHADOZ network data from Nairobi for the period 1998-2013. Meteorological parameters including air temperature, relative humidity, atmospheric pressure as well as ozone partial pressure have permitted to provide the first comprehensible tropospheric ozone climatology over this region. Mean seasonal tropospheric ozone distribution displays two distinct peaks occurring in winter with 43 DU (July) and 46.8 DU in spring (October). Comparison of mean seasonal ozone partial pressure with relative humidity profiles shows a logarithmic trend with strong regression coefficient for ozone partial pressure ($0.81 < R^2 < 0.92$). Conversely relative humidity variation displays a linear trend with a weak seasonal regression ($0.57 < R^2 < 0.74$). Seasonal vertical tropospheric ozone variation displays two ozone peaks of 121 ppbv in JJA and 126 ppbv in SON at 100 hPa respectively. A minimum photochemical source contribution from local and neighbouring countries has been noted at surface to mid latitude. Investigation of individual profiles chosen as case studies for JJA (25/07/2001) and SON (09/10/2002), to assess the origin of high tropospheric ozone concentration have been performed by using back trajectory HYSPLIT model. The strong role played by the Indian Ocean in the long range transport of easterly air mass into eastern Africa at mid and upper troposphere in both seasons has been confirmed. However mean monthly NCEP/NCAR Reanalysis model used to assess the contribution of STE, shows a positive mean eddy divergence values during the months of June to July 2001, with evidence of high vorticity 1 sigma values occurring over the same period. In summer higher positive 1 sigma divergence as well as 1 sigma vorticity values have been noted showing stronger STE activity occurring in SON period. These parameters suggest that STE contribution to ozone enhancement in equatorial east Africa is stronger during SON than in JJA. Given the complexity of climate patterns over the equatorial region, in which Nairobi is located, the influence of ENSO and QBO in the STE occurrence cannot be excluded as noted by previous studies.

Key words: *Climate change, climatology, impact, model, tropospheric ozone*

5.1 Introduction

Tropical and subtropical Africa is considered to be leading sources of air pollution from biomass burning (Hao and Liu (1994). Although biomass burning is highly rated as the main tropospheric ozone contributing sources in these regions, a few studies on this topic have been undertaken, especially in eastern and equatorial Africa where the levels of tropospheric ozone have been increasing since the last past decades of the 20th century (Fishman *et al.* 1996). Tropospheric ozone, as secondary pollutant and a greenhouse gas, has negative effects on human health and the environment. Its concentrations depends on precursor emission levels from natural and anthropogenic activities. Dynamical factors that

determine its dispersion and transport into the troposphere also play a crucial role. In recent years, trends on tropospheric ozone have been exacerbated by change on climate parameters at global level. However, in Africa these trends have been poorly documented and understood. African continent, particularly the East Africa, is among the most vulnerable to climate change impacts due to its geographical position and the lack of resilience capacity to mitigate these impacts (IPCC, 2001). This is because observations on ozone concentration over tropical Africa were only available from TOMS (Total Ozone Mapping Spectrometer) instrument aboard the Nimbus 7 satellite (Fishman and

Brackett, 1997; Hudson and Thompson, 1998) and no *in situ* measurement data existed.

Previous results from TOMS satellite data in this region displayed elevated ozone levels, which coincided with biomass burning season over the tropics (Fishman *et al.* 1986; Cros *et al.* 1988; Marenco *et al.* 1990; Laucaux *et al.* 1996). Furthermore, sporadic ozonesonde operations undertaken in the region (Bundi, 2004) presented significant uncertainties (Fishman and Brackett, 1997; Kim *et al.* 2001), and limited ozone research in the tropics (Bundi, 2004; Thompson *et al.* 2000; 2003a). Likewise, the lack of ozone profile measurements restricted the assessment of its regional budget, and validation of both global models, and satellite information (Sauvage *et al.* 2005).

In eastern equatorial Africa, Nairobi (Kenya) constitutes the unique site location for the detection of ozone, where a few ozone monitoring campaigns have been undertaken, under the active involvement of the World Meteorological Organization (WMO) through Global Ozone Observing System (GO3OS) (Thiongo, 2011). This campaign encompassed monitoring ozone concentrations at the surface using TEI 49C instrument, and the vertical profile, and total column ozone in the atmosphere, using Dobson spectrophotometer number 18, since the year 2005. Monitoring campaign results showed that data from this programme were not consistent until the year 2002, and could not be used for research purpose. Hence, tropospheric ozone characteristics were only studied at individual scale, with no specific characteristics from regional pattern.

Ozone known as greenhouse gas plays negative role in human health (McKee *et al.* 1993), on vegetation (Ashmore, 2005) and in the environment (Logan and Kirchhoff, 1986; Crutzen, 1987). Due to lack of sufficient data in African continent, additional ozone measurement stations distributed in the tropical and subtropical southern hemisphere were launched by NASA's Goddard Space Flight Center, NOAA/ CMDL (Climate Monitoring and Diagnostics Lab) under SHADOZ (Southern Hemisphere Additional Ozonesonde) network. This programme intended to complete the sparse amount of tropospheric and stratospheric ozone data, and consequently remedy data discrepancy in the tropics (Thompson *et al.* 2000; Thompson *et al.* 2003a). SHADOZ network has the advantage of providing ozone profiles on regular basis, with detailed information on the troposphere, and the lower stratosphere in a particular location (Shilenje *et al.* 2015).

The first investigation on tropospheric ozone profile in African tropic were undertaken during SAFARI 2000

campaign for the period 1998—2000 using short term SHADOZ data from Nairobi (Thompson *et al.* 2002). The aim of SAFARI 2000 (Southern Africa Regional Science Initiative) campaign, which also included Lusaka (Zambia) and Irene (South Africa), was to obtain more information concerning the vertical distribution of ozone, and its origin above these locations. Results from SAFARI 2000 indicated high tropospheric ozone concentration during the fire period in September (Austral spring). Nairobi, which is located hundreds kilometers from biomass burning displayed on average, ozone levels ranging between 29 - 69 ppbv, which is far lower than the average observed in other sites. Based on this discrepancy, it was assumed that Nairobi was under distinctly different meteorological transport regimes in comparison with southern Africa sub-region, and was clearly free from any biomass burning influence during the study period. The prevailing wind regime for Nairobi during the month of September is mainly north-easterly from the Arabian Desert in the Middle East, a region devoid of any biomass fire (Bundi, 2004). Further investigations on ozone in African tropics were carried out by Ayoma *et al.* (2002, Paper not published) who studied the variability in the observed vertical distribution of ozone over Eastern Africa as shown in the map in Fig. 5-1.

According to these authors, a statistical analysis of ozone profiles over Nairobi split into three layers reveals strong yearly variation in the free troposphere and the tropopause region, while ozone in the stratosphere appears to be relatively constant throughout the year. Total ozone measurements by Dobson instrument confirm maximum total ozone content during the short-rains season, and a minimum in the warm-dry season. However, no specific tropospheric ozone climatology features over this region were provided. Further investigation on tropospheric ozone undertaken by Bundi, (2004), on the spatial and temporal distribution of tropospheric ozone over southern Africa aimed at understanding of factors affecting the precursors, formation and distribution of regional tropospheric ozone over southern and eastern Africa. Findings of this study revealed that eastern Africa had much less ozone concentration in September, and is not under the influence of biomass burning. This was corroborated the work undertaken by Shilenje *et al.* (2015) who used ozonesonde flight data from Kenya Meteorological Service (KMS) for the period 2000 – 2014. This work, which focused on the variation of upper tropospheric and stratospheric ozone included that seasonal and vertical distribution over Nairobi County showed a negative ozone profile trend upwards within the troposphere, up until the tropopause due to lower exchange rate between the regions. Unfortunately none of these studies, which

were limited to the sources contributing to tropospheric ozone in the region did not provide a comprehensive tropospheric ozone climatology. In order to bridge this gap, the purpose of this paper is to provide a comprehensible tropospheric ozone climatology by using long term SHADOZ data coupled climate change parameters and ozone partial pressure parameters.



