# ASSESSMENT OF OZONE, NITROGEN OXIDES, AIR PARTICULATE MATTER ($PM_{10}$) AND TRACE ELEMENTS LEVEL IN THE AMBIENT AIR OF NAIROBITY CITY

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A thesis submitted in partial fulfilment for the award of Degree of Master of Science in Nuclear Science of the University of Nairobi

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# DECLARATION

I declare that this Thesis is my original work;
and that it has not been submitted previously
as Dissertation or Thesis for any Degree
at any other University.

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This Thesis has been submitted for examination with our approval as

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## ABSTRACT

Motor vehicle emissions are a major source of air pollution in most urban centers. In Kenya, Nairobi city has the highest traffic density and is therefore a particular cause for concern due to the poor maintenance standards of most vehicles plus the use of leaded gasoline. This study was carried out to determine the levels of nitric oxide (NO), nitrogen dioxide ($NO_2$), ozone, and air particulate matter ($PM_{10}$), in the ambient air of Nairobi city. The $NO-NO_2-NO_x$ were measured by Thermo Environmental Instruments Inc. (TEI) Model 14B Chemiluminescence $NO-NO_2-NO_x$ Analyzer, ozone by DASIBI Series 1003 UV Photometer and air particulate matter by the "Gent" Stacked Filter Unit (SFU), a dichotomous sampler. An automatic vehicle counter was used for determining the vehicle density at the sampling point. Gas measurements and analysis was done simultaneously at the sampling site, while the air particulate matter was by gravimetry and elemental composition by Energy Dispersive X-ray Fluorescence (EDXRF) technique. Sampling was done once every week for a period of three months (February to April 2000). Hourly average concentrations of $NO_2$, NO and $O_3$ were measured simultaneously from 9:00 a.m to 5:00 p.m., at a roundabout connecting two main highways (University and Uhuru) in the city. The findings of the study show that the values obtained for Pb, Mn, Fe, Br, Zn, Cu and Ca are within the World Health Organisation (WHO) guidelines. Lead concentrations ranged from 0.051 to 1.106 $\mu g/m^3$; Fe, 0.149 to 3.154 $\mu g/m^3$; Mn, 0.002 to 0.526 $\mu g/m^3$; Cu, 0.041 (Lower limit of detection-LLD) to 0.150 $\mu g/m^3$; Br, 0.016 (LLD) to 0.430 $\mu g/m^3$; Zn, 0.025 (LLD) to 0.140 $\mu g/m^3$ and Ca, 2.180 to 5.389 $\mu g/m^3$. Concentrations of $NO_2$, NO and $O_3$ were also within the 8-hour World Health Organisation (WHO) limits with levels ranging from 0.011-0.976 ppm for NO, 0.001-0.263 ppm for $NO_2$ and LLD-0.126 ppm for ozone. The $O_3$ levels were slightly higher in the afternoons when solar intensity was high especially the days with cloud cover of less than 3 Oktas. The mean level of $PM_{10}$ was 239±126 $\mu g/m^3$ while the range was 66.66 - 444.45 $\mu g/m^3$.. In the dry months of February and March, coarse particulates accounted for more than 70 % of $PM_{10}$. Analysis of the data shows strong correlation (r=0.966) between fine (0.4μm) particulates and NO, indicating the importance of traffic as a common source for both fine particulates and NO.

However, coarse particulates, $NO_2$ and $O_3$, showed poor correlation with motor vehicle density. There was also positive correlation between Pb and Br (r=0.930), while Fe, Ca and Mn were also positively correlated (r= 0.868, 0.010 and 0.326, respectively) with the coarse particulate matter. The high correlation between Pb and Br and motor vehicles suggests their main source being motor vehicle emissions. Ca, Fe and Mn are most probably from resuspended dust particles since they correlated well with the coarse particulate. The WHO as well as other studies show that the values obtained in this study, especially for fine particulate matter, lead and ozone could result in adverse health effects such as acute respiratory infection, asthma attacks, and low IQ and hyperactivity in human. The health implications of these results are also discussed.

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Finally, and most important, I owe a lot of thanks to my God for the good plans He has for me. This work wouldn't be possible without His comfort and special provision. To Him be all the glory!

# DEDICATION

This thesis is dedicated to my uncle Mr. Philip Jabura Oliech whose selfless sacrifice enabled me to attain university education

## SUMMARY

Air pollution from transport sources is a major environmental problem experienced in both developing and developed countries. Its effects include localised health problems and welfare disruptions in urban areas where traffic densities are high. In Kenya, Nairobi city has the highest traffic density and is therefore a particular cause for concern due to the poor maintenance standards of most vehicles plus the use of leaded gasoline. There is very little or no information on most priority pollutants emitted by motor vehicles in Nairobi. The little information available on motor vehicle related pollution are on Air Particulate Matter (APM), and trace elements on dust particles. Research was therefore necessary to investigate the role of motor vehicles, which is one of the main sources of air pollutants, in the city.

This study was carried out with the following objectives:

- to determine concentration of nitrogen oxides (NO and $NO_2$), ozone ($O_3$), trace elements and air particulate matter ($PM_{10}$) in the ambient air
- to determine the variation of NO, $NO_2$ and $O_3$ with pertinent meteorological parameters.

In this study, sampling was done for three months (February to April 2000) once every week. Hourly average concentrations of $NO_2$, NO and $O_3$ were simultaneously measured from 9.00am to 9.00pm at a round about connecting two main highways (University and Uhuru) in the city. Nitrogen oxides ($NO_2$ and NO) were measured by Thermo Environmental Instruments Inc. (TEI) Model 14 B chemiluminescence NO- $NO_2$-$NO_x$ analyser, ozone by DASIBI series 1003 UV. photometer and air particulate matter by the "Gent" Stacked Filter Unit (SFU), a dichotomous sampler. An automatic vehicle counter (SYX-RRL) was used for determining the vehicle density at the sampling point. Gas measurements and analysis was done automatically at the sampling site, while the particulate matter was by gravimetry and elemental composition by Energy Dispersive X-ray Fluorescence (EDXRF) technique.

