MEASUREMENTS OF SURFACE OZONE AND ITS PRECUSRORS WITH RELEVANCE TO URBAN AIR POLLUTION; A CASE OF NAIROBI COUNTY.

BY

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DECLARATION

This research study is my original work and has not been presented to any other institution. No part of this research should be produced without the authors consent or that of Moi University.

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DEDICATION

I dedicate this work to my great parents, Mr. Charles D. Okoth Apondo and Mrs. Mary Apondo, for all their love, support and encouragement: my family and friends.

ABSTRACT

Ozone is an important greenhouse gas and a key global air pollutant. It is known to be the most damaging air pollutant whose concentrations continue to rise globally to beyond tolerable levels, and attributed mainly to human activities. Nairobi city is important to Kenya's economy and acts as regional headquarters for many organizations. The city faces many challenges associated with high population, which include lack of an effective public transport network resulting in frequent vehicular traffic jams leading to increased emissions of air pollutants. The dynamic changes in air quality, due to atmospheric pollutants and more specifically surface ozone is of interest in this work because it influences the quality of life in the city, therefore it needs to be systematically monitored and analyzed. This study focused on: The current levels of surface ozone over Nairobi taken from the continuous and mobile measurements; the types of the precursor gases of surface ozone over Nairobi; their current levels from various selected locations around the city and finally; the past trends and contributions of vertical profile ozone over Nairobi. The continuous surface ozone measurements were obtained from a stationary surface ozone analyzer Thermo scientific Model 49i and the mobile surface ozone alongside the precursor gasses taken from Ecotech Serinus analyzers for Ozone, NOx, NMHC, CO and CH_4 mounted on a mobile air pollution laboratory deployed to several sites around the city and the ozonesonde for the vertical profile ozone measurements. The main results show that the continuous surface ozone measurements have diurnal and seasonal variations being the same for the past four years. Day time ozone levels were seen to peak at mid-day hours, then the seasonal levels seen to have two prominent peaks twice a year in the months of March having hourly mean concentrations 32 +/- 5 ppb and August/September with 36 +/- 5 ppb. Mobile measurements were found to be within the WHO limits. Ozone diurnal variations were found to be within WHO limits of 50 ppb for 8 Hr. mean, with Valley road exhibiting the highest with an 8 Hr. mean of 14.9 ppb. The study concludes that, surface ozone over Nairobi is majorly contributed by vehicular sources as precursors such as NOx and NMHC were high in most mobile site measurements. Based on this work, it is recommended that more continuous and mobile measurements around the city be adopted to enable a diverse data base, which may assist in evaluating the impacts of surface ozone, more so with regards to health and agriculture, critical to inform policy makers and the general public of the trends and the risks posed by the increasing urban air pollution.

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ABBREVIATIONS

ALT	Altitude
ASL	Above Sea Level
BC	Black Carbon
CO	Carbon Monoxide
FAO	Food and Agricultural Organization
GAW	Global Atmospheric Watch
IPCC	Intergovernmental Panel on Climate Change
KMD	Kenya Meteorological Department
KNBS	Kenya National Bureau of Statistics
LPG	Liquefied Petroleum Gas
MAPL	Mobile Air Pollution Laboratory
NMHC	Non-Methane Hydro Carbons
NCAR	National Centre for Atmospheric Research
NOx	Nitrogen Oxides
NTSA	National Transport Safety Authority
NMVOC	Non-Methane Volatile Organic Compounds
PSV	Passenger Service Vehicle
SHADOZ	Southern Hemisphere Additional Ozonesondes
UNECE	United Nations Economic Commission for Europe
UVB	Ultra Violet radiation B
WHO	World Health Organization
WMO	World Meteorological Organization

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Tropospheric ozone is a critical global air pollutant and an important greenhouse gas (IPCC, 2012) known to cause harmful effects on the ecosystem and human health (Ainsworth and Yendrek, 2012). It is found most abundant in atmospheric smog (Mauzerall and Wang, 2001) and exists as a special form of oxygen allotrope, constituting of three oxygen atoms (O_3). Ozone is a strong oxidizing agent weighing about 1.5 times heavier than air with a vapor density of 24 units and has its solubility in water greater than that of oxygen, at about 49% by volume at 0 °C (Naik, *et al.*, 2016).

While ozone is a harmful pollutant in the troposphere and near ground level (Ainsworth, *et al.*, 2012: Xiaodu, 2005) where plants, animals and humans are exposed, it is important in the stratosphere (ozonosphere) where it shields the Earth from intense UV radiation (UNECE, 1999) by absorption and thus accounting for a direct change in the atmospheric energy i.e. Radiative Forcing (RF) of 3.5 – 3.7 Wm^2 (Ainsworth, *et al.*, 2012: Forster and Bodeker, 2007). From pre-industrial times, tropospheric ozone concentrations have been observed to be on a continual increase, with a projected increase rate of 2% per year. Elevated ozone levels, particularly in urban areas, are detrimental and have been known to cause an estimated 5-16% global temperature change (Forster, *et al.*, 2007), substantial decrease in plant health and productivity (Feng and Kobayashi, 2008) as well as resulting in an estimated 0.7 million human deaths every year (Anenberg, *et al.*, 2010: WHO, 2010), in addition to about 7 million premature deaths every year (WHO 2010).

1.1.1 Mechanisms of Ozone formation in the troposphere

The troposphere contains a mixture of gases where ozone constitutes 0.6 ppm of the air. As an atmospheric pollutant, tropospheric ozone is produced from a complex series of photochemical reactions involving sunlight on air containing nitrogen oxides NO_x, ($NO + NO_2$), hydrocarbons (HC), and carbon monoxides (CO) and according to Mauzerall and Wang, (2001) it is also deposited from the ozone in the stratospheric region. The major sources of ozone production are light photon reactions on nitrogen oxides ($NO_x = NO + NO_2$), the NO oxidation in photochemical smog then leads to the formation of NO_2 (light brown), which then absorbs light and dissociates to form ozone. Photochemical reactions leading to zone formation are proportional to the amount of solar radiation and so during hot periods of sunlight, more ozone is formed as a result of high ultraviolet reactions on atmospheric pollutants (Gray and Finster, 1999). A set of expressions in equation 1 shows the chemical reactions leading to formation of tropospheric ozone.

$$OH + CO \rightarrow HOCO + O_2 \rightarrow HO_2 + CO_2$$

$$HO_2^{\bullet} + NO \rightarrow {}^{\bullet}OH + NO_2$$

.....(1)

$$NO_2 + h\nu\ (\lambda < 430\ nm) \rightarrow NO + O\ (^3P)$$

The free oxygen atom ($O\ (^3P)$ then combines with molecular oxygen and results in the formation of ozone as shown in equation 2.

$$O(^3P) + O_2 \rightarrow O_3\ (Ozone)$$ .....(2)

1.1.2 Important precursors of ozone

I. Nitrogen oxides (NOx)

NO_x ($NO + NO_2$) is produced primarily from transport (motor vehicles, motorbikes, planes and trains), fossil fuel combustion, energy use in power plants and industrial facilities (petroleum refineries, fertilizer, glass, and cement manufacturing), and also from other contributing sources such as biomass burning, lightning and soils (Diao, *et al*., 2013).

II. Non-Methane Hydrocarbons

Non-Methane Hydrocarbons (NMHCs) are major subset Organic pollutants made up of Volatile Organic Compounds (VOCs). They are basically hydrocarbons without methane. NMHCs are the second most abundant source of ozone in the atmosphere, produced from a range of human activities including fossil fuel burning, fuel desertion, Liquefied Petroleum Gas (LPG) leakage, organic solvents and wide scale manufacture of chemicals (Mauzerall and Wang, 2001). The major components of Non Methane Hydrocarbons (NMHC) include ethane, propane, propene, benzene, ethyne, and toluene. NMHC make up most of fossil fuels thus indicating pollutions mainly related to vehicular/transportation emission (Poisson and Kanakidou, 2000).

III. Methane

Methane (CH_4) is the second most prevalent greenhouse gas and also an important contributor to ozone production. Methane emission can be linked to natural gas and petroleum systems usually industrial as the major component of natural gas. Methane emission into the atmosphere occurs during the production, processing, storage, and transportation of petroleum and natural gas (Miller, *et al.*, 2013).

IV. **Carbon Monoxide**

Carbon monoxide (CO) is a toxic colorless gas. It is mostly produced from incomplete combustion of carbon containing fuels, natural gas, coal, oil and firewood. With anthropogenic sources being the major sources, CO in urban air pollution is dominantly/primarily from vehicular emissions. Crowded and busy urban areas such as Nairobi have high concentrations of CO. Cities characterized by huge crowds and high vehicular traffic at certain times of the day like rush hours have limited free air circulation and tend to have low pollutant dispersion. This leads to accumulated concentrations of CO and consequently the formation of surface ozone. Tremendous ozone concentrations are usually experienced in the dry seasons characterized by high temperature and pressure conditions where, warm air is trapped over cold air and thus pollutants often get trapped resulting in high ozone concentrations (Muhammad, 2011). A larger influx of stratospheric ozone into the troposphere has also been discussed by Dentener, *et al.,* 2006, to lead to a general increase of free tropospheric ozone.

The contributing anthropogenic activities (NO_x and VOC's emissions) have led to the tremendous additions of ozone in large amounts. Studies have suggested that these activities have increased the ozone amount by 40 to 60%, and that the actual change could be even larger (Mickley, *et al*., 2001). It is chemically favored in certain meteorological conditions such as strong sunlight and high temperatures (Munir *et al*., 2014). The hydroxyl (OH), which is a byproduct, is a key controller of the atmospheric lifetime of many gases. It was noted in the 1960s, that in situ photochemical ozone formation in the troposphere was from the breakdown of hydrocarbons causing ozone episodes in urban environments during hot seasons (Smit and Fox, 1956; Imboden, *et al.,* 1961).

In some countries in Africa such as South Africa and Egypt, few experimental and simulation studies have been conducted to help assess the current situation in terms of air pollution, and crop exposure by ozone. The projected increases were seen to be within limits and are still not potentially severe, an increase of up to +7 ppb annual mean surface ozone was experienced between the years 2000 and 2003 (Zunckel, 2006). It was found that the average modeled hourly concentrations over South Africa ranged between 20 and 50 ppb in all months between October 2000 and April 2001 during the cross-border air pollution impact assessment project (Dentener, 2006).

1.1.3 Stratospheric ozone

The stratosphere contains the highest ozone composition with up to 90% (Boynard, *et al.,* 2009). Over Nairobi, a study by Shilenje, *et al.,* (2015) found that the concentration of ozone in the stratosphere is close to 87%. The region with the highest concentration in the stratosphere is known as the ozone layer and the ozone here is regarded as good since it protects the earth's atmosphere by absorbing about 98% of the suns UV radiation i.e. 200 to 315 nm, third only to carbon dioxide (CO_2) and methane (CH_4), (Cooper, *et al*., 2014). Stratospheric ozone is however known to contribute to about 10% of tropospheric ozone by intrusion (Pitts, *et al*., 1999), the possible mechanisms for the downward transport within the boundary layer have been known to include; normal convective mixing, organized convection associated with cloud and precipitation processes, and organized downward motion within frontal zones (Johnson and Viezee, 1981).

Stratospheric ozone is produced by a series of photolysis reactions by short wave Ultra Violet radiations (240 nm), and then transported pole-ward in the brew Dobson Circulation to form the ozone layer (Lelieveld and Dentener, 2000).