Fig. 5-1. Map of African continent showing Eastern region and study area. Adapter from original map available at: <http://www.mapsofworld.com/africa/regions/eastern-africa-map.html> 07/11/2015

The following objectives set to achieving the purpose of this study are: to assess the seasonal and annual variation of tropospheric ozone in the region; to investigate its vertical distribution with regard to meteorological parameters; and predict future trends on tropospheric ozone climatology over this region and its consequences at regional level. The sections below provide information on the data and the method used to achieve this study, the circulation pattern over east equatorial Africa as well as the results obtained and their discussion.

5.2 Data and Method

We use tropospheric ozone data from SHADOZ network at Nairobi for the period 1998-2013, to achieve the objective of this paper. Information related to SHADOZ network as well as the equipment and data acquisition method used are well explained in a recently published paper by Mulumba *et al.* (2015), which is available via internet (<http://dx.doi.org/10.4172/2169-0049.1000151>).

Ozone parameters including partial pressure (nb), concentration (ppbv) and total tropospheric columns (DU) have been used to assess vertical tropospheric ozone variability and horizontal distribution over eastern Equatorial region for the study period. Monthly meteorological parameters including air temperature ($^{\circ}\text{C}$), relative humidity (%), and atmospheric pressure (hPa) have been computed from individual daily profiles, and averaged in daily, monthly and annual profiles. A total of 674 ozonesonde profiles retrieved for the period from 1998 to 2013 has constituted the basis of this study. Due to instrument measurement anomalies, these profiles have been scrutinized using quality assurance technique to discard profiles with missing data, and instrument measurement errors. Only profiles with quality data (with non missing data from surce to 15 km) were retained to compute monthly and annual averages. On the basis of these averages, mean monthly and seasonal total tropospheric ozone (TTO) been plotted to provide the horizontal ozone variation. Seasonal and annual ozone variations have been plotted and compared with meteorological data. Vertical coordinates used in this study is expressed in atmospheric pressure instead of ordinary elevation or altitude. The reason being that many atmospheric motions and temperature properties occur along constant pressure surfaces, as opposed to constant altitude surfaces.

(http://www.ccpo.odu.edu/SEES/ozone/class/Chap_3/3_4.htm).

Thus, atmospheric motions tend to frequently be interrupted by the topography of mountains, so they easier follow constant pressure surfaces. Partial pressure refers to the fraction of the atmospheric pressure at a given altitude for which ozone is responsible. Divergence and vorticity models have been used to determine the dynamic behind stratospheric ozone intrusion. HYSPLIT_4 model analysis has also been used to determine the origin of ozone precursors that affect ozone levels in the region. Ozone levels are governed by local and regional circulation, which are worth understanding prior to any conclusion.

5.3 Circulation over east equatorial Africa

A few authors who studied the climate characteristics over equatorial eastern Africa (Nicolson, undated; Chan *et al.* 2008; Mutai and Ward 2000; Ogallo, 1987, etc.) come to a conclusion that the equatorial eastern Africa has one of the most complex meteorological system in the African continent. In this study, we provide a brief summary of previous work encompassing the main circulation features, in order to undertand the dynamic that governs the tropospheric ozone variation over this region.

The climatic patterns of equatorial eastern Africa, are markedly complex and change rapidly over short distance due to large scale tropical controls, which include several major convergence zones superimposed by regional factors associated with lakes, topography and maritime influence (Nicolson, undated).

<http://www.met.fsu.edu/people/nicholson/papers/clidyn.pdf>.

The complexity of the climate is due to a complex combination of changes in air humidity, precipitation, cloudiness, and incoming shortwave radiation that might be the key components in determining tropical high-altitude climate (Chan *et al.* 2008). In consequence, climate over this region is dramatically illustrated by the rainfall patterns, which present one, two or three maxima in a seasonal cycle. Besides the complexity of climatic patterns in this region, rainfall variability is governed by large scale global tropical climate.

Winds and pressure patterns include three major airstreams and three convergence zones. The air stream flow includes the Congo air stream with easterly and southerly flows, the northeast monsoon and the south east monsoon. The flow from the Congo is humid and thermally unstable and therefore associated with rainfall. The monsoon streams are thermally stable and associated with subsiding dry air. These three streams are separated by two surface convergence zones, the ITCZ and the Congo air boundary, the former separates the two monsoons, and the other the easterly and westerly. The third convergence zone aloft separates the dry stable northerly flow from the Sahara and the moist southerly flow. At low levels, southeast and north east monsoon prevail during the high and low sun season. The northeast monsoon is made up primarily of a dry air stream, which has traversed the eastern Sahara but during the NE monsoon season relatively humid current from the Atlantic Ocean occasionally penetrates the region (Nicolson, undated).

East African rainfall is highly seasonal, as can be expected from its tropical location (Chan *et al.* 2008). Precipitation primarily occurs during boreal spring and autumn seasons as the solar-driven Intertropical Convergence Zone (ITCZ) crosses the equator from south to north, then north to south, respectively (Camberlin and Philippon 2002; Mutai and Ward 2000). The confluence of tradewinds along the ITCZ causes gradual wind change from northeasterlies in January to easterlies in March, southeasterlies in July and again to easterlies in October (Gatebe *et al.* 1999). Therefore, the mean annual rainfall is divided into four periods: January–February, March–May (long rains), June–September, October–December (short rains), and

accounting for roughly 18, 42, 15, and 25% of the mean annual rainfall, respectively (Indeje *et al.* 2000). In general, precipitation events during the long rains season tend to be heavier and longer in duration, with less interannual variability, and are more likely associated with local factors. In contrast, precipitation events during the short rain season are less intense, with shorter duration and stronger intra-seasonal and inter-annual variability that mirrors large-scale phenomena such as El Niño-Southern Oscillation (ENSO), and the varying intensity of the zonal circulation cell along the equatorial Indian Ocean (Indeje *et al.* 2000; Mutai and Ward 2000; Camberlin and Philippon 2002; Hastenrath *et al.* 2004; Vuille *et al.* 2005).

5.4 Mean Total Tropospheric Ozone (TTO) variation in eastern Equatorial Africa

Mean TTO computation constitutes a useful tool for the comprehension of tropospheric ozone variation (daily, monthly, seasonal and annual) at a given geographic location. Fig. 5-2 presents monthly TTO column variation in equatorial eastern Africa such as observed at Nairobi for the period 1998-2013.