The findings of this study show that the values obtained for Pb, Mn, Fe, Br, Zn, Cu and Ca are within the WHO guidelines. Lead concentrations ranged from 0.051 to 1.106 $\mu g/m^3$; Fe, 0.149 to 3.154 $\mu g/m^3$; Mn, 0.002 to 0.526 $\mu g/m^3$; Cu, lower limit of detection (LLD) to 0.150 $\mu g/m^3$; Br, LLD to 0.430 $\mu g/m^3$; Zn, LLD to 0.140 $\mu g/m^3$ and Ca 2.180 to 5.389 $\mu g/m^3$. Concentrations of

$NO_2$, NO and $O_3$ were also within the 8-hour WHO limits with levels ranging from 0.011-0.976 ppm for NO, 0.001-0.263 ppm for $NO_2$ and LLD-0.126 ppm for ozone. The $O_3$ levels were slightly higher in the afternoons when solar intensity was high especially the days with cloud cover of less than 3 Oktas. The mean $PM_{10}$ was 239±126 μg/$m^3$ while the range was 66.66 - 444.45 μg/$m^3$. In the dry months of February and March, coarse particulate matter accounted for more than 70 % of $PM_{10}$. Analysis of the data shows strong correlation (r=0.966) between fine (0.4 μm) particulates and NO, indicating the importance of traffic as a common source for both fine particulates and NO. Coarse particulates, $NO_2$ and $O_3$, however showed poor correlation with motor vehicle density. There was also positive correlation between Pb and Br (r=0.930), while Fe, Ca and Mn were positively correlated (r= 0.868, 0.010 and 0.326, respectively) with the coarse particulate matter. The high correlation between Pb and Br and motor vehicles suggests their main source being motor vehicle emissions. Ca, Fe and Mn are most probably from resuspended dust particles since they correlated well with the coarse particles. These values are higher than those obtained in most cities in developed countries, but compares closely with those obtained by other researchers in large cities in other developing countries with less strict pollution control measures. Considering the adverse health effects associated with these pollutants, and the high levels in which they are present in the ambient air in the city, it is of critical importance that appropriate measures are taken to address this problem before situations similar to those experienced in cities such as the London smog of 1952. From the data analysis of the of this study, it is clear that motor vehicles are the main sources of the pollutants studied and therefore control measures should focus on reducing motor vehicle emissions. Control measures, such as use of cleaner fuels (e.g. non-leaded gasoline), regular vehicle inspection and maintenance as well as strict enforcement of environmental legislation, should be taken.

## TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# LIST OF ABBREVIATIONS

**APEG**-Airborne Particulates Expert Group

**ATP**-Adenosine Triphosphate

**ATS**-American Thoracic Society

**CMDL**-Climate Monitoring and Diagnostics Laboratory

**CNS** - Central Nervous System

**FEV** - Forced Expiratory Volume

**FVC** - Forced Vital Capacity

**GEMS** - Global Environment Monitoring Systems

**HEI**-Health Effect Institute

**ICRP**-International Commission on Radiation Protection.

**PAN**-Peroxyacetylenitrite

**TEL** -Tetra Ethyl Lead.

**TML** -Tetra Methyl Lead

**UNCED**- United Nations Conference on Environment and Development

**UNEP**-United Nations Environment Program.

**UN** - United Nations

**US EPA**-United States Environmental Protection Agency

**WHO** -World Health Organization.

## CHAPTER ONE

# INTRODUCTION

### Background

The deterioration of environmental quality, which begun when mankind first congregated into villages, has existed as a serious problem since the industrial revolution. In the second half of the twentieth century, under the ever-increasing impacts of exponentially growing population and of industrializing society, environmental contamination of the air, water, soil and food has become a threat to the continued existence of many plant and animal communities of various ecosystems, and may ultimately threaten the very survival of the human race.

Air pollution is defined as the presence in the outdoor or indoor atmosphere, of one or more gaseous or particulate contaminants, in quantities, characteristics, and of duration such as to be injurious to human, plant and animal life, or to property, or which unreasonably interferes with the comfortable enjoyment of life and property (Williams, 1987).

Since the late 1940's and early 1950's, air pollution disasters have become more frequent. Smog episodes are now constantly recurring phenomena in some areas such as Los Angeles in USA (Cornwell, 1998). Air pollution has lately been covering larger proportions of the globe, and on some occasions the problem has increased to hemispherical levels (UNEP/WHO, 1992).

Urban air pollution has been increasing since the industrial revolution. Rapid industrialization, burgeoning cities and greater dependence on fossil fuels have brought in their wake increased production of harmful pollutants in most urban centers (UNEP, 1996).

The two sources of air pollutants ubiquitous in the urban areas are transportation and fuel combustion from stationary sources such as residential, industrial heating and thermoelectric power plants. Air pollution from transport sources is also a major environmental problem experienced in both developing and developed countries. Its effects include localised health problems and welfare disruption. Available data shows that much of the world's air pollution levels exceed recommended WHO guidelines (WHO, 1987). About a half of the world's cities have high concentrations of CO, and up to a third of lead (Pb) in the ambient air (UNEP/GEMS, 1991).

Response to air pollution problem varies from country to country. Unlike the industrialised countries where much research has been done leading to the evolution of practical policies and standards, little seems to have been done in most developing countries. The little information available on transport related pollution in Nairobi City indicates high pollutant emissions (Gatebe, 1992; Karue et al., 1992). High concentrations of lead were found in edible portions of a variety of food crops and in the soil within the vicinity of busy arterials (Surtan, 1987; Freeman, 1991). Lead levels of up to 127 μg/g against the normal range of 0.1 to 10 μg/g were found in vegetables and cereals (Surtan, 1987).

Air pollution levels in Nairobi are high, as is the case in most developing countries. This arises mainly due to economic reasons. A high proportion of city residents work in open areas (commonly known in Kenya as "*juakali*") and are adjacent to the major urban roads. There are also numerous street vendors at road junctions (Freeman, 1991).

Efforts are now being expanded to define the specific hazards posed by these emissions. As the problem of hazardous pollutants becomes more clear, it's seriousness becomes more. In particular, the dangers associated with long term low level exposure to specific pollutants for example lead, cadmium and other trace metals, respirable particulate matter and acidic gases are just beginning to be recognised and defined in this country. There is therefore, a need for concerted and effective action to improve the quality of air in urban environments.

In order to assess the potential impact of air pollutants on human health and in the environment; and to develop appropriate air quality management plans, it is necessary to have a reliable knowledge of the source(s), levels and distribution of air pollutants in an area, an issue recognised in the Agenda 21 of the United Nations Conference on Environment and Development (UNCED) held in Rio de Janeiro in June 1992. (UNEP/WHO, 1994a). Agenda 21, the sustainable development action plan for the 21st century, highlights in several chapters the importance of urban air pollution and calls upon nations and local governments to increase their efforts towards obtaining reliable and accessible data and information on pollutants concentrations, sources and effects. More specifically it states that:

- Sustainable development requires timely information to help decision-makers and the general public in making sound decisions.
- The existing information activities of earthwatch should be strengthened especially in the areas of urban air pollution and global atmosphere.

This research project was therefore carried out with the main aim of determining the concentrations of ozone ($O_3$), air particulate matter ($PM_{2.5}$-$PM_{10}$), trace elements and nitrogen oxides ($NO_x$), which are known to be mainly emitted by motor vehicles in the city of Nairobi.