1.2 Statement of the Problem

Nairobi City has a very rapid industrial and socio - economic growth which has led to it developing into a very important part of Kenya's economy and a regional hub for many local and international organizations. The city's population according to KNBS (2009) stands at about 4 million persons. Certain straining factors such as an ineffective public transport policy and traffic congestion has placed the City's environment under increasing pressure due to air pollutants (Ng'ang'a, 1992, Kinney, *et al.,* 2011). Most if not all modes of public and personal transportation around the city uses fossils fuels that have been found to result in tremendous amounts of emissions and laddening the ambient air with attendant pollutants of major species of air pollutants. Some of these species are major contributors of surface ozone that continue to increase over time resulting to adverse effects. Typical values for the vehicle share in total air pollution range from about 40% to 90% for carbon monoxide, hydrocarbons and nitrogen oxides and are somewhat lower for fine particulate matter (Yang, *et al*., 2004). Health complications due to poor quality of air have become quite common in Kenya especially in the urban areas (Omanga, *et al.,* 2014; Egondi, *et al*., 2013). Understanding the dynamics linked to air quality such as atmospheric pollutants and more specifically the sources, key location and the contributors that lead to the increase in surface ozone for systematic monitoring and analysis becomes relevant/paramount and is of interest to this study.

1.3 Objectives of the Study

1.3.1 General objective

The main objective of this study was to examine and analyze the past and current concentrations of surface ozone, as well as its major precursors over Nairobi City with an emphasis on urban air pollution that will help to provide recommendations for future policy formulations on urban ozone pollution and the need to inform of the detrimental effects of the pollutant.

1.3.2 Specific Objectives

The specific objectives of the study were to;

1. Determine the current levels of surface ozone over Nairobi city from continuous point measurements.
2. Evaluate the past trends and implications of vertical profile ozone over Nairobi city.
3. Measure the several precursors of ozone over Nairobi city from various selected mobile locations.
4. Analyze and determine the levels and the contributions of the detected precursors of surface ozone in Nairobi city.

1.4 Significance of the Study

Nairobi city has seen a very rapid growth for the last 5 years. This has led to the emergence of several concerns such as population increase which now stands at about 4 million people (KNBS 2009), lack of a well-planned and effective public transport system, fast increase in the number of vehicles and subsequently vehicular accumulation and traffic congestion on the City roads, and several industries coming

up and located not so far from the city. According to the official data from the National Transport Safety Authority (NTSA), the number of vehicles including motorcycles and trailers in Kenya by 2014 was 2.2 million. This inevitably leads to serious environmental difficulties and concerns should be raised that only a small percentage of these events have been recognized and are being acted upon. Nairobi is located in a tropical region and is known to have fluctuation in the relative humidity in every season. This in turn is bound to affect the ozone formation and being a big and heavily populated city, the high density is likely to result in large scale ozone exposure. The projected increases and ozone concentrations for the East African region indicated by National Center for Atmospheric Research (NCAR) chemical forecast global output for 6-hour frequency are estimated at 10 ppb to 50 ppb annual mean surface concentration, and changes projected between the years 2000 and 2030 suggest that the conditions may well significantly worsen in the near future.

It has to be clarified that the present serious and a possibility of escalating situation has been recognized then the current steps towards the pollution control needs to be fast tracked and actualized. It is therefore important to know the major contributors and the sources of tropospheric ozone. Further, clean air is a basic right and the Kenya Environmental Management and Coordination (Air Quality) Regulations 2014 states that: “ambient air quality is the air quality standard specified under these regulations which, in the judgment of the authority, are requisite to protect human health and allow an adequate margin of safety”.

Figure 1 below shows an environmental Kuznets curve showing the increase of carbon IV oxide (CO2) emissions in in Kenya with time. Over ten years ago, there were lower CO2 emission as compared to the levels being experienced now.

Figure 1: Greenhouse Gas Emissions trend in Kenya.
Source: FAOSTAT 2015.

Figure 2 below displays a recent study by Muhammad (2011), indicating the potential areas likely to be affected by ozone damage due to climate change shaded by red while the other areas in white are less likely to be affected or where little knowledge exist about.

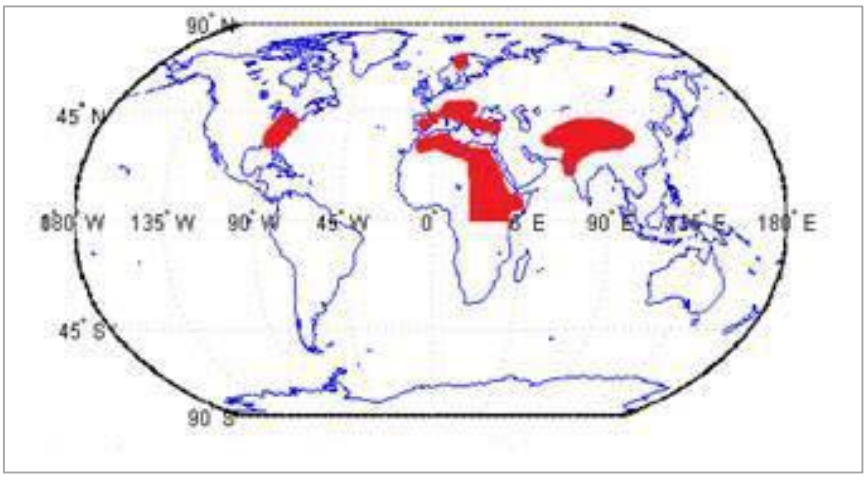


Figure 2: Projected ozone damage areas promoted by climate change around the world.

Source: (Muhammad, 2011)

1.5 Limitations of the Study

This study generally focuses on ozone measurements and concentration trends approach and the impacts on a small geographical scale focused in Nairobi city, Kenya (1.2667° S, 36.8000° E).

There are not so many Ozone measuring and monitoring stations across Nairobi city and Kenya as a whole and that the ones available are mainly focused around Nairobi city and Mount Kenya. It was thus not possible to get a good diverse data from several functioning ozone measuring stations and thus a grid resolution, spatially and temporally to conduct a modeling approach of surface ozone by using the Dagoretti corner surface ozone data.

The study used measured surface ozone data from few local sites around Nairobi city18 sites taken for a short time, and more specifically towards the end of the year.

The logistical arrangements to deploy the Mobile Air Pollution Laboratory to many sites and longer times around Nairobi city were very costly and sophisticated: This was because of the generator fuel, security, more personnel and other challenges like parking permit from the county government.

1.6 Scope of the Study

The study focused on the analysis of surface ozone contributors and its sources around Nairobi region and was conducted between September 2015 and April 2016. It looked at the surface ozone contributions by natural and man-made trace gas emissions, its distribution through photochemistry on the surface and on the vertical profile, as well as determine the importance of Stratospheric Tropospheric Exchange. Ozone alongside

other suspended particulates was sampled at 18 sites around Nairobi city including, along major urban roads (Ngong road, Landhies road, Outer Ring road roundabout, Mbagathi road, City Mortuary roundabout, Enterprise road, Imara Daima estate - residential area, and Valley road. Surface ozone was sampled both during periods of high traffic (weekdays) and low traffic (weekends) as well as day and night in a few sites to get insights on concentrations and chemical compositions which may be related to the emission source. The continuous ozone data was measured and collected from KMD, Nairobi regional GAW Division.

CHAPTER TWO

LITERATURE REVIEW

2.1 Surface Ozone

Since the discovery of ozone by Schonbein in 1839, its measurement began afterwards in various parts of the world such as the USA, Europe and Asia to determine its concentrations (Finlayson-Pitts, 1999). Air pollution has increased quite rapidly and considerably since the pre-industrial times, and the levels of atmospheric pollutants, greenhouse gases, aerosols and several pollutants among them ozone (regarded as the second most important air pollutant), has had steady increasing trends in cities of several developed countries around the globe (Ainsworth, *et al.,* 2012).

Ozone measurements during the late 19th century in Europe, South America and North America showed concentrations of around 10 ppb (Volz and Kley, 1988). However today, measurements are typically 30 ppb to above 40 ppb in concentrations, basically in most parts in the industrialized and heavily populated areas of the world. Presently, surface ozone concentrations have been found to be much higher than they were in the 1970's, 1980's, and 1990's. In the early 90's in Europe, ozone levels were estimated to be 10 ppb, and the figures reached 15 – 20 ppb in the mid 90's then eventually 30 ppb in the late 90's (Reid, *et al.,* 1998). The USA has also had considerable increase in the levels of Ozone, mostly in the Northern and the Eastern USA with the levels ranging from 50 -80 ppb and episodically higher at about 100 ppb, and also much higher recordings of up to 200 ppb in urban and rural areas during heat wave episodes (Cooper, *et al*., 2014).

In Africa, mostly the Southern Africa, there have been surface ozone measurements by the Global Atmosphere Watch (GAW) site since 1983 and the surrounding

concentration levels having an annual average of 22 ppb (15 ppb in summer and 30 ppb in winter). Kenya as a signatory to the International Conventions and Treaties on Climate Change and Environmental Protection has also had active participation in ozone measurements and through the World Meteorological Organization (WMO) and KMD, there has been ozone measuring activities in four stations around the country namely:

- Mount Kenya Global Atmosphere Watch (GAW) station
- Jomo Kenyatta International Airport (JKIA) Urban Air Pollution Monitoring Station.
- Nairobi Regional GAW station
- Chiromo Urban Air Pollution Monitoring Station.

Analysis of ozone profiles in Nairobi can be split into 3 layers which have shown strong annual disparities in the free troposphere and the Tropopause, whereas stratosphere ozone seemed to be relatively constant throughout the year. Using Dobson instrument, total ozone measurements have confirmed maximum total ozone content in the short rains season and a minimum in the warm dry season (Shilenje, 2013).

The global GAW station in Mt. Kenya has shown diurnal and seasonal ozone variations with the average diurnal amplitude of 15 ppb. This pattern has been seen to recur in all months annually from 2003 to 2006, and increased amplitude ranging between 25–30 ppb in July and September as observed from figure 3 below.

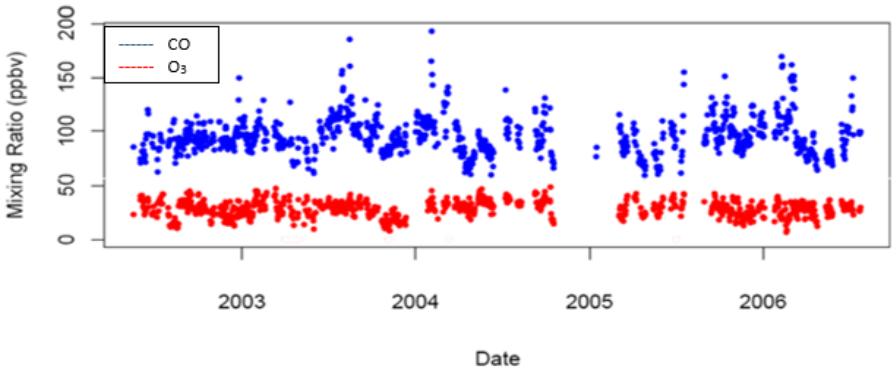


Figure 3: Surface ozone and CO time series from Mount Kenya GAW.
Source: Shilenje, 2013.

The Kenya national climate change response strategy has linked some evidence of climate change in Kenya. These incidences include; temperature rise throughout the country with the minimum temperature increasing by 0.7 – 2.0 °C, and the maximum temperatures increasing by 0.2 – 1.3 °C, depending on the season and the region. Irregular rainfall patterns and unpredicted rainfall, extreme and harsh weather is also becoming a common occurrence in several regions across the country (Wakachala, *et al*., 2015).

Tropospheric ozone concentration measurement and monitoring in developing countries is still at its infancy, yet these countries are becoming significant contributors of greenhouse gases due to their rapid industrialization. Further, such countries still lack good measurement frameworks and proper air quality regulations and guidelines essential for the control and regulations of the rising levels of emission of atmospheric pollutants. Additionally, little data is available on the ambient and destructive levels of ozone pollution in fast developing cities and rural areas which are massively the agro – economic regions (Mauzerall and Wang, 2001).