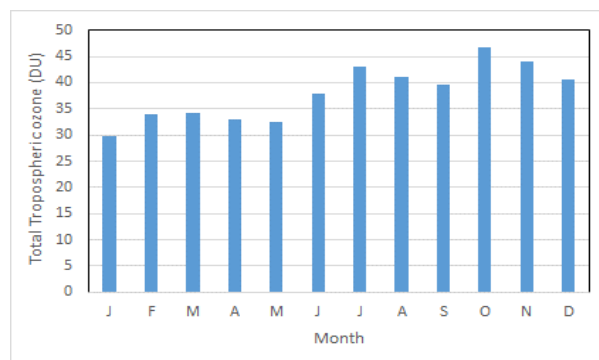


Fig. 5-2. Mean Monthly Total Tropospheric Ozone column variation for the period 1998-2013.

Two ozone maxima occurring in July (43.0 DU), and in October (46.8 DU) are noted respectively. July maximum corresponds to biomass burning season in the tropics as depicted by satellite and previous ozone measurement studies (Fishman *et al.* 1986; Cros *et al.* 1988; Marengo *et al.* 1990; Laucaux *et al.* 1996). Low ozone concentration is observed in January with 29.7 DU. Computation of mean seasonal and annual TTO variation is presented in Fig. 5-3. This figure shows that high ozone concentrations levels occur in austral spring (SON) with 43.8 DU. This period corresponds with the dry and biomass burning season in the tropics. The lower ozone concentration is recorded in austral summer (DJF) with 32.6 DU. This period corresponds to long rain period when the ITCZ is moving from the

northern to the southern hemisphere. Annual ozone concentration of 38 DU is observed for the study period.

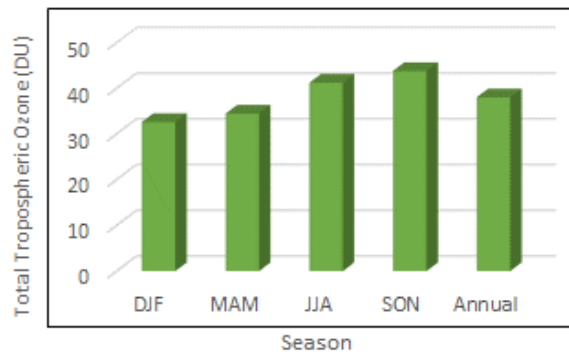


Fig. 5-3 Mean Seasonal Total Tropospheric Ozone column variation from 1998-2013

5.5 Mean seasonal temperature and relative humidity variation

Fig. 5-4 shows mean seasonal temperature (C°) columns with the highest mean temperatures recorded in DJF and the lowest in JJA. In contrast, mean seasonal relative humidity observed for the study period (Fig.5-5) shows high values in JJA, whereas low values are observed in DJF.

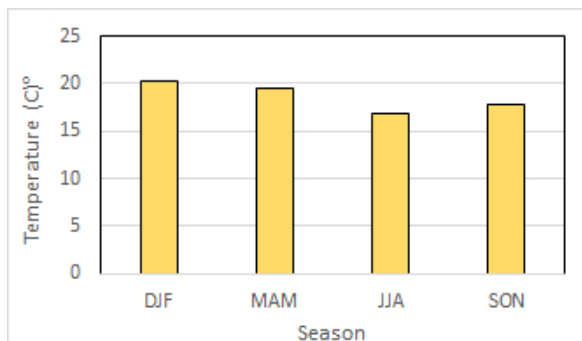


Fig. 5-4. Mean Seasonal surface temperature (C°) variation at Nairobi

These figures present temperature and relative humidity “paradox” which may be useful to understand tropospheric ozone distribution in at Nairobi.

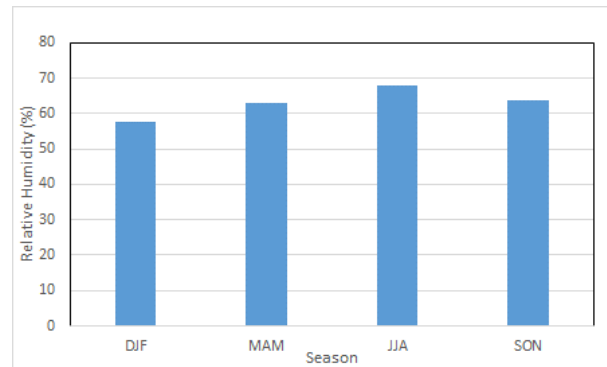


Fig. 5-5. Mean seasonal relative humidity for the period 1998-2013

5.6 Tropospheric ozone distribution in eastern Equatorial Africa

Vertical ozone distribution provides detailed information on the variation of its concentration in different tropospheric layers. It also pictures the role played by photochemical and dynamical factors. Fig. 5-6 (a,b,c,d) present mean seasonal ozone distribution such as observed at Irene for the study period in comparison with seasonal relative humidity profiles for the same period. Maximum ozone concentration of 472 ppbv is observed in JJA at 200 hPa with 25 ppbv at the surface (823 hPa). The minimum ozone concentration of 306 ppbv is observed during DJF at 200 hPa, and 25 ppbv at the surface. SON and MAM present maximum ozone concentrations of 404 and 364 ppbv at 200 hPa and 23 and 26 ppbv at the surface respectively. Relative humidity profile maximizes in JJA with 82% at 792 hPa and corresponds to ozone concentration of 32 ppbv at the surface. Minimum relative humidity of 69 % during DJF, which corresponds to ozone concentration of 30 ppbv at surface. SON and MAM present the relative humidity of 78 and 76%, which correspond to equal ozone concentration of 30 ppbv at the surface respectively. Ozone mixing ratio equals relative humidity at intersection point with varies on seasonal basis. Tropospheric ozone concentration varies according to the logarithmic equation as follows:

$$Y = t \ln(x) + c$$

and relative humidity varies in linear equation

$$Y' = ax' + b$$

with Y and Y' representing the barometric pressure at which ozone concentration and relative humidity have the same mixing ration (m).

t = ozone concentration lapse rate as function of barometric pressure,

a = relative humidity lapse rate as function of barometric pressure

x = ozone concentration (ppbv)

x' = relative humidity in percent

b = relative humidity coefficient

c = ozone coefficient

The intersection point of these parameters can be determined by the equation system (1) and (2)

$$\begin{cases} Y = t \ln(x) + c & (1) \\ Y' = ax' + b & (2) \end{cases}$$

The intersection point of these parameters is found through the equation (3) where we suppose $Y=Y'$ (3)

and we obtain the equality

$$t \ln(x) + c = ax' + b \quad (4)$$

with (x, y) and (x', y') represent the mixing ratio point (M) coordinates.

Because $Y = Y'$ $M = (x, y; x' y')$ then

$$M = (x, y; x', y) \quad (5)$$

This model will serve to analyze the seasonal tropospheric ozone and relative humidity correlation as function of atmospheric pressure. Table 5-1 presents seasonal equations determining the atmospheric pressure at which relative humidity and ozone present a common mixing ratio. These seasonal models can be used for statistical hypothesis testing the relationship between mean atmospheric pressure and these two parameters (ozone concentration and relative humidity).

Table 5-1. Seasonal models for the determination of common mixing ratio as function of barometric pressure.