## Previous Air Pollution Assessment Studies in Kenya

Most studies on air pollution that have been done in Nairobi have concentrated on $SO_2$ and total suspended particulate matter (UNEP/WHO, 1996). Some studies have also been carried out on lead (Pb) pollution (Karue et. al., 1992; Kinyua et. al., 1998; Onyari et. al. 1992. The work by Karue et al. (1992) was carried out with the aim of determining the concentration of total suspended particulate matter (TSP) within the city centre, industrial area and one residential area, as well as to characterise the TSP for trace elements by the EDXRF technique. Their findings showed that various activities in the city such as construction work, industrial processes, use of unroadworthy vehicles, and dust blown off unpaved roads contributed enormously to suspended particulate matter in the air. Studies have shown that the mass concentration of total suspended particulate matter (TSP) is rather poorly related to the actual pollutant burden on exposed individuals as the human respiratory system can remove large particles. Therefore, data on the concentration of TSP may not provide adequate information on the health implications of suspended particulate matter in the ambient air in the city. In the USA, as in most other industrial countries, ambient monitoring of suspended particulate matter has therefore been revised to measure levels of $PM_{10}$ rather than total suspended matter. This is because the smaller particles have been found to present greater risks to human health (US EPA, 1992; Dockey et al., 1993).

Information on other priority urban air pollutants e.g. CO, NOx, $O_3$, respirable particulate matter ($PM_{10}$) and trace elements, which have very adverse effects on human health and the environment, are therefore very limited or lacking. The only available data on vehicular emissions here in Nairobi are those obtained by Gatebe (1992) and Oketch (1994). From the findings of the study done by Gatebe (1992), levels of HC's and CO were found to be significantly high, especially in traffic congested areas mainly due to slow movement of vehicles. $NO_x$ levels were however in low concentrations. This study was carried out a decade ago and since then the number of vehicles in Nairobi have increased tremendously. Other priority urban air pollutants such as fine particles emitted from vehicular exhausts and ozone, both of which have been shown to have adverse health effects, were not considered in this study by Gatebe (1992). The results obtained are simulations of the pollutants using the Gaussian model. On the other hand, the study by Oketch (1994) was carried out to model the levels of CO and $NO_x$ at the arterials connecting the main highways in the city. No actual data on vehicular emissions of $PM_{10}$, $NO_x$ and $O_3$ for Nairobi is available.

## Objectives

In trying to fill this gap, this study was carried out with the aim of determining the concentrations of NOx, $O_3$, trace elements and particulate matter (particularly the respirable portion, $PM_{2.5}$-$PM_{10}$), focusing mainly on motor vehicle emissions. The hope is that the data obtained will provide a sound basis for the development of air quality management plans and / or policies for the city, as well as inform the public about the quality of their environment. The study also forms a good foundation for future research in the area of urban air pollution not only in Nairobi, but also in the country as a whole. The aims of this study are therefore to:

- Determine concentration of nitrogen oxides (NO and $NO_2$), Ozone ($O_3$), trace elements and the respirable fraction ($PM_{10}$) of the suspended particulate matter in the ambient air within the city of Nairobi and, to

- Monitor variation of NO, $NO_2$, $O_3$, and $PM_{10}$ levels with meteorological parameters like temperature, solar intensity and wind velocity in Nairobi.

## The Study Region

This study was carried out within the city center of Nairobi. Nairobi is located $10^0$ S and $40^0$ E at a mean altitude of 1700m. This is a rapidly growing area with a population of over 2 million people (UN, 1997) and a great deal of commercial and residential activities.

Nairobi is currently the third fastest growing city in the world after Guadeloupe, Mexico and Mozambique (UN, 1997). The population is currently growing at a rate of 7%. The commercial center is concentrated within the city center while most of industries are located to the southeast in the industrial area.

Nairobi experiences two distinct rainfall seasons, albeit with a lot of deviations of late, with the long rain season around April and the short rain season around November. During the long rain season, periods of heavy rains and showers are frequent. In between the two rain seasons, we have the warm dry season. This covers the period of December to the beginning of March when sunny and dry conditions prevail. The other is October. The prevailing winds in Nairobi are mainly north easterly (Ng'a ng'a, 1980).

# CHAPTER TWO

# LITERATURE REVIEW

## Urban Air pollution

Many of the major cities of the world are beset by a series of environmentally related problems, not the least of which is their deteriorating air quality. Exposure to air pollution is now an almost inescapable part of urban life throughout the world. Urban air quality is increasingly recognised as a major public health and environmental issue in both developed and developing nations; posing a substantial threat to human well being and to the environment.

Urban air pollution has been growing since the industrial revolution largely as a result of rapid industrialization, burgeoning cities and greater dependence on fossil fuels. These fuels have brought in their wake, increased production of harmful pollutants, making life in many cities increasingly unpleasant and unhealthy.

Among the most common and most virulent air pollutants are sulphur dioxide ($SO_2$), nitrogen oxides ($NO_x$), carbon monoxide (CO) and lead (Pb). There is also evidence of a growing threat to human health from indoor pollutants such as radon, formaldehyde, asbestos, mercury and organic substances.

Many industrialised countries have succeeded in controlling and reducing the most toxic pollutants, but in several others, e.g., less industrialised western countries and many developing countries, the problem continues. In many developing countries, urban air pollution is worsening (UNEP/WHO, 1992). Rapidly growing cities, more traffic on roads, use of dirtier fuels, reliance on outdated industrial processes, growing energy consumption and lack of industrial zoning and environmental regulations are continuing to contribute to falling urban air quality and deteriorating public health (WHO/ECOTOX, 1992).

World wide, more than 1.1 billion people live in urban areas with unhealthy air exposed to a cocktail of pollutants released from industrial, energy and vehicular sources (Dietrich, 1995). Air quality seems likely to worsen with rapid urban growth unless rigorous pollution control measures are put into effect.

In the cities with high air pollution levels and a combination of geography and weather that prevents pollutants from dispersing, ambient air pollution can pose a significant health risk. The problem is particularly pronounced in cities with large numbers of poorly maintained vehicles and widespread use of leaded gasoline as is the case in Kenya where the lead content of gasoline is 0.4g/litre (Karue et al., 1992).

Studies confirm the ill effects of outdoor air pollution on health (WHO, 1987). Pollution at the levels typically found in the air of large cities has been implicated in both acute and chronic illnesses, such as asthma and chronic bronchitis. Those most vulnerable are children, the elderly and those who already have respiratory difficulties.

## Sources of Air pollution in Urban Areas

### Air pollution from Motor Vehicles

Mobile source emissions are extremely complex and comprise hundreds of compounds that are present in the atmosphere as gases, aerosols and particulates. Many of these compounds are transformed in the atmosphere producing secondary pollutants such as tropospheric ozone, acid aerosols and carcinogenic hydrocarbons, which are sometimes more harmful than their directly emitted precursors.

Major air pollutants emitted by motor vehicles include carbon monoxide (CO), particulate matter (PM), nitrogen oxides (NOx) and a variety of gaseous organic carbon compounds, chiefly hydrocarbons (HCs) and Volatile Organic Compounds (VOCs). The presence of several highly reactive species in VOC emissions makes them, along with NOx emissions, the major motor-vehicle related precursors of tropospheric ozone ($O_3$).

In areas of high population densities, particularly in cities, motor vehicle emissions pose direct risks to human health. Health effects linked to mobile source emissions include aggregated respiratory symptoms, morbidity, and increased cancer mortality associated with exposures to polycyclic aromatic hydrocarbons (WHO/ECOTOX, 1992). While it is generally in the urban centres that these pollutants are present in amounts exceeding current air quality guidelines, they are also responsible for several forms of environmental degradation on the regional and global levels. Environmental damage linked to motor vehicle emissions range from negative aesthetic effects and crop or materials damage to more profound disruptions of regional ecosystems and aggravation of global environmental problems such as greenhouse gas accumulation (Spengler et al., 1990).