2.2 Ozone Deposition

The most usual terrestrial sink for greenhouse gases is the natural ecosystem like trees, vegetation and crops. Transportation of ozone can occur vertically based on a number of factors such as; surface urban emissions being transported into the mixed layer; free troposphere, mountain slopes venting up through surface solar heating (chimney effect) and clouds (Muhammad, 2011). Ozone deposition occurs in many ways and one important deposition is on terrestrial ecosystems. This occurs when ozone is brought to plants canopy, and is greatly controlled by stomatal uptake, wind turbulence, landscape type and density of the vegetation. It has been cited by Cieslik (2004), to account for between 30% - 90% of the total ozone ecosystem uptake raising the concern for the relationship between high ozone pollution and damage to agricultural crops (Reich and Amundson, 1985).

Plants are seen to be the worst affected by high ozone pollution where unlike other organisms; their proximity, constant exposure to the natural environment and harsh meteorological conditions make them the more vulnerable and thus succumb to the effects of ozone exposure (Wahid, 2006). Most research has focused on above threshold ozone damages estimation to plants and incorporating this metric into regulatory standard. The increasing impacts of ozone are likely to be experienced due to the development and rapid industrialization, which are associated with high emissions of ozone precursor levels. Other studies have focused on surface ozone concentrations in developing countries and its projected increase and its effects on the crop used as staples and cash crops by chamber exposure experiments e.g. in South Africa (Sitch, *et al*., 2007).

2.3 Effects of Tropospheric Ozone

Tropospheric ozone has been found to be one of the most damaging air pollutants known, and whose concentrations continues to rise globally to beyond tolerable levels, this has been seen to impact negatively on living organisms and on the environment. Unlike other greenhouse gases, ozone has a known phytotoxicity and oxidizing nature, and whose effects could worsen with continued increase in the concentration of the surface level and also broadening to various geographical areas (Ashmore, 2005).

2.3.1 Effects on the natural ecosystem

A number of effects have been experienced and remain evident about the effects of surface ozone on the environment. Several studies have been conducted and developments made in ozone exposure effects to the ecosystem. Fuhrer et al. (1997) for example have shown some effects based indices and approaches that have shown critical levels of damage. Some of the effects on the natural ecosystem are;

- Trees and whole forests or ecosystems being affected and thus adversely impacting on ecological functions such as water movement, mineral nutrient cycling, carbon sequestration and habitats for various animal and plant species.
- Weakening sensitive vegetation by ozone makes plants more susceptible to disease, pests, and environmental stresses (Mauzerall and Wang, 2001).
- Fish deaths and algae blooms in water from ozone sink are other cases occurring in sensitive waterways.
- Other issues include the damage of leaves resulting to their falling off sooner or become spotted and brown thus significantly decreasing the natural beauty of areas like national parks and recreational facilities.

- Contribution from global warming that causes prolonged drought and rain which impacts negatively on the natural system and a shift in the climate.

2.3.2 Effects of ozone on human health

Human health remains to be one of the most affected by air pollution. It has been reported by Ostro & WHO (2010) that, in the last five years alone, outdoor air pollution has risen by 8%, with fast-growing cities in the developing world seen to be worst affected. According to new data compiled by the World Health Organization WHO (2016), in the past five years alone, billions of people around the world are now known to be exposed to dangerous air, and this is from more than 3,000 cities globally. While all regions are affected, fast-growing cities in the Middle East, south-east Asia and the western Pacific are the most impacted with many showing pollution levels at above 6 times above WHO recommended levels (WHO 2016).

According to the new WHO database, levels of ultra-fine particles of less than 2.5 microns (PM2.5s) are highest in India, which has 16 of the world's 30 most polluted cities.

Some of the health effects of surface ozone include;

- Ozone inhalation causes the inflammation and irritation of the tissues lining airways. This worsens variety of symptoms associated with breathing complications as well as making it difficult for deep and vigorous breathing (Adgate, *et al.,* 2014).
- Ozone exposure leads to the aggravation of lung diseases such as asthma, emphysema, and chronic bronchitis. It also causes chronic obstructive pulmonary disease (COPD). (Sousa, e*t al*., 2013).

- Exposure to ozone can reduce the volume of air that the lungs breathe in and cause shortness of breath and as a result suffocation due to insufficient supply of oxygen.
- High doses of ozone increase the permeability of the lung cells and thus rendering them more vulnerable to toxins and microorganisms leading to infections.
- Exposure to ozone leads to continued damage of the lungs even when the symptoms have disappeared.

The occurrence and severity of health effects from ozone exposure vary widely among individuals, even when the dose and the duration of exposure are the same.

2.4 Geostatistical data analysis

Mapped concentration data outputs can be obtained from Geostatistical Analyst extension of the ArcGIS software, which can be customized to give regional maps. Simulating ozone concentrations and exposure usually requires a comprehensive emission inventory, meteorological data and an applicable atmospheric transfer model. Using measured ozone values at the various locations, and where surface ozone values are not known, interpolation can be done using Raster tools to create a model to generate a surface of ozone concentration.

Figure 4 below shows the conceptual framework of how the different emission sources combine with factors that facilitate the formation of surface ozone.

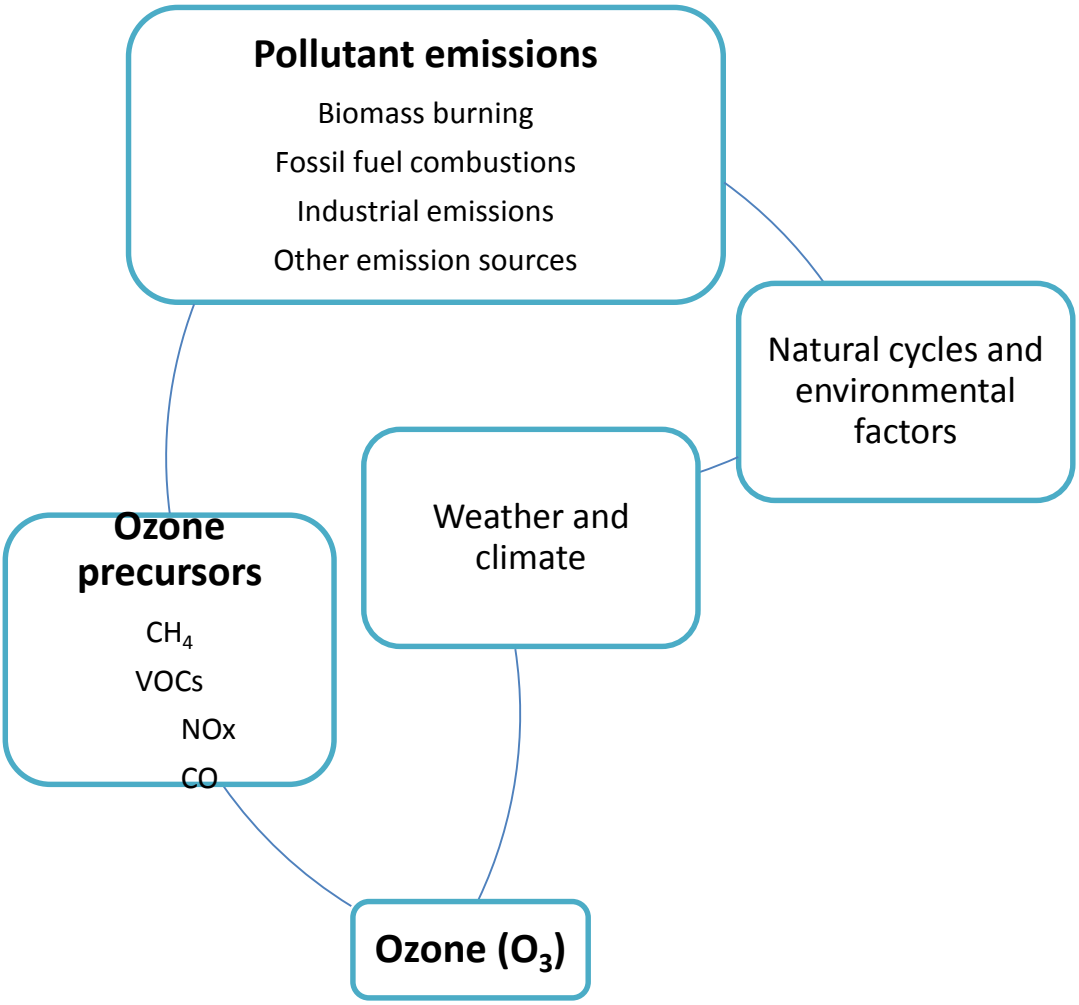


Figure 4: Conceptual frame work.

CHAPTER THREE

METHODOLOGY

3.1 Measurement Instruments

Through the World Meteorological Organization (WMO), KMD is recognized as active participant and contributes by measuring and collecting air pollution data. KMD has a few air pollution observation stations around the country (Mount Kenya GAW station and JKIA station). These measure and monitor atmospheric pollutants by an active involvement in the WMO, Global Ozone Observing System (GO_3OS) and GAW, for a total ozone monitoring Programme launched in 1984. The measurements from the Nairobi Regional GAW station was considered having that, there are few working monitoring stations for surface ozone in Nairobi and Kenya as a whole, and that it is located close to the equator Altitude (ALT): 1795 M Above Sea Level (ASL), Lat: 1.30 S, Lon: 36.75 E) agrees to the facts that it is a unique site for the detection of surface ozone in the tropical region around Eastern Africa. These instruments are under thorough routine maintenance, calibrations by the Swiss Meteorological (MeteoSwiss) and operated by specially trained officers. The air quality data are also subjected to quality assurance by the officers.

Ozone measurement were conducted using two main instruments i.e. the surface ozone analyzer and the Ozonesonde, which were all stationed at KMD, regional headquarters at Dagoretti corner in Nairobi. The continuous surface ozone measurements from the ozone analyzer are conducted 24 hours, seven days with a time resolution data of 5 minutes and have been running for the last 6 years. The study hourly average data for a period of four years (from 1st Jan 2013 to 31st Dec 2016) has been considered. It was retrieved and analyzed from 5 minutes to hourly average then to daily average, and

compiled to monthly average data. Month hourly average data was then plotted of the surface ozone over Nairobi by R statistical programming software.

3.1.1 Surface Ozone Analyzer Thermo Scientific model 49*i*

Figure 5: the Surface Ozone Analyzer Thermo Scientific model 49*i*.

This is a stationary instrument mounted at the Global Atmospheric Watch operations room. It is a time shared dual cell Ultra Violet (UV) photometric ambient ozone instrument capable of measuring ambient level ozone concentration on a continuous, real time basis. It has a dual-cell, UV photometric, and is capable of measuring the amount of ozone from 0.05 ppb concentrations up to 200 ppm. The instrument operates on the principle that; ozone molecules absorb Ultra Violet (UV) light at a wavelength of 254 nm and that the light absorbed is directly related to the ozone concentration as defined by the Beer-Lambert Law in equation 1;

$$I/I_o = e^{-KLC} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where:

-K= molecular absorption coefficient, 308^{cm-1} (at 0°C and 1 atmosphere)

L = length of cell, 38 cm

C = ozone concentration in parts per million (ppm)

I = UV light intensity of sample with ozone (sample gas)

I_o = UV light intensity of sample without ozone (reference gas)

The sample is drawn through the sample bulkhead then split into two gas streams. One gas stream flows through an ozone scrubber to become the reference gas (Io). The reference gas then flows to the reference solenoid valve. The sample gas (I) flows directly to the sample solenoid valve. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A contains reference gas, cell B contains sample gas and vice versa. UV light intensities of each cell are measured by detectors A and B. When the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for several seconds to allow the cells to be flushed. The Model 49*i* calculates the ozone concentration for each cell and outputs the average concentration to the front panel display, the analog outputs, and also makes the data available over the serial or Ethernet connection. Figure 6 below shows the flow schematic of the instrument, from the sample input to the display output.