Seasons	Y	Y'	R^2	R'^2
DJF	$-302 \ln(x) + 1653$	$10.969 x' + 149$	0.66	0.92
MAM	$-278.1 \ln(x) + 1576$	$9.6254 x' + 162$	0.66	0.90
JJA	$-229.4 \ln(x) + 1397$	$8.1344 x' + 193$	0.57	0.81
SON	$-268.3 \ln(x) + 1559$	$8.6185 x' + 179$	0.74	0.85

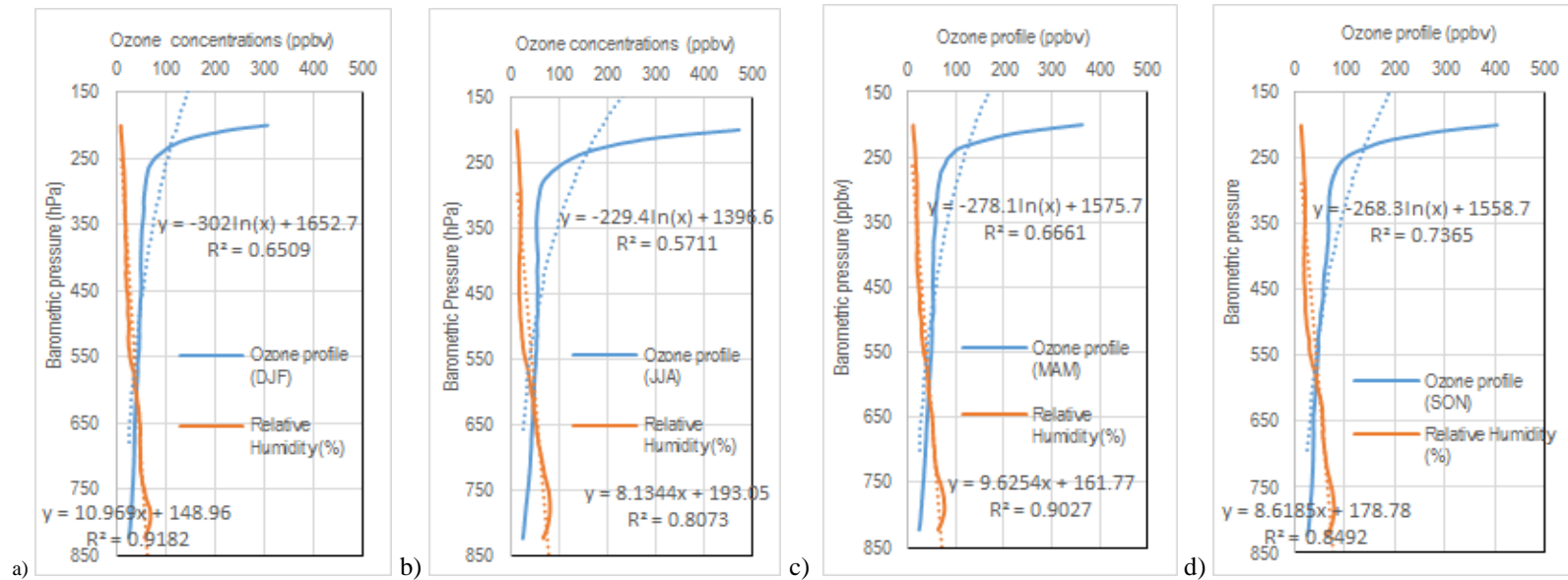


Fig. 5-6. Mean seasonal vertical tropospheric ozone with Relative Humidity profiles at Nairobi as function of Barometric pressure (850-200hPa): a= DJF; b=MAM; c=JJA; d=SON

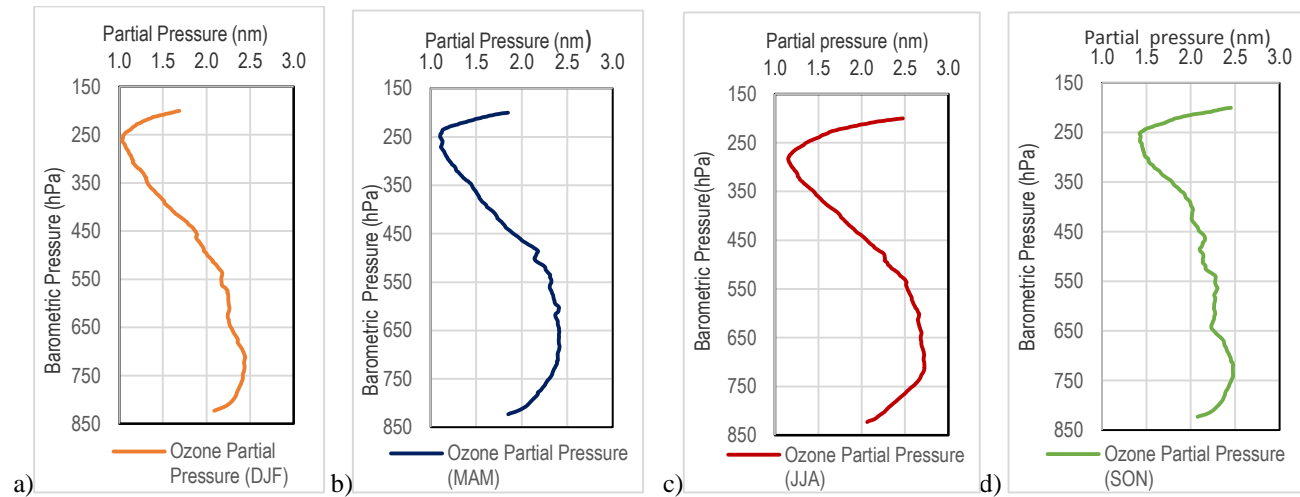


Fig.5-7. Mean seasonal tropospheric ozone and partial pressure at Nairobi for the period 1998-2013

5.7 Mean tropospheric ozone partial pressure variation

Mean seasonal tropospheric ozone partial pressure computed for the period 1998-2013 determines its mixing ratio in the atmosphere at a given altitude or barometric pressure. As such, partial pressure measures the frequency of collisions of gas molecules with surfaces and therefore determines the exchange rate of molecules between the gas phase, and a coexistent condensed phase (Levine, 1995). It is thus a useful parameter to determine dynamical and chemical properties of the troposphere as well as the tropopause characteristics. In this study, we use seasonal ozone partial pressure to determine stratospheric ozone exchange process which can be detected by ozone pressure lapse rate profile, which is expressed by the formula:

$$\frac{dT}{dz} = \frac{1}{c_p \rho} \left(\frac{dp}{dz} \right) \quad (5)$$

where T = air Temperature

z = Altitude

p = Atmospheric Pressure

c_p = Caloric heat

ρ = air density

Suppose Q = Ozone partial pressure which change as function of atmospheric pressure, humidity and temperature, the following equation can be obtained :

$$\frac{dQ}{dz} = \frac{1}{c_p \rho} \left(\frac{dp}{dz} \right) \quad (6)$$

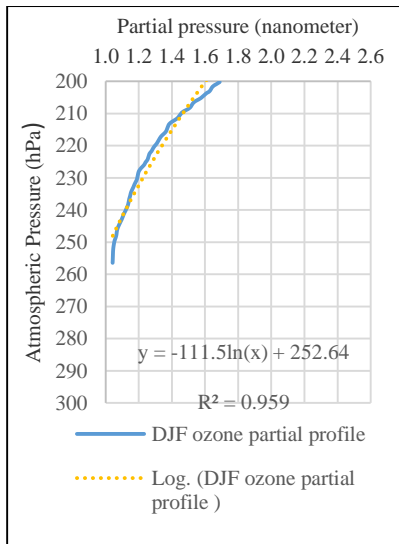


Fig. 5-8 a). Ozone partial pressure lapse rate for DJF

Computation of seasonal ozone partial pressure profiles (Fig.4-7) displays inversion lapse occurring at different atmospheric pressure values in all seasons. A remarkable inversion atmospheric pressure is noted in JJA and SON where ozone partial inversion profiles evolve at 298 hPa and 261 hPa in JJA and SON respectively and reach the highest value of 2.5 nm (nanometer) at 200 hPa considered at a tropopause pressure in the tropics. Therefore ozone partial pressure lapse rate increase as function of $\left(\frac{dQ}{dz}\right)$, implies stratospheric tropospheric ozone exchange between the upper troposphere and the lower atmosphere. This dynamic process is normally accompanied by strong radiative heating due to latent heat release at low latitude such as equatorial Africa. This change may spawn tremendous climate parameters change such as high surface temperatures with all the consequences that may follow in the region. Fig. 5-8a, b, c, d, present the seasonal ozone partial pressure inversion logarithmic model together with their respective regression coefficients (R^2). All seasons present a strong regression coefficient, which implies that STE activity occur in all seasons at Nairobi.