The increase of vehicles in large cities is responsible for the greater part of motor vehicle related emissions. Consequently, lakes, streams, and even remote forests have also experienced significant degradation. As evidence of anthropogenic impacts on the upper atmosphere accumulates, concern that motor vehicles are contributing to global changes that could alter the climate of the planet are increasing (Broecker, 1987). Thus, motor vehicle emissions are associated with virtually all the major air pollution problems at the local, regional and global scale (UNEP, 1987).

Direct health risks from motor vehicle related air pollution is common in urban areas where large percentages of the population are regularly exposed to high concentrations of pollutants (WHO/ECOTOX, 1992). According to a study on urban air quality conducted by the United Nations in 1988, only 20% of the world's 2.26 billion urban dwellers, lived in cities with acceptable air quality (UNEP/GEMS, 1991).

Ambient air pollution measurements and calculations of air pollution levels in built-up areas have shown that pollutants from motor vehicles including carbon monoxide, lead, air particulates, nitrogen dioxide and oxidants such as ozone are often present in concentrations exceeding international health standards (UNEP/WHO, 1992). In the following sections, pollutants assessed in this study are briefly discussed.

## Nitrogen oxides (NOx)

The oxides of nitrogen present in the atmosphere are $N_2O$, NO and $NO_2$. In addition, nitrous and nitric acids have been found, free, or in the form of their salts. Nitrous oxide ($N_2O$) is present as a regular atmospheric component at concentrations on the order of 0.5 ppb. Its stability makes it appear unlikely that it plays an important role in low-level atmospheric reactions. The higher oxides of nitrogen are formed in chemical processes such as nitrification, but by far the largest contributor is combustion at high temperatures whereby nitric oxide is formed (Seinfeld, 1989).

$$2N + O_2 \rightarrow 2NO \text{..................................} 1.1$$

Nitric oxide (NO) then reacts with ozone to form nitrogen dioxide ($NO_2$) according to:

$$NO + O_3 \rightarrow NO_2 + O_2 \text{..................................} 1.2$$

At equilibrium conditions, most of the NO is oxidized to $NO_2$. At a concentration of 1000ppm colourless NO is seen to turn brown with the formation of $NO_2$ in a matter of seconds. At the low concentrations occurring in the atmosphere the oxidation rate is much slower. For example, at 1 ppm 100 hours are needed for a 50% conversion of NO to $NO_2$. At 0.1 ppm the half-life is 1000 hours (Seinfeld, 1989). Ozone, however, oxidises nitric oxide much more rapidly and it is calculated that at concentrations of 1 ppm the half-life of NO is 1-8 seconds in this reaction. If both reactants are present at 0.1 ppm, only 18 seconds are needed for total oxidation.

Photochemically, nitrogen dioxide absorbs light over the entire visible and ultraviolet range of the solar spectrum available in the lower atmosphere. From 6000 to about 3800 Å, the spectrum indicates the formation of excited molecules (Leblanc, 1999). Below 3800A, $NO_2$ dissolves to produce NO and oxygen atoms:

$$NO_2 + h\nu \rightarrow NO + O \quad \text{..................1.3}$$

In the atmosphere, atomic oxygen combines with molecular oxygen forming $O_3$:

$$O + O_2 + m \rightarrow O_3 + m \quad \text{......................1.4}$$

Where m is any third body (usually $N_2$ or $O_2$).

In this two-step process equal amounts of NO and $O_3$ would be produced and rapid reaction between NO and $O_3$ will greatly decrease the total amount of ozone found. When nitrogen dioxide is present in a concentration of 1 ppm, the ozone formed in this process is 0.1 ppm; at 0.1 ppm of $NO_2$ it is 0.03 ppm (Leblanc, 1999).

In areas where ozone concentration is high, $NO_2$ is readily oxidised to $N_2O_5$, which is subsequently hydrated to nitric acid.

$$2NO_2 + O_2 \rightarrow N_2O_5 + O \ldots\ldots\ldots\ldots\ldots\ldots 1.5$$

At a nitrogen dioxide concentration of 1 ppm, it is estimated that the half-life of ozone is only 8 minutes (Seinfeld, 1989). The same end results can be obtained in fog droplets, where hydration and catalytic oxidation lead to complete conversion of $NO_2$ to nitric acid as shown:

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3 \ldots\ldots\ldots\ldots\ldots\ldots 1.6$$

In general, the atmospheric processes tend to bring the oxides of nitrogen to the nitric acid stages. This oxidation may take place in hours or days, and during this time the nitrogen oxides participate in a number of complicated reactions in which they are switched back and forth between the various oxidation stages. Eventually, however, they end up largely as nitrates, which are removed from the nitrogen oxides atmospheric pool by rain. A smaller percentage is found in aerosols as nitroderivatives of large-organic polymers.

$NO_x$ emissions from vehicles and other sources produce a variety of adverse health and environmental effects. Once in the atmosphere, $NO_x$ emissions also react chemically with other pollutants to form tropospheric ozone (the primary component of photochemical smog) and other highly toxic pollutants (Leblanc, 1999).

Exposure to nitrogen dioxide ($NO_2$) emissions is linked to increased susceptibility to respiratory infection, increased airway resistance in asthmatics and decreased pulmonary functions (WHO/ECOTOX, 1992). Short–term exposure to $NO_2$ has been associated with a wide-ranging group of respiratory problems in school children (cough, runny nose and sore throat are among the most common ones) and an increased sensitivity to urban dust and pollen by asthmatics.

The GEMS/ Air survey showed that 25 % to 30 % of the cities monitored exceeded 24 hour and 1 hour WHO guidelines (UNEP/GEMS, 1991). It was estimated that 15 % to 20 % of urban residents of North America and Europe (about 70-90 million people) suffer increased health risks from $NO_2$ exposure (UNEP/GEMS, 1991).

Oxides of nitrogen have also been shown to adversely affect vegetation. This effect is even more pronounced when nitrogen dioxide and sulphur are simultaneously present in the atmosphere (Wittemore and Korn, 1980). After $SO_2$, nitrogen oxides are the most important pollutants contributing to the formation of acid rain and acid deposition. It is therefore the aim of this study to monitor the levels of this pollutant in Nairobi City.

## Suspended Particulate matter (SPM)

Suspended particulate matter emitted from motor vehicles vary in size and usually consists of a number of compounds adsorbed on a solid carbonaceous core. The smaller, more easily respirable particles, particularly those below 10 microns in diameter ($PM_{10}$) are the most dangerous to human health, since they are capable of penetrating deeper into the lungs. Road traffic is a major contributor to primary particulate matter emissions and recent measurement data for $PM_{10}$ and $PM_{2.5}$ and particularly that pertaining to traffic-influenced sites, indicate that vehicular emissions contributes more than 90 % of fine particulates in urban centres (WHO, 1999).