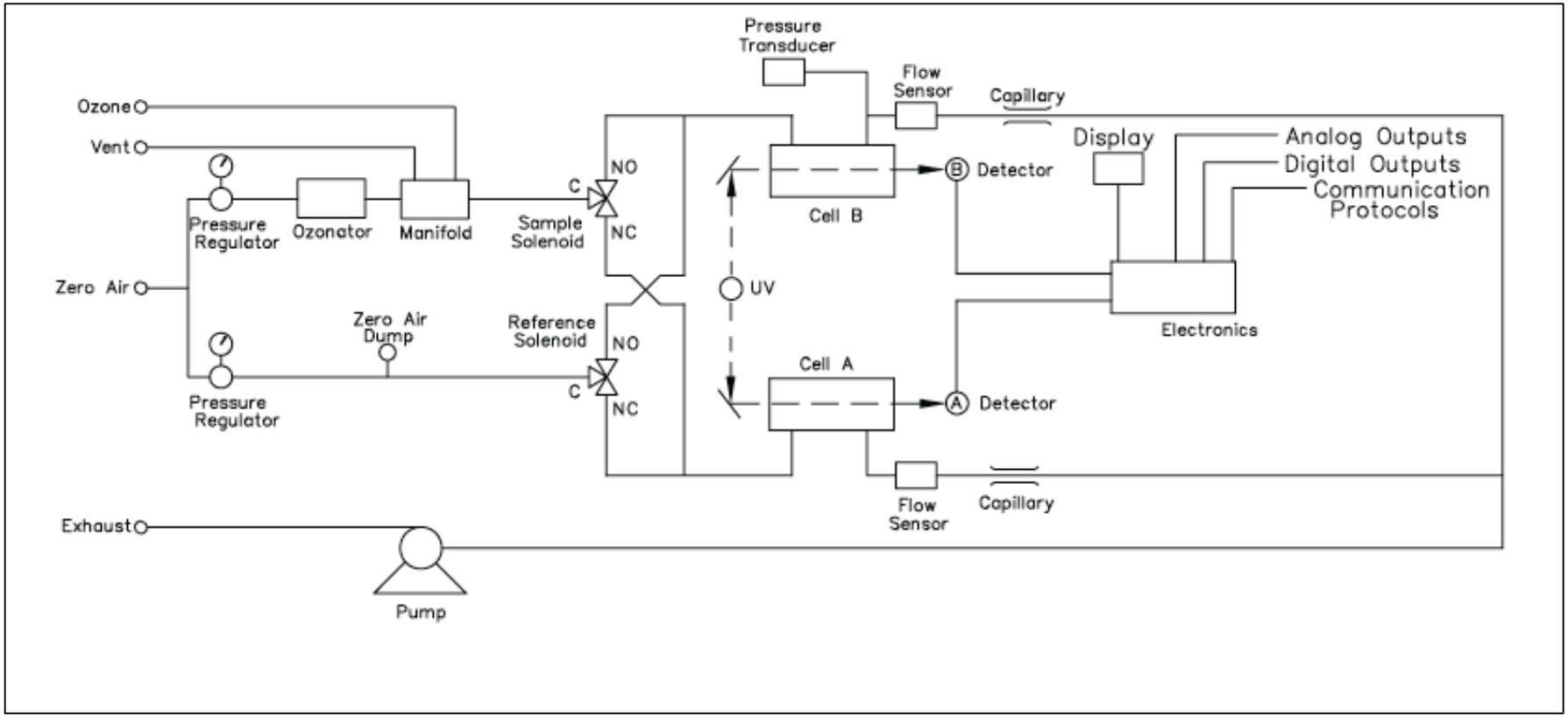


Figure 6: Surface Ozone Analyzer model 49i flow schematic.

3.1.2 Ozonesonde

The Electrochemical Concentration Cell (ECC) Ozonesonde is a lightweight, balloon-borne instrument usually interconnected to a meteorological Radiosonde during measurements. Usually, the balloon carrying the instrument package makes vertical ascends through the atmosphere and the Ozonesonde transmits the measured ozone and standard meteorological parameters such as pressure, temperature and humidity data to a ground receiving station. On a typical day, the balloon normally ascends to altitudes of about 110,000 feet (32 km) at pressure levels of about 7 hPa before it bursts. There are about 50 stations around the world that make regular (approximately weekly) ozone vertical profile measurements using Ozonesonde**.** The Ozonesonde consists of an ECC, which is an iodine/iodide redox electrode having; two half cells containing potassium iodide solutions of different concentrations (dilute in Cathode and concentrated in Anode) connected by an ion bridge, a small Teflon pump, and an electronic interface. The ion bridge allows the flow of electrical current between the two half cells while impeding mixing of the two different solutions. During the flight, sample air is pumped in containing trace amounts of ozone through the cathode of the ECC, ozone reacts with KI in an aqueous solution to form iodine as described in equation 2 below;

$$2KI+O_3+H_2O \rightarrow 2KOH+I_2+O_2 \quad \text{..... (2)}$$

The change in iodine concentration leads to a change in electrochemical equilibrium between the two half cells and causes 2 electrons to flow in the cells external circuit when the iodine is reconverted to iodide by the cell. A weak electrical current proportional to the ozone concentration is then generated as described in equation 3 below;

$$I_2+2e^- \rightarrow 2I^- \quad \text{..... (3)}$$

This flow of electrons through the cells external circuit can be measured and is directly proportional to the partial pressure of ozone in the sampled air (Johnson *et al.*, 2002):

$$PO_3 \rightarrow cT\ t100\ (I - Ibg) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

In equation 4 above;

PO_3 is in [mPa], I is in [μA] and is the measured cell current, and Ibg is taken as the background current that is generated by the cell in the absence of ozone.

$$C = R/\ X^F \rightarrow 4.309\times10^{-4} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (5)$$

In the equation 5 above; C Is the ratio of ideal gas constant R, and Faraday Constant F divided by the yield ratio of 2 electrons per ozone molecule.

T[K] is the temperature of the air getting into the cell, approximated by the temperature of the pump; t100 in [s] is the flow rate time to the pump 100 ml; and is the pressure dependent pump efficiency, which corrects the reduced pump efficiency at low pressure. For laboratory measurements under normal surface pressure equals 2, i.e. they do not require a flow rate correction as these measurements are performed with direct flow rate measurements, otherwise essential in the stratospheric measurements (Johnson, *et al*., 2002). Several important terms contribute to the total uncertainty of the ozone partial pressure derived from the Eq. (4). Equation (3) assumes a yield ratio of 2 electrons per ozone molecule. However, secondary reactions that are not described by the basic chemistry described in Eq. (2) and Eq. (3) could change this yield ratio slightly as stated by Davies, *et al.,* (2000). The ozone yield ratio has also been seen to be influenced by specifics of the ion bridge and the surface chemistry on the platinum electrodes (Komhyr, 2008). Not much has been investigated on the details leading to the quantification of a possible deviancy from that is =2. The pump temperature (T) is measured by a thermistor inserted in the Teflon pump to estimate the temperature of

the airflow entering the ECC cell and it is assumed to be the same as the pump temperature (Bonyard, *et al.,* 2009).

3.1.3 The Mobile Air Pollution Laboratory

Various gas analyzers measuring concentrations of various atmospheric pollutants and aerosols are positioned in a Mobile Air Monitoring Laboratory (MAML) and the van moves to the site of interest. The instrumentation includes an automated weather station that is mounted on top of on the van laboratory, with the wind measurement done at 10 m above the ground. Every site was measure twice for 24 hours (once during the weekdays and once in weekends). The analyzers generate and store data a one-minute time resolution. The vans interior is air conditioned, with the temperature kept close to 26℃. All the one-minute data measured and used in this study were visually inspected. Erroneous data were flagged as invalid. Figures 7 and 8 below shows the exterior and interior of the MAPL laboratory respectively.

Figure 7 : The exterior of the Mobile air pollution laboratory at a measurement site.

Figure 8: The interior of the mobile air pollution laboratory with the various monitoring instruments.

An overview of the instrumentation installed in the mobile van used for the measurement of various parameter is presented in table 1 below, showing the model and the corresponding parameter.

Table 1: Summary of the instrumentation types in the MAPL

Instrument Model	**Parameter (s) measured**
Ecotech Serinus 10	Surface ozone (O_3)
Ecotech Serinus 30	Carbon monoxide (CO)
Ecotech Serinus 44	Nitrogen oxides (NO_X) and Ammonia (NH_3)
Ecotech Serinus 51	Hydrogen sulphide (H_2S) and Sulphur dioxide (SO_2)
Ecotech EC 9820 Series	Carbon dioxide (CO_2)
Environmental Dust Monitor Model 180	Particulate Matter (PM_{10} and $PM_{2.5}$)
Aethalometer	Black Carbon (BC)
Automated Weather Station	Ambient and screen temperatures, Solar radiation, precipitation, Atmospheric pressure, Relative humidity, Wind speed and direction

3.2 Research Area

The research was conducted in Nairobi County, the capital city of Kenya, at an altitude of between 1,600 and 1,800 M ASL. With an estimated area of about 700 km^2, the region has predominant low-level easterly winds characterized by bimodal rainfalls mainly influenced by the migratory trend of the Inter-Tropical Convergence Zone (ITCZ). The short rains are usually observed in October, November, December (OND) and the 'long' rains in March, April, May (MAM). The cold wet season is normally June, July, August, (JJA), while late December, January, February (DJF) is considered warm; giving it a mean annual temperature of 17 $^{\circ}C$. The region represents an area of extensive air pollution activities, which is the focus of this study in terms of ozone pollution. The continuous air quality monitoring station is located at KMD. It is located away from the central business district in order to avoid the direct influence of rapid changes in the wind patterns and the city's concrete jungle. A major roadway (Ngong road) passing near the monitoring location enables the trapping of pollution from vehicular sources. Nairobi city also has a huge industrial complex at industrial area mostly on Enterprise road and part of Mombasa road which is located on the South-Eastern side of the city and KMD, and therefore, it is very important to study the sources and levels of surface ozone around the city owing to its high population density, high traffic and dynamic metrological conditions.

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter presents the research findings and analysis. A series of graphs and tables were plotted of the surface ozone measurements and the vertical profiles ozone levels followed by their descriptions. These findings were then interpreted and discussed thereafter.

4.1 Surface Ozone Measurements Results and Discussions

Day hourly mean, Month hourly mean and yearly annual mean graphs of surface ozone over Nairobi city are presented. The plots were made by R statistical programming software.

4.1.1 Annual surface ozone graph

There is a common trend of two distinctive peaks of the highest ozone concentration experienced in all the four years. The two distinctive peaks of the highest surface ozone concentration over Nairobi City were experienced particularly in the months of February and October.

Figure 9 below shows the annual means plotted for 2013 to 2016 showing the monthly mean distributions of surface ozone. All the months of March had common distinctive peaks for the four years considered (2013 to 2016), were predominantly high due to the dry season, common with high ozone concentrations. The second high peak in all the four yeas considered was experienced in the month of August. The general trend for annual hourly average surface ozone concentrations was observed to be high in the first three months of the year then get low during the mid-year in May and then starts to increase from June through July and attains maximum levels in August and September.