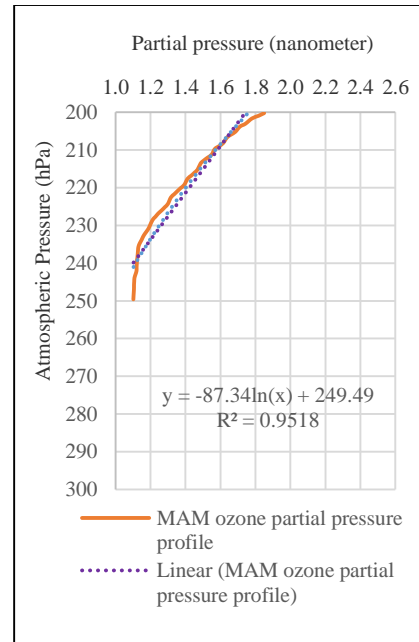


Fig. 5-8 b). Ozone partial pressure lapse rate for MAM

However, a seasonal variation of ozone partial pressure inversion has been observed at different barometric pressure. JJA and SON present the same ozone pressure value of 2.5 nm Table 3 presents the seasonal ozone partial pressure inversion pressure. Thus seasonal change in ozone partial pressure can be associated with the seasonal variation of ozone mixing ratio with altitude

that occurs just above the tropopause such as observed by Holton *et al.* (1995). To better understand these processes and the role played by dynamic factors contributing to seasonal changes on ozone concentration in the troposphere, two ozone enhancement events have been chosen as a case study.

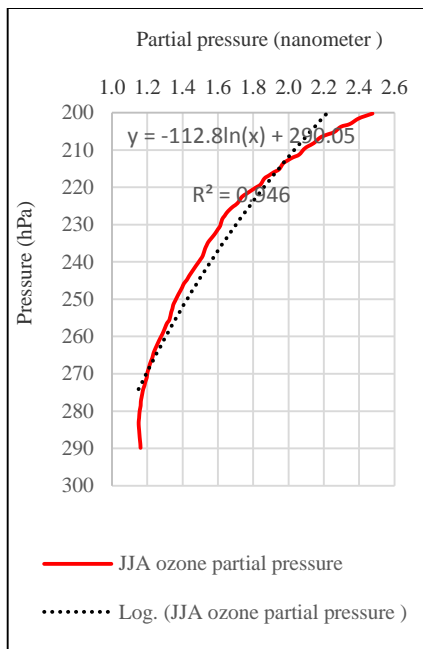


Fig. 5-8 c). Ozone partial pressure lapse rate for JJA

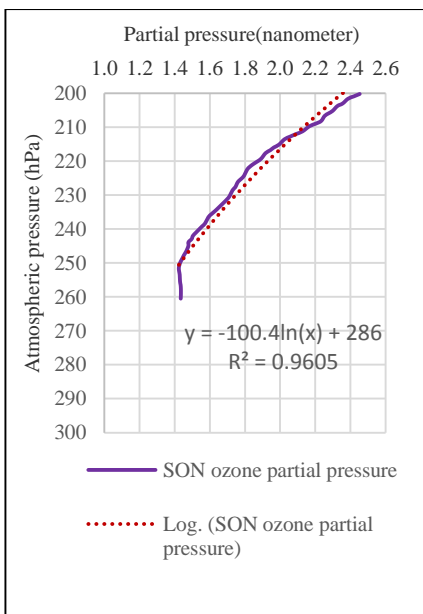


Fig. 5-8 d). Ozone partial pressure lapse rate for SON

Table 5-4 presents seasonal ozone partial pressure inversion variation at 200 hPa.

Table 5-2. Seasonal ozone partial pressure inversion point variation as function of barometric pressure

Season	Ozone Partial pressure	Barometric Pressure inversion point (hPa)
DJF	1.0	256
MAM	1.1	250
JJA	1.2	290
SON	1.0	261

Table 5-3: Seasonal ozone partial pressure inversion variation at 200 hPa

Season	Barometric Pressure with high value (hPa)	Ozone Partial pressure
DJF	200	1.0
MAM	200	1.8
JJA	200	2.5
SON	200	2.5

5.8 Analysis of case studies

Computation of inter annual ozone concentration shows that high tropospheric ozone concentrations of 68 DU were recorded in July 2001 and October 2002 respectively. In order to understand the mechanisms responsible for these high ozone concentration events two case studies have been chosen and analysed. The ozone profile events on 25 July 2001 and on 09 October 2002 have been chosen as profiles presenting the highest ozone concentrations event of 126 ppbv at 100 hPa, and 121 ppbv at the same altitude (Fig.13 and Fig.17). Back trajectory computation from HYSPLIT trajectory Model has been used to determine the air mass trajectory that may have contributed to ozone enhancement events at Nairobi. Composite 24 hours trajectory modeled at three different altitudes, i.e. 3 000 m, 5 000 m, and 7 000 m above ground level and at 8000 m, 10 000 m, and 12 000 m were chosen with isobaric vertical motion. Two plots for individual event have been computed, and the results are presented in Fig. 14 a and 14 b and Fig. 15a, and 15b. Mean eddy divergence plot have together with potential vorticity have been used to determine STE contribution to high ozone events on the days.

5.8.1 Case study of 25/07/2001

Analysis of 25/07/2001 tropospheric ozone and relative humidity profiles (Fig.5-9), shows two ozone peaks

occurring at lower troposphere with 57 ppbv at 590 hPa and in the upper troposphere 126 ppbv at 100 hPa. These peaks are well in line with the findings made by Mulumba *et al.* 2015 on the positive correlation between ozone and relative humidity at surface and upper troposphere.

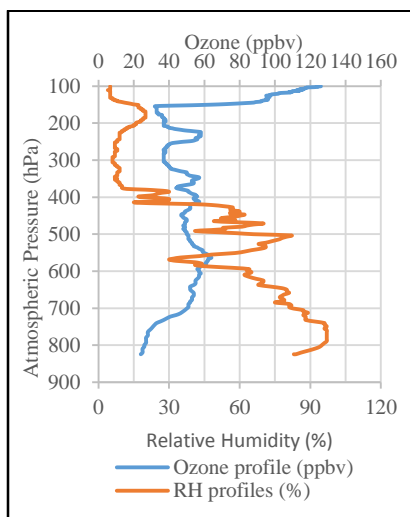


Fig.5-9. Ozone profile with corresponding relative humidity on 25 July 2001 at Nairobi.