Current problems with emissions of suspended particulate matter have been aggravated by lack of stringent emission regulations on the increasing number of diesel-powered vehicles being used for freight transport. According to the studies done, SPM is the most severe air pollution problem affecting the world's population especially in the urban areas (UNEP/WHO, 1992).

An ambient air quality standard based merely on the mass concentration of total suspended particulate matter (TSPM) is rather poorly related to the actual pollutant burden on exposed individuals. The human respiratory system can remove large particulates and therefore air quality standards based on TSPM alone may not provide adequate protection. The respiratory system acts as a highly effective filter for coarse particles, removing a large percentage of those inhaled particles of an aerodynamic diameter greater than 3 µm. The smaller particles are capable of penetrating deep into the lungs where their presence can cause increased air way resistance and susceptibility to infection, and reduction of lung function. In severe exposure, fibrosis, silicosis and other pathophysiological changes can occur. Even if the particles are chemically inert, they can act as irritants and can impair lung function. In the USA as in most other industrial countries, ambient monitoring of suspended particulate matter has therefore been revised to measure levels of $PM_{2.5}$ rather than general suspended matter. This is because the smaller particles have been found to present greater risks to human health (US EPA, 1999; McDonald and Duncan, 1979).

Depending on chemical and elemental species present, the toxicological effects of fine particulate matter can vary from insignificant to severe. In recent toxicological and epidemiological studies, observable health effects have been associated with exposure to respirable particles ($PM_{10}$) (Jakubowski, 1991; Pope et. al., 1995). One study in the USA that followed some 150,000 people in 151 cities for over 7 years, found that residents of the cities most polluted with suspended matter have a 15 to 17 % higher risk of premature death from all causes than those residents of the least polluted cities (UNEP/WHO, 1992).

The deposition of irritant particulate matter inhaled into the respiratory tract can cause acute symptoms such as cough, bronchial constriction and over-secretion of mucus (WHO/ECOTOX, 1992; WHO, 1987). Chronic exposures may result in the impairment of lung elasticity and gaseous exchange efficiency and cause an increased susceptibility to infections. In extreme cases lung tissues may become fibriotic.

Health hazard evaluation of suspended particulate matter in the ambient air cannot be based only on the size of the particles. Particulate matter from vehicle exhaust contains a considerable number of chemicals or elemental species that can be adsorbed after deposition in the upper airways. In addition, materials deposited in the upper respiratory tract and removed by cilliary action are often ingested. If these particles contain toxic materials that can be adsorbed in the gastrointestinal tract, they will contribute to the body burdens. A major component of particulate matter from motor vehicle exhaust is lead, which is discharged into the ambient air by the combustion of gasoline containing lead additives. It was therefore the aim of this study to assess the levels of air particulate matter in ambient air of Nairobi.

### Lead

As a result of the addition of tetra-ethyl and tetra-methyl lead to gasoline as an octane enhancer, motor vehicles have traditionally been the major source of lead compounds in the ambient air of most cities. Smelting operations and smoke from refuse burning and furnaces also make a contribution of Pb in the environment. During the combustion of gasoline in motor vehicles, alkyllead reacts with ethylene dihalide (EDH) "scavenger", with consequent emission of the lead in an inorganic particle form predominantly Pb Br Cl. The theoretical mass ratio of Br/Pb is 0.386 (Harrison and Sturger, 1983). The lead / bromine ratio (Pb/Br) in atmospheric particles has therefore been commonly used as an indication of vehicle emitted lead, since the two elements are associated in autoexhaust.

Motor vehicles exhaust has been shown to be the major contributor to fine particle mass concentration in the ambient air (Barmbach et al., 1995). The mass emission of lead is dependent on the lead content of the fuel. In cities with heavy traffic and ineffective (or non existent) fuel quality controls, lead emissions from motor vehicle exhausts can be responsible for up to 90 % of total urban lead emissions (WHO/ECOTOX, 1992). Only about 10 % of the lead emitted by vehicles is deposited within 100 meters of the road: the rest is widely dispersed (Butler, 1987). Khandeker and Tripathi (1989) reported a significant correlation between airborne lead concentrations and vehicular traffic density at the time of sampling in Bombay.

Among the heavy metals, lead has raised concern about its quantity in the environment, as it is not known to have any biological function in the body. The levels of lead in the body seem to rise with the environmental levels. Information based on epidemiological evidence has been given by Goldsmith and Hexter (cited in Butler, 1987) that the relationship between blood lead concentration and atmospheric lead is given by the empirical equation:

$$Log_{10} BLL = 1.265 + 0.2433 \log PBL \ldots\ldots\ldots\ldots 1.7$$

where BLL is the blood lead concentration in μg/100ml of whole blood and PBL is the atmospheric lead concentration in μg m$^{-3}$.This equation gives reasonable predictions in agreement with the blood lead concentrations and respiratory exposure to lead found by Kehoe (1996).

The general presence of a metal as toxic as lead in the urban environment has attracted considerable attention and the possible effects of direct inhalation of lead discharged in motor vehicle exhaust are of interest to clinicians and public health authorities. Indeed the health implication of the presence of lead in petrol has become a concern of environmentalists and a major public issue. This heavy metal gets into the body mainly through inhalation and at times ingestion of contaminated vegetables and other food crops grown along highways. The majority of lead exhausted from motor vehicles is less than 1 μm in diameter and therefore readily penetrates the lung as far as the alveoli from which transfer to the blood stream takes place.

Several studies have shown that children with high levels of lead accumulated in their baby teeth exhibit more behavioral problems, lower IQs and a decreased ability to concentrate (Bellinger, 1987 and Davis and Svendsgaard, 1987). Available evidence is convincing that exposure to levels of lead commonly encountered in urban environments constitute a significant detrimental biological effect in children, especially those less than three years old (Damji and Richtens, 1989). In a study of 249 children from birth to two years of age, it was found that those with prenatal umbilical cord blood lead levels of 10 μg/dl consistently scored lower on standard intelligence tests than children with lower blood lead levels (Bellinger, 1987).

Evidence of adverse health effects at lower levels of lead continues to grow, and statistical evidence has even been found to link lead to increased incidences of high blood pressure in adults (WHO, 1987). In order to keep blood lead levels below the threshold at which adverse health effects begin, the World Health Organization (WHO) has suggested a guideline of 0.5- 1.5 $\mu/m^3$ (annual average for ambient lead) (WHO, 1987).

Generally, lead concentrations in urban areas are decreasing in nearly every industrialised country, due to lowered lead content in gasoline and the use of unleaded fuel (Jensen and Laxen, 1987; Jones and Stephens, 1983). However, in Kenya lead concentrations in ambient air is expected to rise with the increase in number of motor vehicles since there has not been any control on the use of leaded petrol. This study was therefore carried out with the aim of continuing with the assessment of this pollutant in Nairobi.

### Ozone

Most of the earth's atmospheric ozone is found in the stratosphere- the portion of the atmosphere between about 10 and 50 km altitude- where it plays a critical role in absorbing ultra violet radiation emitted by the sun. A much smaller portion of naturally occurring ozone is found in the troposphere.