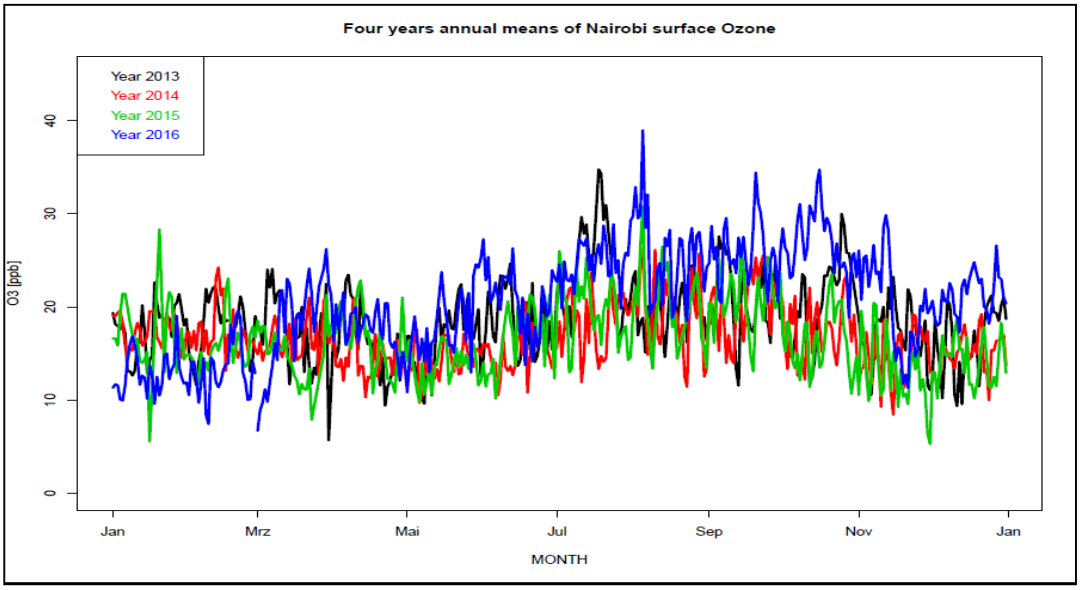


Figure 9: Four years annual means of Nairobi surface ozone distribution (2013 and 2016).

The possible explanation for the cycle and the Inter-annual variation trends of surface ozone as observed from Figure 9 above is that, low hourly average surface ozone observed in May, June, July are contributed much by the low temperatures usually experienced and accompanied by the rainy periods in Nairobi. Rainy seasons usually presents upper limits cloud covers that lessens the presence of Ultra Violet B (UVB), this will in turn reduce the temperature levels, and increase the humidity, which then leads to a low ozone transformation from photochemical reactions (Santurtun, *et al.*, 2015).

Moreover, rainfall cleans the atmosphere and thus removes away pollutants such as nitrogen oxides (NO_X), the precursor of ozone. Unlike the dry hot periods in December, January, February then August and September with broad summer maximum trends with conditions favoring ozone formation from atmospheric pollutants and also the possibility of contribution from southern African biomass burning from the larger grassland areas usually happening in August and September then transported towards Kenya. However, it has been stated by Liousse, *et al (*2014), biomass burning has little

direct influence on ozone measurements and that only introduces inter-annual variability in the background concentrations of the southern hemisphere that consequently gets to Kenya. The error bars on the plotted values on figure 10 below represent the standard deviation on the Nairobi's KMD station monthly means. They do not include the individual station's standard deviations on higher temporal scales, or the analytical uncertainty. Figure 10 below, shows the mean monthly surface ozone distribution in Nairobi city measured at KMD.

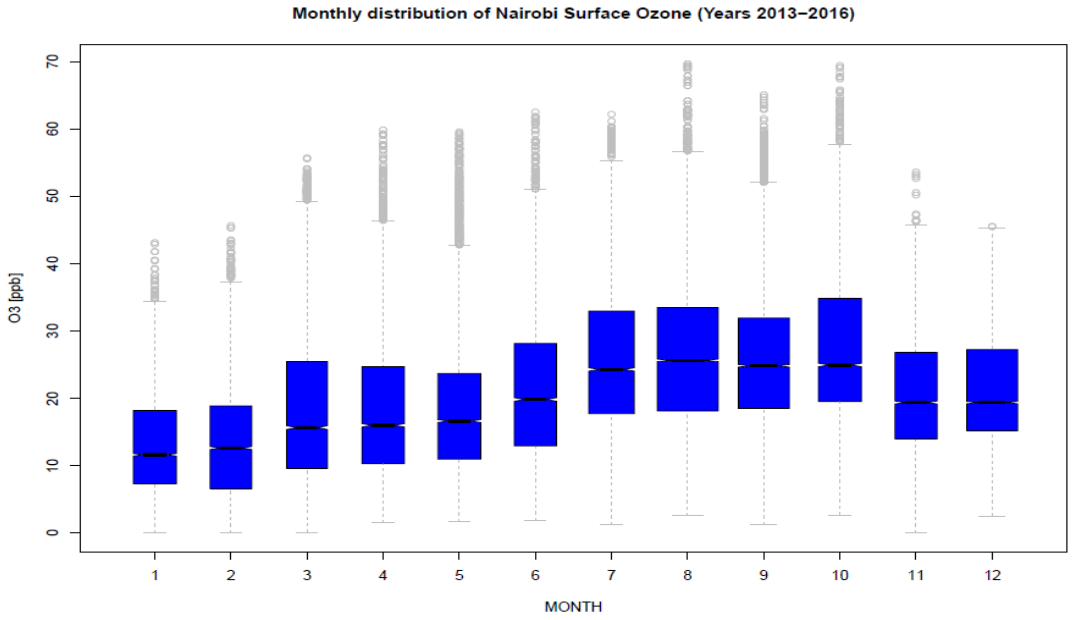
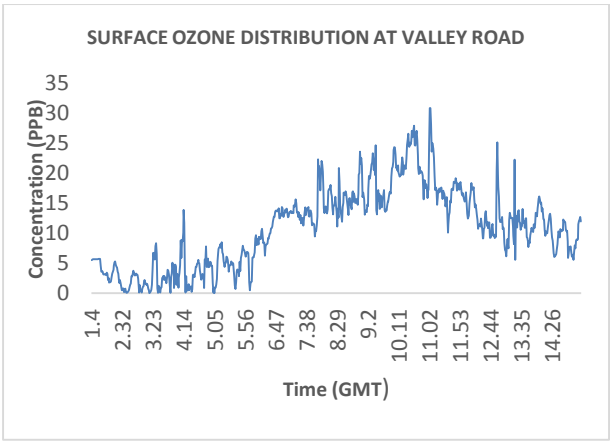


Figure 10: The monthly average distribution of surface ozone over Nairobi from 2013 to 2016.

For the day mean distribution, there was an observed common trend of concentrations starting to rise at morning hours, peaks at mid-day then drops back down in the late afternoons. Maximum diurnal ozone concentrations are usually recorded at mid-day times, this is because ozone formation is usually favored in the presence of high temperatures in the photochemical reactions (Roy, *et al.*, 2008). Figures 11 and 12 below shows the diurnal variations of surface ozone at Valley road and at Highrise.



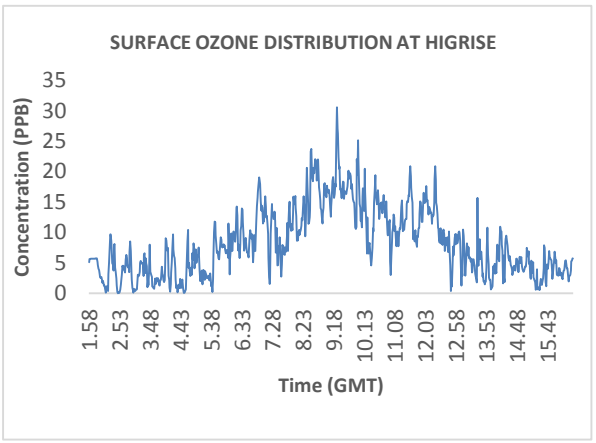


Figure 11 and Figure 12: The diurnal variations of surface ozone at Valley road and Highrise.

The concentrations were seen to start increasing at 7am, with values of between 5 – 12 ppb (±5 ppb), get to maximum at values between 25 – 42 ppb (±5 ppb) at around noon time, then starts dropping toward the evenings at 5 pm. The day mean surface ozone distribution recoded for Nairobi City for 2013 to 2016 is shown in figure 13 below. This general trend of low concentrations at early mornings, high concentrations in the mid-day, then again low concentrations late in the evenings and nights is common for all surface ozone measurements as also observed by Shilenje (2014). Surface ozone concentration trends and cycles have been observed to be directly proportional to the increase in temperatures, since it favors photochemical reactions, which is also true for many other parts of the world (Mohammed, 2011).

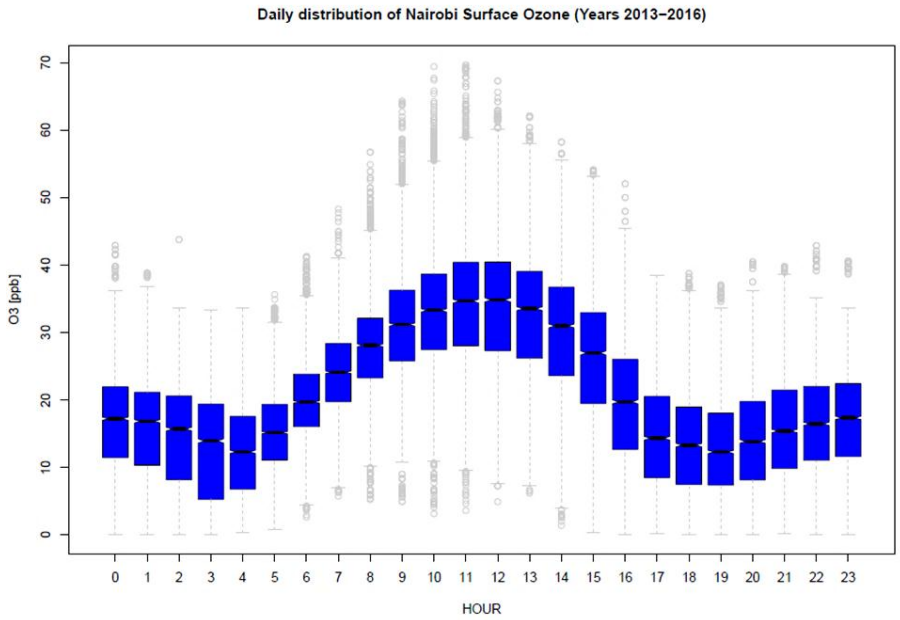


Figure 13: Daily distribution of Nairobi surface ozone for years 2013 to 2016.

The hot dry seasons in Kenya are characterized by high temperatures due to intense solar radiation. This is very crucial in providing stable and stagnant situations that favor higher concentrations of ozone. The Nairobi city seasonal cycle for surface ozone accounts for the monthly variability in the levels of ozone.

4.1.2 Mobile sites surface ozone measurements

A total of 14 sites were sampled that included industrial facilities along known busy roads and roundabouts. There were two round of measurements; the first round was conducted at high traffic times (days of high vehicular movements i.e. weekdays) and the second being the low traffic times (periods of low vehicular movements i.e. weekends). Figures 14 and 15 below shows the daily mean levels of surface ozone plotted for the road sites and the industrial sites.