Surface to middle altitude display a decrease on ozone concentration value below 50 ppbv showing the minor photochemical sources contribution from local sources as shown in Fig. 10a, at the altitude 3000 m, 5000 m and 7000 m. Photochemical contribution from neighboring Somalia can be observed at 350 hPa in the upper troposphere. The possibility of photochemical sources contribution cannot be excluded at this time of the year when north east monsoon prevail during the low sun season. However, the work done by Bundi, (2004) evidenced ozone enhancement episodes over equatorial and southern Africa at mid-troposphere at locations distant from potential precursor source regions. These findings may be in agreement with approach developed by Holton *et al.* (1995), on STE contribution to lower levels ozone these regions.

Fig. 5-10 b, plotted at the altitude of 8000 m, 10000 m and 12000 clearly shows air mass trajectory from Somalia from a distance as far as 700 km away from Nairobi. Local contribution of ozone enhancement on this day is from convective air mass driven by easterly flows. These flows are motivated by the proximity of the Indian Ocean which plays a crucial role on synoptic weather system in eastern Africa. Further analysis on dynamic parameters through NCEP/NCAR Reanalysis model shows a positive mean eddy divergence values during the month of June to July 2001 (Fig.5-11). Evidence of high vorticity 1 sigma occurring over the same period has been also noted with

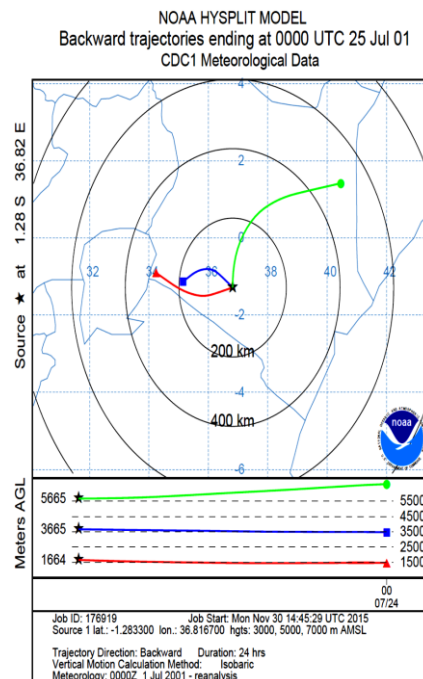


Fig. 5-10 a) Composite HYSPLIT Back trajectory representing the air mass pathway at three different altitude 3000 m, 5000 m and 7000 m over Nairobi on 25/07/2001.

Sources: <http://ready.arl.noaa.gov>

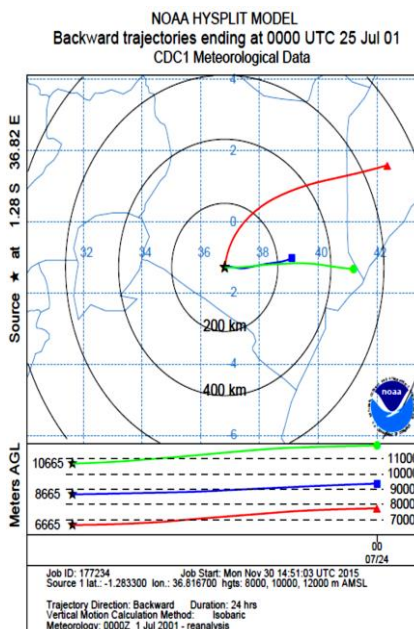


Fig. 5-10 b) Composite HYSPLIT Back trajectory representing the air mass pathway at three different altitude 10000 m, 8000 m and 6000 m over Nairobi on 25/07/2001.

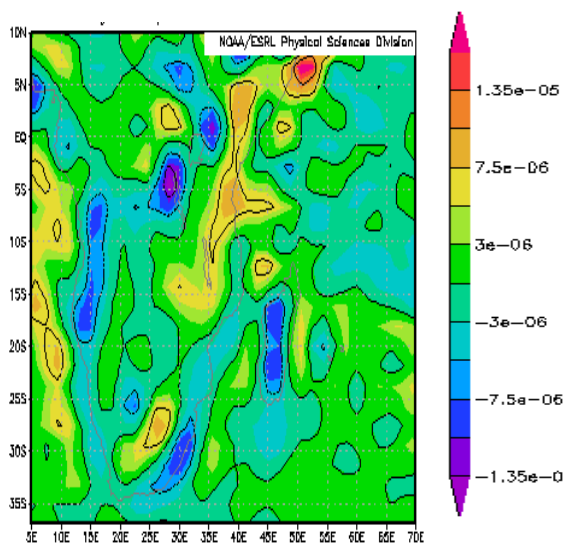


Fig. 5-11. Mean Eddy divergence average over June and July 2001
Sources: <http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.html>

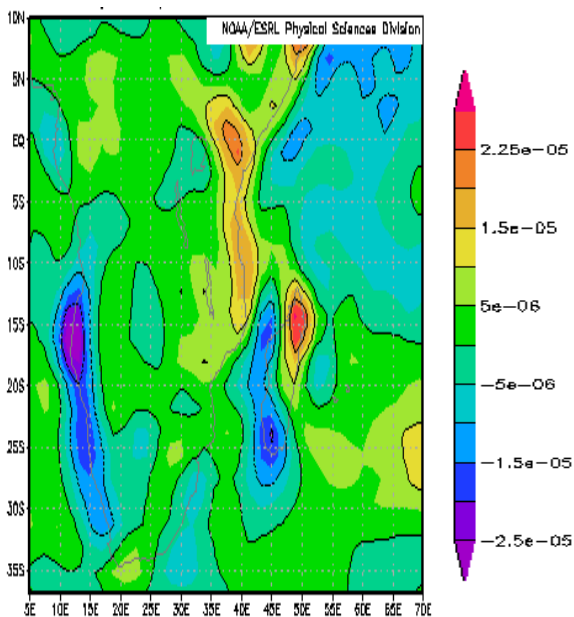


Fig. 5-12 Vorticity Mean eddy vorticity June-July 2001
Sources: <http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.html>

positive values varying from $1.5e$ to $2.5e$ (Fig.5-12). STE process contributing can be depicted through the sharp increase of ozone that occurs at 153 hPa with a concentration of 36 ppbv to peak up at 124 ppbv at 100 hPa under diabatic condition such was determined by ozone pressure positive lapse rate.

5.8.2 Case study of 09/10/2002

Analysis of 09/10/2002 tropospheric ozone and relative humidity profiles (Fig. 5-13), shows two ozone peaks occurring at mid-troposphere with 108 ppbv at 400 hPa and in the upper troposphere 120 ppbv at 100 hPa.

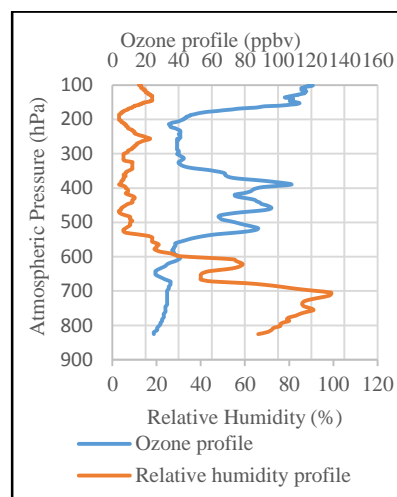


Fig. 5-13. Ozone profile with corresponding relative humidity on 09/October 2002 at Nairobi.