Of late there has been concern with the problem of elevated tropospheric ozone concentration, particularly in densely populated urban and sub-urban areas. Such elevated ozone causes damage to exposed people, plants and animals (Varshney and Mneesha 1987).

The build-up in tropospheric ozone has broad implications for atmospheric chemistry. Ozone and associated atmospheric oxidants play a significant role in controlling the chemical life times and reaction products of many atmospheric species and also influence organic aerosol formation. In addition, tropospheric ozone is a greenhouse gas that traps radiation emitted by the earth and an increase in tropospheric ozone might contribute to a warming of the earth's surface (Schjoldager and Peringe, 1984; Olcese and Toselli, 1999).

The presence of tropospheric ozone is generally attributed to a combination of its *in situ* photochemical production and destruction coupled with regular incursions of ozone-rich stratospheric air (Logan, 1985). Worldwide expansions in agriculture, transportation and industry are producing a growing burden of waste gases, most particularly oxides of nitrogen (especially NO and $NO_2$, designated as $NO_x$) and volatile organic compounds, designated as VOCs which enter the atmosphere and enhance the photochemical production of ozone. Computer models have been used to extrapolate the response of tropospheric ozone production as a function of atmospheric concentrations of VOCs and $NO_x$ both backwards and forward in time. These models estimate the low concentrations of tropospheric ozone of the past century and forecast increasing concentrations for the future, unless projected emissions of precursor trace gases are curbed (Hough and Derwent, 1990; Thomson et al., 1990).

The most critical aspect of the tropospheric ozone problem is its formation in and down wind of large urban areas, where, under certain meteorological conditions, emissions of $NO_x$ and VOCs can result in ozone concentrations as high as 200-400 ppb. Such production of ozone and related oxidant species, referred to as photochemical air pollution, was first recognised in the Los Angeles basin in the 1940s, when vegetable crops begun to show damage (Seinfeld, 1989). Work in the 1950s by Haegen-Smit established the photochemical nature of the agents that were causing plants damage (Haegen-Smit, 1951, 1953; cited in Butler, 1987). This work elucidated the key role of NOx and VOCs in ozone formation.

## Chemistry of ozone formation

Ozone is produced from the photochemical reactions of hydrocarbons and oxides of nitrogen, which in urban atmospheres are primarily of motor vehicle origin (WHO/ECOTOX, 1992). The concentration of ozone in polluted air is determined by rapid reactions 1.8-

1.11 below (Joos and Maffiolo, 1989):

$$NO_2 + h\nu \xrightarrow{k_1} NO + O \quad \text{..........} 1.8$$

$$O + O_2 + m \xrightarrow{k_2} O_3 + m \quad \text{..........} 1.9$$

$$NO + O_3 \xrightarrow{K_3} NO_2 + O_2 \quad \text{..........} 1.10$$

In the photo stationary state:

$$2N + O_2 \rightarrow 2NO \quad \text{..........} 1.11$$

Hence the ozone concentration is determined by the value $k_1$, highest when insolation is at its peak value, and by the ratio $[NO_2]/[NO]$. Since pollutant NOx is primarily emitted, as NO, this ratio is likely to remain small in the absence of other reactions converting NO to $NO_2$ without consumption of ozone. This conversion is known to occur by reactions with peroxy radicals formed in air masses polluted with hydrocarbons and CO as well as $NO_x$ (reactions 1.12 and 1.13)

$$NO + HO_2 \rightarrow NO_2 + HO \quad \text{..........} 1.12$$

$$NO + RO_2 \rightarrow NO_2 + RO \quad \text{..........} 1.13$$

The concentrations of the $HO_2$ and $RO_2$ radicals depend on solar intensity resulting in peak concentrations around midday within an urban area. There is, therefore, a pronounced diurnal variation in the ozone concentration. This variation is caused by a combination of meteorology and photochemical production. During daytime hours, photochemical production takes place, and at the same time the mixing height increases, causing ozone-rich air from a loft to be brought to the ground (Schjoldager and Pering 1984). These two phenomena result in maximum ozone concentrations in the afternoon in most cities. Areas with high traffic density and poor dispersion such as Los Angeles and Mexico City experience $O_3$ concentrations of the order of $600\text{-}700 \mu g/m^3$ which seriously damages peoples health especially sensitive individuals (Joos and Maffiolo, 1989). This is the major reason why developing countries must plan for emission controls now before their development leads to similar conditions.

Pollution of the lower atmosphere by ozone is a growing problem in many urban centers. In the troposphere, ozone not only behaves as green house gas, but is also a respiratory irritant and potentially damaging to plants. As photochemical $O_3$ formation was first observed in cities, surface ozone has traditionally been viewed as a predominantly urban pollutant. Research in both Europe and North America has since established that extensive ozone formation frequently occurs throughout the Northern hemisphere mid-latitudes during the summer months, most noticeably downwind of major cities and industrial regions (UNEP, 1996).

Due to the sparcity of the reliable long-term records (i.e. > 15 years), the evidence for large-scale increases of surface ozone is somewhat fragmentary (Penkett, 1991; Lehon et al., 1992). Evidence for increases over the past 100 years rely heavily on analysis of records from a handful of rural sites in Europe and North America, the reliability of which is impaired by uncertainties in the accuracy of older $O_3$ measurement techniques. Surface $O_3$ has been routinely measured at NOAA/ CMDL observatory sites since the early 1970's. The most significant trend observed in these data is a 0.7 percent year increase observed over the past 20 years at the Barrow Alaska monitoring stations (CMLD, 1992, cited in UNEP/WHO, 1994a). This is largely attributed to the longer summer (May-September) increases of over 25 percent since the start of measurements. A small but significant increase has also taken place at the Mauna Loa Observatory Station. Elsewhere, i.e. in the Southern Hemisphere, weekly negative trends in the surface $O_3$ concentrations have been reported (CMLD, 1992, cited in UNEP/WHO, 1994a).

In the United Kingdom, the occurrence of elevated $O_3$ concentrations is now fairly well documented. Measurements at several sites done by Eggleston et al., (1992) show that under anticyclonic conditions the maximum hourly mean $O_3$ concentrations often exceed 100 ppbv, a useful benchmark in the evaluation of $O_3$. The association of the elevated ozone concentrations with air masses containing photochemically reactive pollutants originating in urban areas, has been straight forward, and is based on poor vertical dispersion; the presence of other chemical products, namely peroxyacetylenitrite (PAN), sulphuric acid and ammonium sulphate aerosol; and oxidation of NO to $NO_2$ in urban areas. The meteorological conditions favouring the photochemical production of surface $O_3$ in the UK are typically, anticyclonic producing a generally easterly airflow with light winds, high temperatures and light cloud cover (UNEP, 1996). To date all episodes of elevated $O_3$ levels reported in the UK have been observed under these conditions. Studies done by researchers in different parts of the world supports this view. For instance, Bruntz et al. (1984) showed that a strong correlation exists between $O_3$ concentrations and some meteorological parameters on Welfare Island (New York). From a multiple regression analysis, where $O_3$ data were fitted with maximum daily temperature, solar radiation and wind speed resulted in a correlation of 0.84. Also, Wisse and Velds (1980) reported that in Vlaardingen (a heavy industrialised region in Netherlands), high $O_3$ levels predominantly occurred during stable atmospheric conditions and a considerable amount of sunshine.