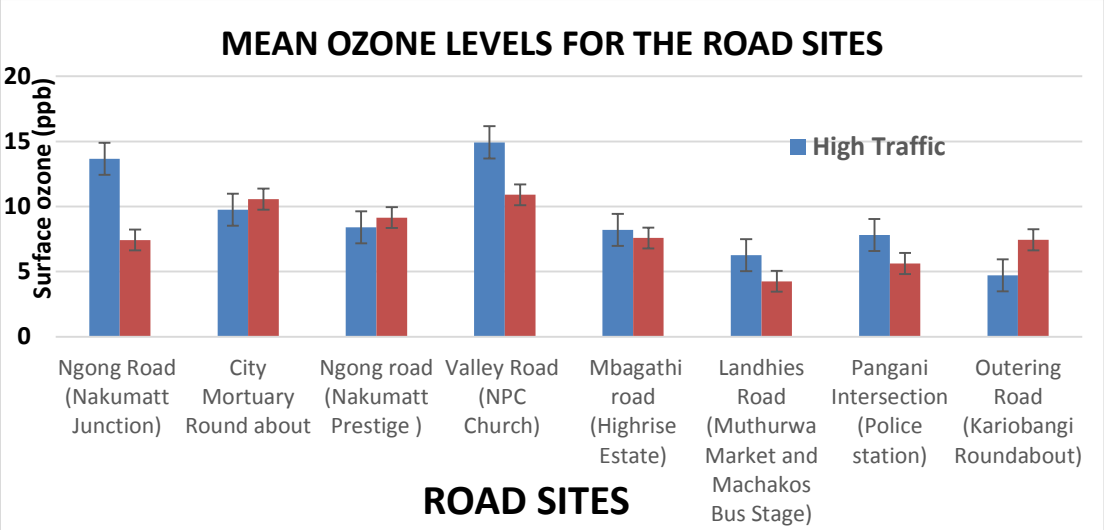


Figure 14: The mean surface ozone values for the various road sites measured.

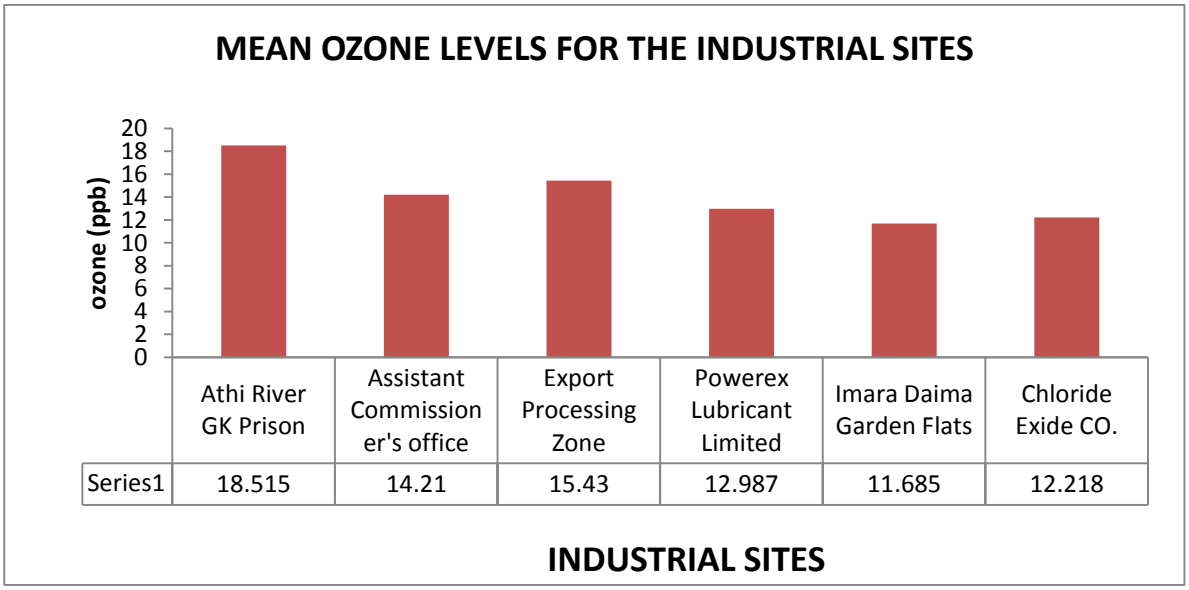


Figure 15: The mean surface ozone values for the various industrial measured.

Like the continuous surface ozone measurements by the stationary analyzer at the Laboratory, the mobile locations surface ozone levels exhibited the same trend. All of the mobile sites had low morning levels followed by a gradual increase, attained high noon peaks and again gradual decrease to low evening concentrations. The daytime increase and the attained peaks in surface ozone concentration in Nairobi City is typical of all urban air pollution scenarios. This is basically as a result of the precursor gases photo-oxidation (CO, CH_4, and NMHCs) in presence of sufficient NOx. As it can be

seen from the graphs and tables, no measured surface concentrations in Nairobi City were generally found to be above the Air quality limits stipulated for property boundary, domestic or industrial threshold levels as stated in the Environmental Management Co-ordination (Air Quality) Regulations 2014, as detailed on table 2 below.

Table 2 : Ambient air quality tolerance limits for surface ozone in Kenya.

Pollutant	**Time Weighted average**	**Industrial Areas**	**Residential, Rural and other areas**
Ozone (O_3)	1 Hour	200 µg/m^3	0.12 ppm (120 ppb)
	8 Hour (Instant Peak)	120 µg/m^3	1.25 ppm (1250ppb)
	8 hours mean	50 ppb **(W.H. O)**	50 ppb **(W.H. O)**

From the graphs for all the sites measured for surface ozone on Figures 13 and 14 above, the maximum attained value was 36.62 ppb (0.0366 ppm), measured at Kariobangi South Roundabout, located at Outer Ring Road, and followed closely by City Mortuary Roundabout with 36.28 ppb. /Compared with the WHO standards of 8 hour mean not exceeding 50 ppb, the maximum 8-hour mean value from the site with the maximum total average value as seen from Figure 12, was measured at Valley Road near NPC with a concentration of 20.60 ppb and is within the WHO standards, that agrees with the findings from Ongoma, *et al* (2016), which showed levels of ozone at 20.2 ppb at industrial area.

4.1.3 Surface ozone precursors

Similar surface ozone production system takes place for all the precursors (NOx, CH_4, CO and NMHCs), but their yields are much different individually. NOx is known to yield much higher as compared to other precursors. (Roy, *et al.*, 2008). Table 3 below show the respective tolerance limits for pollutants emission at serval environments that if exceeded are harmful to human health.

Table 3: The various surface ozone precursors in Nairobi with their respective tolerance limits.

Pollutant	**Time weighted average**	**Industrial areas**	**Residential, rural and other areas**	**Controlled areas**
Carbon monoxide (CO)	8 hours	5.0 ng/m^3	2.0 ng/m^3	1.0 ng/m^3
Methane (CH_4)	24 hours	5000 ppb		
Non-Methane Hydrocarbons (NMHC)	Instant peak	700 ppb		
Nitrogen Oxides (NOx)	Annual Av.	80 µg/m^3	60 µg/m^3	15 g/m^3

Note: (a) For residential premises in designated industrial areas, the above standards do not apply.

(b) For industrial premises in designated residential areas, standards for residential areas shall apply.

4.1.4 Levels and trends of the surface ozone precursors

Measurement of surface ozone precursors were dine for NOx, NMHC, CO and NH3 for the mobile sites and the plots provided. Figure 16 below shows the daily mean concentrations for NOx measure on the rides sites around Nairobi City.

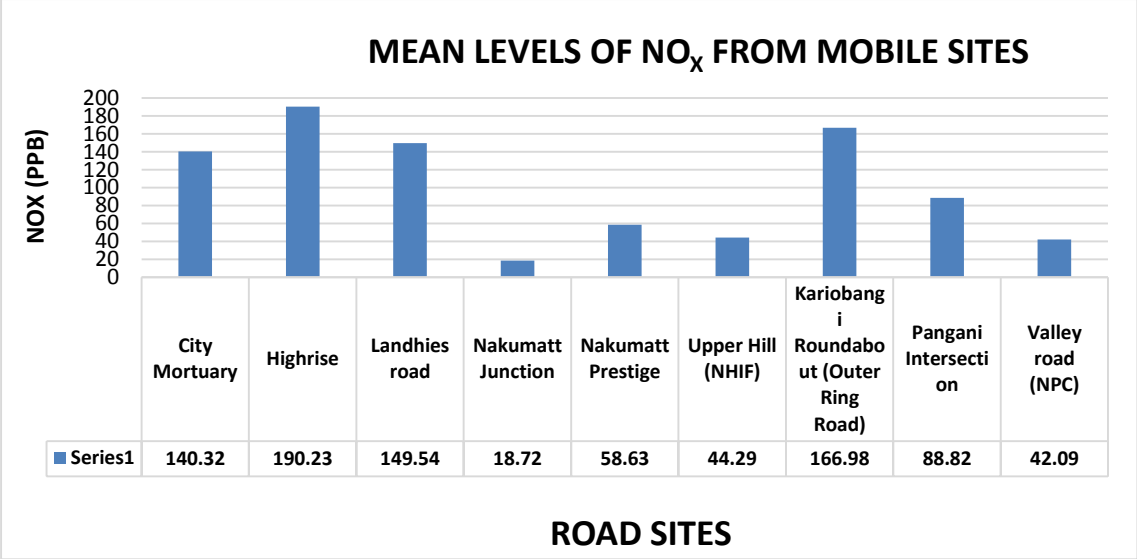


Figure 16: Mean levels of NOx measured from mobile sites.

From Figure 16 above, NOx values are seen to be highest at Highrise area and Kariobangi Roundabout. The roundabout is at a crucial point intersecting Outering road, (heading to Umoja and Donholm estates from Thika road), and Juja road (Heading to Dandora estate from Eastleigh estate. There is also a matatu stage nearby, and thus very busy especially at rush hours. Nakumatt Junction was seen to have relatively low NOx concentrations. It is noteworthy to mention that the lowest concentration was experienced mostly during the afternoons around 15:00 hrs., while the highest concentration ware noted in the mornings and in the evenings which are considered to have high vehicular activity in the city that are characterized with traffic jams in all major roads. The peaks of hourly average concentration of NOx were mostly observed at around the morning hours (around 09:00 am).

The relation between high traffic and low solar intensity common at morning and evening hours and which also negates the chances of photo-dissociation is observed on figure17 below for City mortuary roundabout, Highrise estate (along Mbagathi road), Landhies road and Outer ring road.

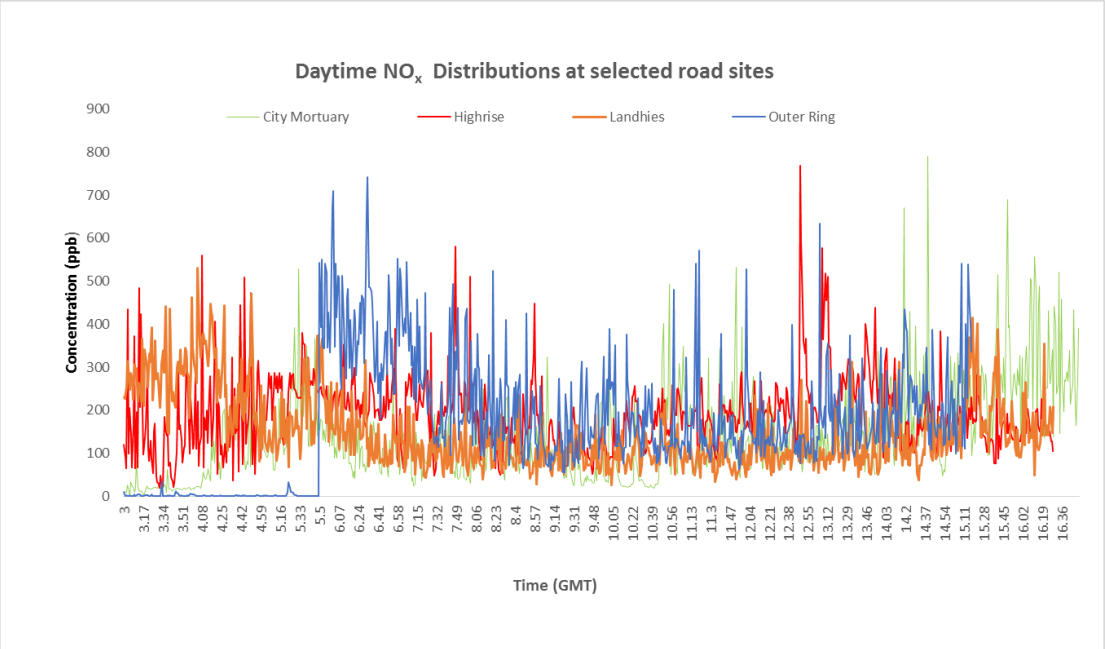


Figure 17: Mean NOx Distribution at City Mortuary roundabout, Highrise, Landhies road and at Outer ring Roundabout.