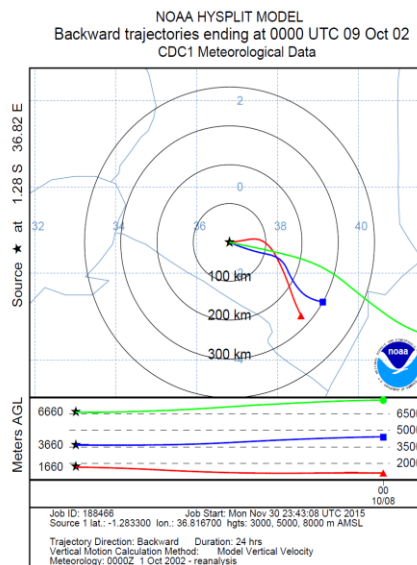


Fig. 5-14 a) Composite HYSPLIT Back trajectory representing the air mass pathway at three different altitude 3000 m, 5000 m and 7000 m over Nairobi on 25/07/2001.

Sources: <http://ready.arl.noaa.gov>

Over this date a sharp relative peak is noted at 700 hPa, which corresponds to ozone value of 33 ppbv. Once again, this is in good agreement with the positive

correlation existing between ozone and relative humidity.

A substantial increase in ozone concentration noted below 700 hPa originates from local photochemical sources and long distance air mass transport driven by easterlies flow as shown in Fig. 5-14a.

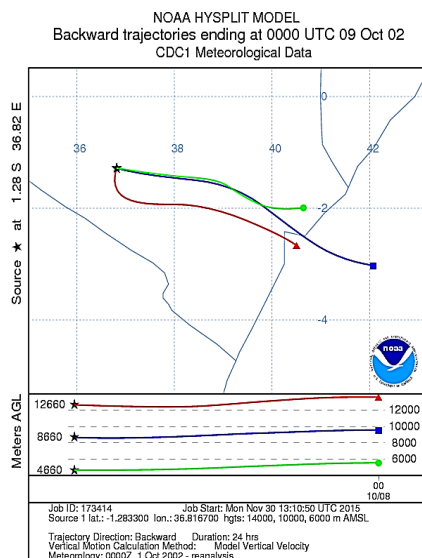


Fig. 5-14 b) Composite HYSPLIT Back trajectory representing the air mass pathway at three different altitude 6000 m, 10000 m and 14000m m over Nairobi on 9/10/2002.

Sources: <http://ready.arl.noaa.gov>

Consequently, a remarkable decrease in relative humidity at the same pressure and below is also noted. A second peak, which originates from 250 hPa with ozone concentration of 38 ppbv to reach 120 ppbv at 100 hPa, denotes a contribution from local and long range air mass transport from photochemical sources in the upper troposphere driven by coupled ocean-atmosphere-land interactions (Kinyoda, undated) as displayed in (Fig. 5-14b). These findings clearly show the role played by Indian Ocean on the synoptic weather system in equatorial eastern Africa. Although photochemical sources contribution from long range transport of air mass from Indian Ocean from easterly jet stream in the upper troposphere, have been noted, the possibility of STE contribution during this period of the year at Nairobi cannot be excluded.

Long term mean eddy divergence 1 sigma computed from NCEP reanalysis model provides evidence positive values higher than winter period, which vary from 1.5e to 4.5 e. (Fig. 5-15). Positive values on one month mean eddy vorticity model computation from NCEP/NCAR reanalysis model have also been noted (Fig.5-16d). These parameters confirm well the higher contribution

of STE to ozone enhancement in equatorial east Africa during SON than during JJA. During this season, the influence of ENSO (El Nino, Southern Oscillation) and the Quasi Biennial Oscillation (QBO) occurring at Nairobi cannot be ignored (Lee *et al.* 2010).

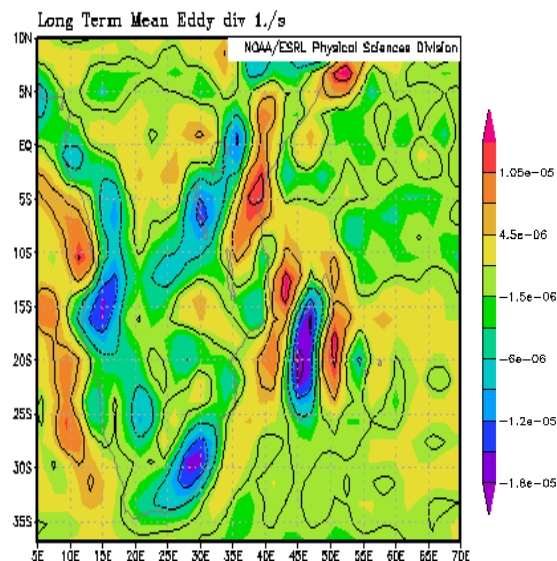


Fig.5-15. Mean Eddy divergence average over June and July 2001

Sources:

<http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.html>
DC Derived NCEP Reanalysis Products Sigma Level Data GrADS image

Sources: <http://www.esrl.noaa.gov/psd/cgi-bin/GrADS>

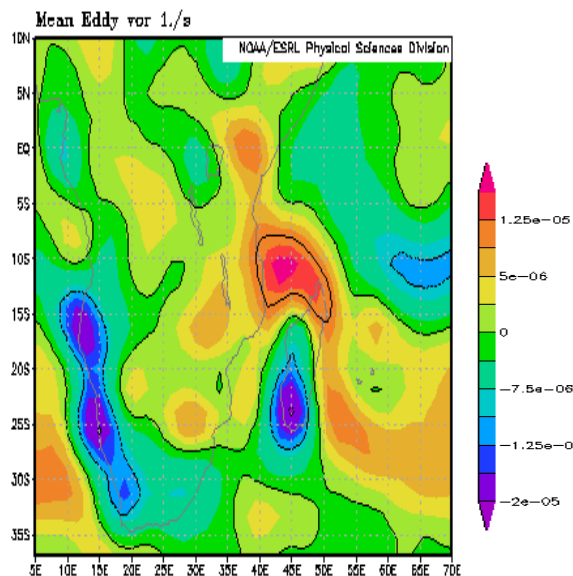


Fig. 5-16 Vorticity Mean eddy vorticity June-July 2001

Sources

<http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.html>

5.9 Conclusion and suggestions

Tropospheric ozone climatology over equatorial eastern Africa has been investigated with data from SHADOZ Network from Nairobi, which is a unique station in this part of the continent where a few *in situ* tropospheric ozone measurements exist. Its geographic position near the equator and a few distance from Indian Ocean makes Nairobi one of the most complex meteorological system in the African continent. In this study, we provide a brief summary of previous work encompassing the main circulation features, in order to understand the dynamic that governs the tropospheric ozone variation over this region. Located in a region of high ozone enhancement, a study of ozone distribution and variation using long term ozone sonde data, may provide a comprehensible tropospheric ozone for the eastern African region where ozone data are scarce and its climatology not well understood. This is in essence the purpose of this study the following objectives: to compute seasonal and annual tropospheric ozone distribution and variation, to assess seasonal variation with regard to climate change parameters, to assess ozone parameters variation and to determine origin photochemical sources as well as dynamical factors contributing to its enhancement in the region, and finally to predict future scenario on ozone enhancement and its consequences in the region.