More recent studies indicate that the pollution of the lower atmosphere by $O_3$ is a growing problem in many urban centers (Oleese and Toselli 1999; Varshney and Maneesha, 1987). In their study of $O_3$ pollution in the urban atmosphere of Delhi, Varshney and Maneesha (1987) showed that the amount of $O_3$ in the ambient air of Delhi City varied from 9.4 to 128.31 ppbv exhibiting wide temporal and seasonal variations. The Ozone concentration invariably peaked at noon and remained high during the early summer and spring periods. The findings of the study show a significant build up of $O_3$ in the urban area of Delhi. This suggests significant load of primary pollutants in the troposphere of Delhi to support tropospheric formation of $O_3$ involving complex chemical reactions.

Nairobi's meteorological conditions are also characterised by light winds, high temperatures and for most part of the year, light cloud cover, conditions which favour the photochemical production of $O_3$. It therefore enhanced the basis of $O_3$ determination in Nairobi since there was no data available and no routine measurements of the same by the relevant authorities.

### Air Pollution from Industries

Industrial emissions contribute to urban air pollution, especially in locations close to industrial areas. With the rapid rate of industrialization in the developing countries, there is bound to be higher contribution to air pollution in the cities in developing countries. Studies carried out here in Nairobi (Gitari, 2000; Karue et al., 1992) have confirmed high pollution within the neighborhood of the industrial areas and the estates located down wind from the industries. Within the Central Business District of most cities, the dominant source of air pollution, however, is vehicular emissions. This study is therefore mainly concerned with the determination of vehicular emissions within Nairobi city centre by assessing the gaseous, particulate emissions as well as trace elements.

## Effects of Air Pollution on Human Health

Several air pollutants have the potential to affect the health of human populations. The only significant exposure route for air pollutants is inhalation (ATS, 1987). Exposure can then be defined as the concentration of air pollutants in the nose and mouth. Pollutants therefore enter the body through the respiratory system, which can be divided into the upper respiratory system, consisting of the nasal cavity up to the pharynx and the lower respiratory tract consisting of the bronchial tubes and the lungs. At the entrance to the lungs, the trachea divides into two bronchial trees, which consists of a series of branches of successively smaller diameter (Figure 1).

The entire bronchial tree consists of over 20 generations of bifurctions, ending in bronchioles of diameters of about 0.005cm (Sterling and McNicol, 1984). . At the end of the bronchioles are large collections of tiny sacs called the alveoli. It is across the alveolar membranes that oxygen diffuses from the air in the sacs into the capillaries and carbon dioxide diffuses in the opposite direction. Although an individual alveolus has a diameter of about 0.02 cm, there are several hundred million alveoli in the entire lung, providing a total surface area for gas transport of roughly 50cm$^2$.

The respiratory system has several levels of defense against invasion by foreign materials. Large particles are filtered from the air stream by hairs in the nasal passage and are trapped by the mucus layer lining the nasal cavity and the trachea. These large particles are unable to negotiate the sharp bends in the nasal passage, and, because of their inertia, impinges on the wall of the cavity as the air rushes down towards the lung. In addition, particles may also be scavenged by fine hair like cilia, which line the walls of the entire respiratory system. These cilia continually move mucus and trapped materials to the throat where they are removed by swallowing. Most particles of sizes greater than 5μm are effectively removed in the upper respiratory system.

Particles of radii less than a few micrometers generally pass through the upper respiratory system, escaping entrapment (Sterling and McNicol, 1984). . Some of the larger particles are deposited on the bronchial walls immediately behind bifurctions in the bronchial tree. The mechanism for this deposition is believed to be inertial impaction, which results from the swirling air motion caused by bifurctions. Very small particles (radii < 0.1μm) are strongly influenced by Brownian mortion (rapid, irregular movement due to collisions of the particles with air molecules). As a result, these particles have a high probability of striking the bronchial walls somewhere in the bronchial tree. Particles in the size range of 0.1 to 1 μm which are too large to be influenced by the Brownian mortion but are too small to be trapped in the upper portion of the lung are able to penetrate deep into the lung.

For gaseous pollutants, the solubility governs what proportion is absorbed on the upper airway and what proportion reaches the terminal air sacs of the lungs (Sterling and McNicol, 1984). For instance, $SO_2$ is quite soluble and consequently, is absorbed early in the airway, leading to airway resistance and stimulated mucus secretion. On the other hand, $NO_2$ and $O_3$ are relatively insoluble and are able to penetrate deep into the lungs to air sacs. Nitrogen dioxide and ozone cause pulmonary oedema (swelling) which inhibit gas transfer to the blood.

A number of air pollutants therefore have the potential to affect the health of humans. Motor vehicles are the major sources of most of these pollutants, in particular nitrogen oxides, carbon monoxide, unburned hydrocarbons, ozone and other photochemical oxidants, lead and particulate matter (HEI, 1988). With the growing urbanization and vehicle density, urban air pollution has become a crucial problem and it is therefore of utmost importance to undertake risk assessments in order to evaluate and prioritize control strategies. In the following section, the health implications of the air pollutants assessed in this study are discussed.

## Health effects of Ozone

Ozone is a highly reactive gas and a strong oxidant. Ozone has been shown to react rapidly, but selectively, with many organic compounds. It reacts with alkanes at room temperature, for example, but is about 400, 000 times more reactive toward alkenes than towards alkanes (Pryor, 1983 cited in Beverly, 1989). Not unexpectedly, then, ozone reacts rapidly with bioorganic compounds containing double bonds, such as unsaturated fatty acids (Pryor, 1983, 1984, cited in Beverly, 1989) many of which are functionally and structurally essential. It exerts its action mainly through two mechanisms: the oxidation of sulfhydril groups and amino acids of enzymes, co-enzymes, proteins and peptides, and the oxidation of polyunsaturated fatty acids. Membranes are composed of fatty acids and lipids, and appear for that reason to be an obvious target for ozone. Cells or organelles with large specific surfaces may be extremely vulnerable.

The primary target organ for ozone is the lung. $O_3$ exposure produces cellular and structural changes, the overall effect of which is the decrease in the ability of the lung to perform normal functions (Beverly, 1987). Ciliated and type 1 cells are the most sensitive to ozone exposure (ciliated cells function to clear the airway of inhaled foreign materials). Proliferation of non-ciliated cells and type 2 alveolar cells occurs as a result of damage and death of ciliated and type 1 cells [1]. The lung air space location where ozone exposure cause a major lesion is the centiacinar area (see fig.1), which includes the first few generation of either respiratory bronchioles or alveolar duct (Lippman, 1989). Thus efficiency of gas exchange can be compromised in the affected areas.