The highest level of NOx was recorded at Highrise (Mbagathi way) with a mean value of 190.23 ppb. The area is characterized by a steep slope and a dual road coming on from a busy road (Langata Road) and also feeding in to a busy road (Ngong road) at City Mortuary roundabout. There is thus the possibility high vehicle emissions from a lot of traffic congestions that could provide a very positive correlation to give high ozone concentrations measured in the area. From the data on figure 17 above, the peaks of hourly average concentration of NOx were observed mostly around the morning hours and late in the evenings. According to this analysis, a strong negative correlation of ozone with NOx exists as shown on Figure 18 below with an R^2 value of 0.106897329.

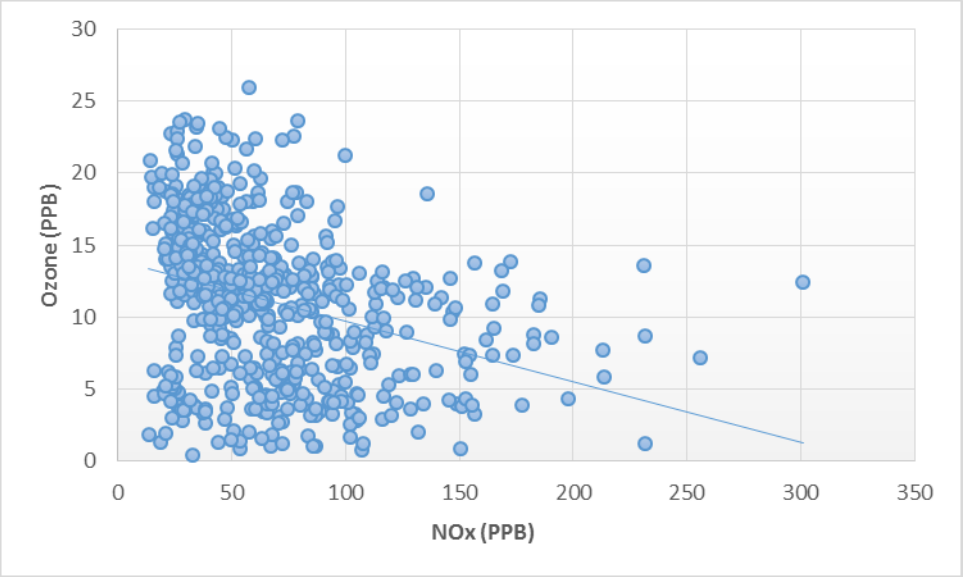


Figure 18: Correlation between daytime NOx and ozone concentrations at Nakumatt Prestige.

This indicates that concentration of precursor pollutants not only plays an important role in the formation of ozone but also in its destruction, and with regards to NOx, ozone formation is usually favored in high temperature where the light photon reacts on nitrogen oxides (NO_x = NO + NO_2). This conversion is a result of actions of oxidizing agents like hydroxyl radicals or ozone itself. The photo-dissociation of NO_2 thus is an important part of surface ozone formation.

The mean levels of the NMHC measured from the various mobile sites are shown in Figure 19 below.

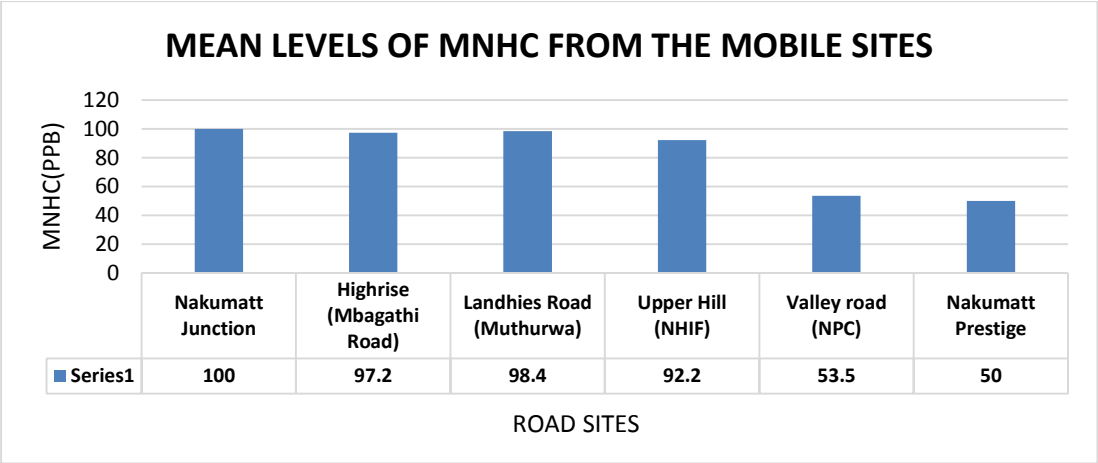


Figure 19 : Mean NMHC levels from the mobile sites.

According to this analysis, the NMHC concentrations were seen to be more prominent at Nakumatt Junction with amounts of up to 100 ppb. At that location, the NMHC peaks were seen to be more prominent at the morning hours, around mid-day and in the evening. At such times, the area is usually characterized by very heavy traffic coming on from Ngong road and to the roundabout where it gets very slow and as a result, a buildup of traffic from Matatus and personal vehicles heading towards Kawangware estate, Dagoretti estate, Wanyee estate, Karen estate and Ngong town. Nyayo Highrise had 97.2 ppb, and followed closely by Landhies road at Muthurwa bus terminus with levels of 98.4. Nakumatt Prestige however showed the least amounts of NMHC with levels of 50 ppb. The NMHC were seen to be high in most of the locations of measurements. The reaction of NO with ozone is usually suppressed by presence of HCs as the affinity of HCs towards NO appears to be higher than that of ozone leading to the formation of NO_2 as a product. At times, the hydrocarbons compete with ozone leading to destruction of ozone molecules.

$RH + OH \rightarrow R^{\bullet} + H_2O$……. (6)

$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$…… (7)

$RO_2^{\bullet} + NO \rightarrow RO^{\bullet} + NO_2$…… (8)

NMHC are important in ozone formation in that their hydroxyl radical oxidation and also to other species such as carbon monoxide and methane helps during the photochemical ozone production processes in the troposphere. All these are favored in durations of sunlight in the presence of nitrogen oxides (NOx).

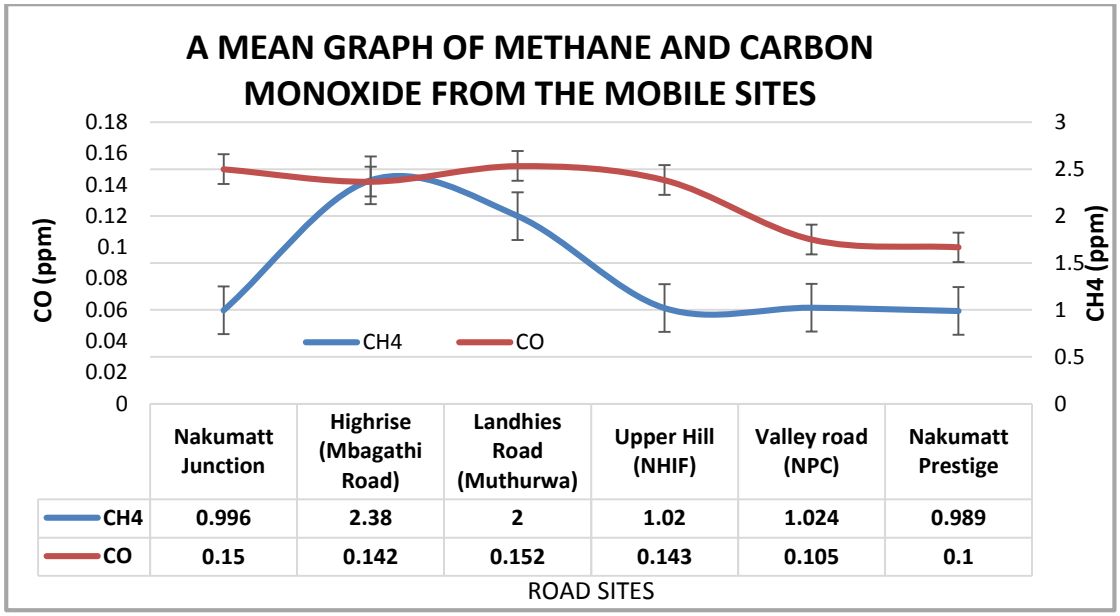


Figure 20: Mean methane and carbon monoxide levels as measured from the mobile sites.

According to Figure 20 above, CH_4 levels were seen to be high mainly at Nyayo Highrise and Muthurwa bus terminus. These two areas are common with vehicular activities throughout the day, Muthurwa bus terminus for example has a lot of Passenger Service Vehicle (PSV) buses from upcountry always parked with their engines running for very long durations. This is a great contributor to the high amounts of CH_4 measured from the site. The area around Nyayo Highrise also experiences bulk of traffic of vehicles with their engines running on a steep slope waiting for traffic to ease into Ngong road up ahead. CH_4 is a key ozone precursor and like other precursors, it contributes to the surface ozone photochemical production by hydroxyl radical oxidation in the presence of nitrogen oxides.

The carbon monoxide levels as seen from the analysis on Figure 20 above were found to be rather high in all the road site measurements. Nyayo Highrise was found to have the highest level of CO with concentrations of 0.152 ppb, this was closely followed by Landhies road at Muthurwa bus terminus. These areas were seen to have high levels of CO because of their locations as they are found in areas with a lot of vehicular flow and

traffic congestion. All of the peaks for the concentrations were seen to be mostly higher during the early morning and in the evening during the rush hours of traffic, suggesting the influence of high vehicular activity around the monitoring site.

Nairobi city is characterized by high traffic congestion typically at the rush hours in the morning and in the evening around most intersections and roundabouts. Usually, emission intensities of ozone precursors are quite higher over the densely populated areas. Ozone formation is usually non-linear with respect to its precursors and, there is no much direct correlation between the precursor emission intensities and ozone concentrations. Higher ozone concentrations are however observed where the emission intensities of the precursors tend to be high up to certain limits, since an ideal proportion of ozone precursors is favorable for the non-linear photochemical production of ozone (Sagar and Murthy, 2015; Monks, *et al.*, 2015). All these are much favorable owing to the conditions of the city that predisposes and enhances the photochemical production of ozone to a great extent as compared to the other parts of Nairobi.

The hours of maximum concentrations of ozone precursor gases and other anthropogenic emissions are also more pronounced in the mornings and evenings due to the combinations of the emissions and boundary layer processes, the atmospheric chemistry as well as local surface wind patterns. Atmospheric conditions during night hours results to the boundary layer descent and remains low till early morning, thereby resisting the mixing of the anthropogenic emissions with the upper layer (Venkama, *et al*., 2015). Hence, pollutants get trapped in the shallow surface layer and show higher levels. Most early Nairobi mornings are also usually characterized by a heavy haze as a result of the boundary layer descent and in these conditions, major ozone contributing precursors such as NMHC tend to be more (Shilenje, *et al.*, 2015). Although the precursor concentrations may seem low, NMHCs such as ethane, ethyne, ethene,

propane, propene, *i*-pentane, benzene and toluene remain abundant in the atmosphere during rush hours than any other times of the day and thus it can be said that these compounds are mainly related to vehicular emission and so vehicular pollution remain a great contributor to ozone precursors.