The main future of this study reveal seasonal tropospheric ozone variation with two maxima occurring in JJA (43 DU) and SON (46.8 DU). Vertical distribution displays two ozone peaks occurring in the same period with 121 ppm and 126 ppbv at 100 hPa. Seasonal ozone partial pressure profiles present strong regression coefficient ($0.81 < R^2 < 0.92$) in comparison with relative humidity ($0.57 < R^2 < 0.74$). The highest ozone partial pressure value of 2.5 nm corresponding to 200 hPa, was observed during JJA and SON implying the intrusion of ozone rich air from lower stratosphere into the upper troposphere. Two case studies used to study the origin of high tropospheric ozone distribution using HYSPLIT back trajectory model suggest local photochemical sources contribution from convective air mass as well as long range transport from north easterly and easterly flow from Indian Ocean in the mid troposphere and upper troposphere. NCEP/NCAR reanalysis model confirm the presence of STE in both seasons (JJA and SON) through positive divergence 1 sigma values and positive vorticity 1 sigma value where SON values are stronger than JJA. Given the complexity of climate pattern over equatorial region, which Nairobi is located in, the influence of ENSO and QBO in the STE occurrence cannot be excluded as noted by previous studies. This study limited to Nairobi which is an isolated location in eastern Africa could be complete if additional data from other station in the region were

associated. Given the importance of tropospheric ozone in global climate and human life, we suggest more *in situ* ozone measurements in the region with various LIDAR or various instrument to provide more insight on ozone trend over the region and predict its evolution due to climate change impact.

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CHAPTER SIX

GENERAL CONCLUSION AND FUTURE WORK

The present work aimed at assessing tropospheric ozone climatology over southern part of the African continent including Congo basin, equatorial east Africa, and subtropical Africa. Due to insufficient data and information regarding ozone characteristics in the region, data from SHADOZ and MOZAIC programme from 1998 -2013 and 1998-2001 respectively have been used to establish ozone characteristics and to determine the impact of climate change on ozone concentrations over these three particular regions. The methodology used to achieve the objective of this study was based on the modelling of tropospheric ozone variation with meteorological parameters including temperature and humidity. Ozone partial pressure and atmospheric pressure were also used to determine the dynamical processes occurring in upper and middle troposphere. NCER/NCAR reanalysis and Hysplit model 4 have permitted to understand air mass circulation over the middle and upper troposphere that may be at the origin of ozone enhancement in the region.

Although results from the three different locations present lot of similarity, one must note that the change in meteorological parameters due to climate change negative impacts on tropospheric ozone concentration, which the effects are well perceived through case studies analysis. In the following sections, we present the summary of results from the three locations that have constituted the basis of this study.

Tropospheric ozone modeling at Irene confirms the seasonal patterns of ozone such as previously observed over southern Africa, 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 been noted, in comparison with previous short term studies undertaken at this location. 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 to 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 used to provide seasonal correlation between ozone and temperature and relative humidity displays strong regression coefficient ($0.96 < R^2 < 1$) between ozone and temperature in all seasons. Similar trends are also observed for relative humidity and TTO concentrations ($0.91 < R^2 < 1$) in autumn, spring and summer. However a weak correlation is noted in winter, when TTO minimum values are recorded ($0.58 < R^2 < 1$).

In the Congo Basin tropospheric ozone climatology investigated using short term aircraft data from MOZAIC programme collected at Brazzaville for the period 1998-2001 also presents two seasonal maxima occurring in August and February with 35.4 DU and 26.1 DU respectively. Seasonal vertical ozone profiles variation shows two peaks occurring in summer (February) and spring (September-October) respectively. These results confirm the role played by ozone precursor's gas from biomass burning emission in the lower troposphere, where ozone peaked at about 100 ppbv at an altitude ~2 km. The spring ozone peak noted, corresponds well with the seasonal biomass burning peak in this region. The summer peak with ~65 ppbv at an altitude of ~4 km, corresponds to onshore transport of ozone precursors from neighbouring coastal Atlantic countries, where biomass burning is also noted during the same period. Further investigation on ozone in the Congo Basin in the mid-troposphere shows the role played by dynamical processes

following its position near the Inter Tropical Convergence Zone (ITCZ) on the movement of air mass from the North Hemisphere to the South Hemisphere. Two case studies on ozone enhancement events occurring in both summer and spring confirm the photochemical sources and dynamical processes affecting ozone concentration at lower layer and mid-altitude respectively. The origin of these sources has been determined using five days back trajectory modeling (HYSPLIT_4 model) and NCEP/NCAR reanalysis model to provide further insight into the circulation pattern on the selected days for case study. Results from these models ascertain the photochemical origin of ozone at 850 hPa, as well as the transport of ozone precursor's gas from neighbouring and remote African countries at 500 hPa.

Over equatorial eastern Africa, which presents one of the most complex meteorological system in the African continent, seasonal ozone distribution has also been noted with two peaks (43 DU) and (46.8 DU) occurring in July and October respectively. These peaks which correspond with those recorded at Irene, are due to local photochemical sources in the lower troposphere where the ozone concentrations has been noted from surface to middle troposphere due to convective air mass movement prevailing in this region. Two individual profiles chosen as case studies including 25 July 2001 (winter) and 9 October 2002 (spring) confirmed the influence of photochemical sources (anthropogenic, biogenic and lightning emission) at the surface to the middle troposphere where ozone profiles presented a peak of 58 ppbv at 590 hPa during winter and 108 ppbv at 390 hPa during spring. In the upper troposphere at 100 hPa, at peak of 121 ppbv and 126 ppbv have been recorded in the both case studies respectively. Analysis on dynamic factors responsible for high ozone concentration in the upper troposphere from these two case studies has been undertaken using HYSPLIT Model and NCEP/NCAR Reanalysis Model. Results from these models show the contribution of long range air mass transport at upper

troposphere, which mainly originates from East African low-level jet or Somali jet, the north-eastern tip of Madagascar from Indian Ocean, and during the movement of the ITCZ air mass from the North Hemisphere to the South Hemisphere from austral winter to austral spring. A positive divergence values were noted in both case studies as negative flux on zonal and meridional wind patterns prevailed at upper troposphere due to a quasi-permanent low pressure system prevailing in the region and the influence of monsoonal streams from Indian Ocean. Computation of seasonal ozone partial pressure profiles display logarithmic inversion lapse which evolves at 298 hPa and 261 hPa in JJA and SON reaching the highest value of 2.5 nm. These dynamic processes, which are normally accompanied by strong radiative heating at low latitude may spawn tremendous climate consequences such as high surface and sea temperature with all the consequences this can entrain in the region.

FUTURE WORK

Ozone over African continent is poorly documented and understood. The lack of data in many countries, especially over sub-Saharan Africa, does not permit much research in the topics. Because ozone has negative impacts of photochemical source emissions, chiefly produced in tropical and subtropical regions, additional monitoring stations are needed to document the trends on this secondary pollutant.

At this regard, the implementation of ambient air quality monitoring stations for the measurement of greenhouse gases including carbon dioxide, methane, and nitrous oxide and ozone in main cities over the continent may be a milestone toward the identification and control of local sources and their mitigation. Inventory of biomass burning and biogenic emissions Congo basin and east Africa may also contribute to fill the gap on the existing data and consequently ensure future scenarios on tropospheric ozone concentrations trends.