4.1.5 Vertical profile ozone measurements results and discussions

Vertical profile ozone measurements at the Nairobi station are usually done once-per-week on Wednesdays in the morning hours. The balloon in most cases attained an altitude of approximately 28 to 32.5 km, but can sometimes burst prematurely. Each launch carries a set of its own new instruments. Figure 21 below refers to a typical vertical profile ozone as measured by the Ozonesondes and transmitted by the received by the Radiosondes above Nairobi.

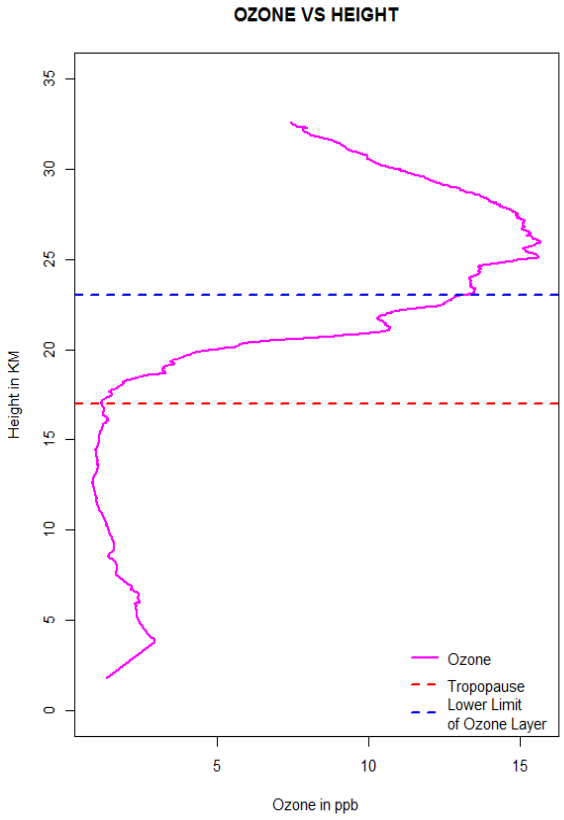


Figure 21: A typical vertical profile ozone over Nairobi.

Table 4 below sums the number of vertical profile ascents made at the Nairobi GAW station on every Wednesdays of the week or on Thursday in case of un-avoided complications (instrument malfunction or loss of telemetry communication). The soundings are made at around 0600 GMT (9 am local time). The data was recorded since 1996 but the years 2013, 2014 and 2015 was chosen and obtained for this study for comparison of the frequency of launch.

Table 4: Summary of vertical profile ozone flights for 2013 - 2015.

Month	**2013**	**2014**	**2015**
January	5	3	3
February	4	4	4
March	4	4	5
April	4	5	4
May	5	3	4
June	5	4	4
July	5	5	3
August	3	4	4
September	4	4	6
October	5	5	4
November	6	3	3
December	2	5	4
Total	**52**	**46**	**48**

One of the primary motivations for the vertical profile ozone measurements at the Nairobi GAW station analyzed here is to monitor the changes in the vertical distribution of ozone over Nairobi. The vertical profiles results are shown for pressure levels placed below 13 hPa as there are uncertainties about the quality of the ECC ozone sensors data above 28 km (Johnson, *et al*., 2002). The Annual profile mean trends are in agreement within 2%/ decade in the stratosphere (Okuku. *et al.*, 2013). Trends in ozone are highly

variable, and depend on region. The mean trend was seen to be generally average and slightly more on the negative by 1- 2%/decade, with a maximum trend in the lower stratosphere of +3 %/year, further distributions have shown good stability of the total ozone columns (Okuku, *et al.,* 2013). Ozone decrease was found to be between about 30 hPa and the tropopause, while the increases above Nairobi were noteworthy between the surface and 10 km (500 hPa) (Shilenje & Ongoma 2012). Tropospheric trends were not found to vary considerably with seasons. From the measurements, analyses here demonstrate a statistically significant increase in ozone in the higher mid-latitude regions between 250 and 30 hPa (10.5-27 km) from 2010 to 2015, with the largest increase being +4 %/year, is located between 200 and 80 hPa (11.5-18 km). The Nairobi tropopause was noted to have a moderate increase in the ozone concentration, and a strident increase in the lower stratosphere level, ozone concentrations were also observed to be at its most in the mid stratosphere region (Shilenje, *et al.,* 2015).

The maximum ozone concentration was recorded as 13.04 ppb, found at about 27 km with pressure levels of 20 hPa. The ozone layer (known to constitute the highest concentration of ozone), is usually found at about 23 – 30 km (within 40 to 10 pressure levels) above mean sea level. In most vertical profiles made, it was observed to be at about 25 km covering a depth of about 7 km, mid stratosphere over Nairobi region. These values of ozone concentration are in agreement with Shilenje, *et al.,* (2015) and Sauvage, *et al.,* (2005). Conventionally it had been presumed that tropospheric ozone is entirely influenced by stratosphere-troposphere exchange (STE) across the extra tropical tropopause based on the observed ozone gradient with altitude and thus suggesting a source at the tropopause and a sink at the surface (Lelieveld and Dentener; Elbern, *et al.,* 1997).

CHAPER FIVE

CONCLUSIONS AND RECOMMENDATIONS

This chapter presents the summary of the study findings from the results obtained in Chapter 4, conclusions, and recommendations for future work.

5.1 Summary of the Findings

The study was based on the surface ozone measurements around Nairobi City. It focused on examining and analyzing the seasonal trends and levels of the continuously measured surface ozone as well as the levels of mobile sites surface ozone and its several precursors measured from several mobile locations around the city that are responsible for surface ozone pollution and resulting to poor air quality. A total of eight sites located on busy roads were sampled for 12 and 24 hours for high traffic and low traffic periods respectively, then a total of six sites located near industrial and a few residential places also measured for 12 and 24 hours. The following conclusions were thus drawn from the research and the recommendations given.

5.2 Conclusions of the Study

Surface ozone measurements results were extracted for the years 2013 to 2016. Daytime ozone levels were realized to peak at mid-day hours, then the seasonal levels found to have two prominent peaks twice a year in the months of March and August towards September. All the months of March in all the four years had consistently high peaks with hourly mean concentrations 32 ±5 ppb, due to the high solar intestines experienced in that dry season that favors ozone formation. This was followed by a decreasing and also minimum values towards April and May with a mean value of 28.39 ±5 ppb and less, from minimal phytochemical reactions caused by the cold wet season. The case was the same for the second peak in August and September which had the same

consistency in all the four years noticed to start rising from late July then attains high values in August and September with concentrations of 36 ±5 ppb mostly at 10 GMT (1 pm local time) favored by extreme solar radiations from high UV concentrations. The final phase of the seasonal trends is then realized to start decreasing from October with maximum hourly averages of 29.51 ±5 ppb towards November and finally December with values of 18 ±5 ppb where again it starts to peak and the cycle continues.

Mobile sites measurement around the city showed a marked diurnal variation of surface ozone and were also found to be within WHO limits of 50 ppb for 8 Hr. mean. Valley road exhibited the highest concentration with an 8 Hr. mean of 14.9 ppb, followed closely by Nakumatt Junction with a mean 8 Hr. value of 13.66ppb, quite evident with the heavy vehicular traffic always experienced at the location throughout the day. The traffic situation is worsened at peak hours due to the uphill nature of the road further causing emissions. Minimum surface ozone mean value measured on the mobile sites was 4.28 ppb at Muthurwa market, this area is characterized by traffic flowing throughout and thus high NOx values that tend to suppress ozone exponentially throughout the day leading to low concentrations.

Overall measurement of the surface ozone precursor revealed concentrations that were found to be quite lower than the prescribed international and local levels. They still however provide a substantial contribution to the ozone in Nairobi as well as the background concentrations responsible for the current air pollution. NOx was seen as the most prevalent precursor for ozone over Nairobi predominantly from vehicular emissions. In all the mobile sites measured, NOx was highest at Nyayo Highrise estate on Mbagathi road. This is due to emission from a long stretch heavy traffic that heads uphill with 190.23 ppb followed closely by Kariobangi roundabout on Outer Ring road with concentrations of 166.68 ppb.

Stratospheric ozone is also an important contributor to tropospheric ozone by stratospheric tropospheric intrusion and Stratospheric – Tropospheric exchange. The intrusions are typically made up of peak ozone concentrations at higher altitudes (6–8 km ASL), ranging from 240–400 ppb in concentration, and spreading about 100–300 km wide in the crosswind direction. Distributions have shown good stability of the total ozone columns and a good linkage with worthy agreements between the different Ozonesonde data sets for Nairobi.

5.3 Recommendations of the Study

The following recommendations were made;

1. There is need to have enough continuous measurements stations to enable a diverse data base of high resolution and quality, this would also help to show exactly the concentrations of the different points around Nairobi and also track the sources of surface ozone pollutions.
2. An extensive evaluation of the various risks associated with compromised air quality by surface ozone on major areas i.e. Agriculture, Health and the Environment and Climate Change as these are of great importance to our country.
3. Measurements and monitoring of trace pollution from the biomass burning regions, waste burning and emissions from other parts of Nairobi city.

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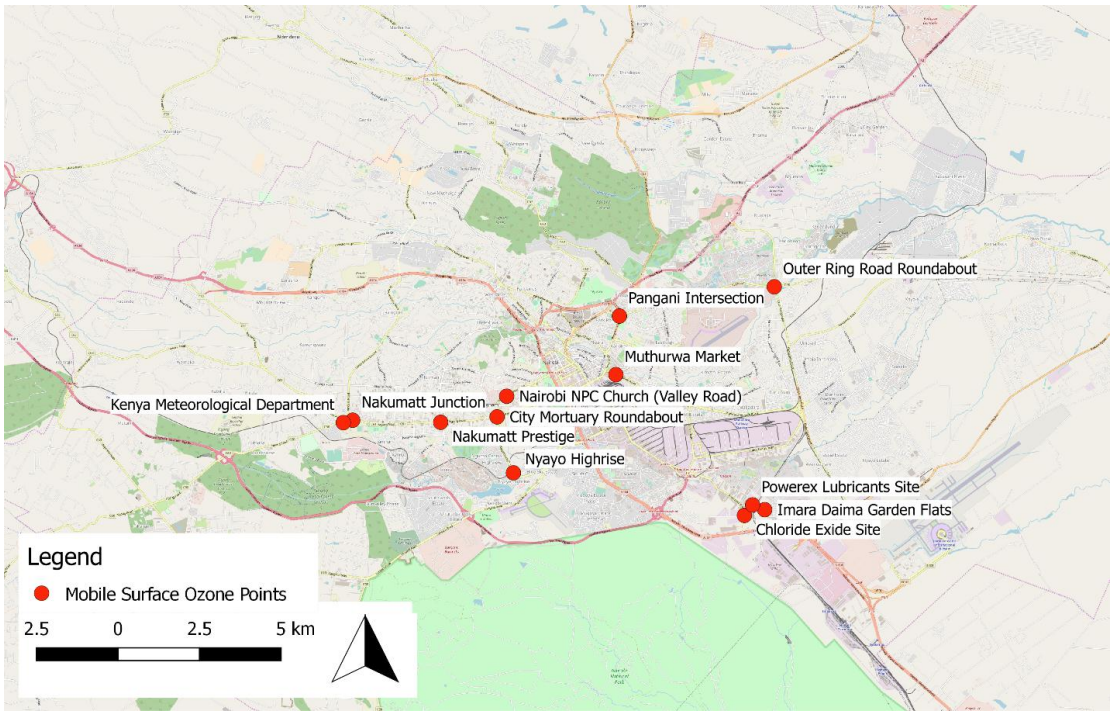
APPENDIX



Appendix 1. A map showing the measurement sites in Nairobi city by locations

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