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[1] Type 1 cells are thin, flat epithelial cells that line the alveoli of the acinus. Type 2 epithelial cells are more cuboidal and their proliferation after ozone-induced injury of Type 1cells results in the exposure of less surface area per cell to air and the ozone in it but that tends to thicken the epithelial membranes of the alveoli (Beverly, 1989)

Most of the studies on the health effects of $O_3$, have focused on short-term (1-2 hours) exposure and have indicated a number of acute effects of $O_3$ and other photochemical oxidants. Studies of hospital admissions in relation to ozone exposure reported an increase in hospital admission rates for respiratory diseases (Bates and Sitzo, 1983) and asthma attacks (Wittemore and Korn, 1980; White and Etzel, 1991). However, due to methodological limitations, these studies cannot demonstrate an association between ozone exposure and respiratory illnesses.

Different authors have investigated symptoms related to $O_3$ exposure. In a clinical study, Avol (1987) studied the occurrence of symptoms in subjects exposed to $O_3$ levels ranging from 0 to 640 µg/$m_3$. Symptoms were classified as upper respiratory (nasal congestion or discharge and throat irritation), lower respiratory (substernal irritation, cough, sputum production, dyspnea and chest tightness), and fatigue and eye irritation. The results of this study showed a dose-response relationship between effective dose of $O_3$ ($O_3$ concentration* time* ventilation rate) and symptoms score. Imai (1985) also reported significant symptom increase in adults during periods of increased ambient $O_3$ exposure in Japan.

The inhalation of $O_3$ causes concentration dependent decrease in the average lung volume and flow rate during expiratory maneuvers and mean decrements with increasing depth of breathing (Lippman, 1989). Decrease in lung functions in healthy children and young adults have been reported at hourly average $O_3$ concentrations in the range of 160-300μg/m$^3$ (0.08-0.150 ppm).

Based on estimates from Spektor et al (1988; cited in Beverly, 1989), moderate physical activity for a range of $O_3$ exposure from 38 to 226 μg/m$^3$ (0.019 to 0.113 ppm) for 1 hour could lead to a decrement of 180 ml for Forced Vital Capacity (FVC) and 0.7 ml/μgm$^{-3}$ for Forced Expiratory Volume (FEV) in one second. The Forced Expiratory Volume at 1-second ($FEV_{1.0}$) is the most commonly used spirometric measure of ozone induced lung function changes. Both $FEV_{1.0}$ and FVC give information about impairment of lung volumes. $FEV_{1.0}$ also gives information about impairment of flow rates resulting from increased flow resistance of the airways. Though ozone induced changes both in lung volume and airflow, its main effect at even the highest ozone concentrations observed in ambient air is to reduce the inspiratory capacity of the lung; that is, ozone limits the ability to take a deep breath.

Epidemiological field studies in children have indicated that pulmonary function decrement can occur at ozone concentrations of 220 μg/m$^3$ (0.11ppm) or somewhat lower (WHO, 1987). Other studies have associated changes in pulmonary function in children or asthmatics with ozone concentrations of 160-340 μg/m$^3$ (0.08-0.17ppm), but there were also associations with changes in temperature or with other pollutants (WHO, 1987).

Long term exposure effects of $O_3$ are still unclear, but there is good reason for concern that repeated exposures could lead to chronic impairment of lung development and function. Animal studies have bronchitis, bronchopneumonia, and acute pulmonary oedema at high concentrations (WHO, 1987).

Morrow (1984) showed that $NO_2$ can be toxic in certain biological systems and acute exposures to $NO_2$ have been reported to affect both the cellular and hormonal immune systems. Other authors (Damji and Richtens, 1989) have reported reduction of T lymphocytes following acute exposure to $NO_2$, which may reflect a function impairment of the immune response.

Recent controlled studies (WHO, 1987), show conflicting results concerning respiratory effects in the range of 190-7250μg/m$^3$ (0.1-4.0 ppm). The lowest observed level to affect lung systems consistently was at a 30 minutes exposure with intermittent exercise, to nitrogen dioxide concentration of 560μg/m$^3$ (0.3 ppm). Asthmatics appear to be more responsive to $NO_2$ and their lung function may be affected by levels of 940μg/m$^3$ (0.5ppm) (WHO/ECOTOX, 1992).

### Health effects of particulate matter

Recent concern about the health effects of air pollution has focused on particulate matter, and several epidemiological studies from the United States have indicated a strong link between increased $PM_{10}$ concentrations and increased mortality and morbidity (e.g. Dockey et al., 1993; Pope et al., 1995 and Schwartz, 1993). The more recent studies have indicated that it is the finer particulate fraction (>2.5 aerodynamic diameter) which have the greatest impact on health, probably because of their ability to penetrate deeper into the lungs and also because they contain more of the trace elements and other toxic chemicals (Schwartz, 1993). While breathing, particles are retained according to their size within the respiratory system. Larger particles are deposited in the upper respiratory tract while smaller particles may penetrate deeper into the lungs, where they are retained for a longer period. The fraction of particles that penetrate and are subsequently deposited within the respiratory system varies widely dependent on the properties of the particles, the individual breathing pattern, the structure of the respiratory system and other influencing factors (Stuart, 1983).

Inhalable particulates with a diameter of about 10 µm are predominately deposited in the nose, the mouth-throat area and in the larynx (Sterling and McNicol, 1984). The residence time of deposited particles in these areas is several hours. Particles below 10 µm in diameter may advance until the thoracic respiratory system (thoracic particles) and mainly deposit in the tracheo-bronchial area, where they are removed within several hours up to a day (Sterling and McNicol, 1984).. Finer particles (< 2.5 µm) penetrate the alveolar area (respirable particles). The deposition probability might amount up to 60 %. The elimination process of particles, which have been deposited in the alveolar areas, takes between days and even years.

The hazards caused by deposited particles in the respiratory system range from respiratory infections, bronchitis, asthma, pneumonia impaired lung function, hospitalisation for respiratory and cardiac disease to increase in mortality. Whereas acute health effects of particulate matter is probably best related to the deposited dose, chronic and long-term effects may be related to cumulative or retained dose but may also arise from recurring cycles of pulmonary injury and repair. Retention of particles is a function of deposition site, clearance of macrophages or the mucociliatory system and particle characteristic (Clarke et al., 1988). The rate increases significantly at high particle level, when "overloading" of respiratory system reduces the clearance mechanisms retention (Stuart, 1983). Lower elimination is also linked with the presence of air pollutants like sulphur dioxide and nicotine, which inhibit the mucociliatory efficiency. Accumulation of particles increases the likelihood for chronic obstructive pulmonary diseases, permanent decrease of the lung function, asthmatic symptoms and cardiovascular disease (EPA, 1999).

Little is known about the toxicological mechanism behind the health effects caused by particles and even less about the synergism with other pollutants. The organic constituents have been shown to induce some inflammation and suppress the defense capability towards infectious microorganism. Recent findings show that very small, ultrafine (< 0.1 µm) particles show a greater inflammation potential linked to surface-area dependent toxicity.

It is assumed that several metals and silica-derived constituents of the particles are cytotoxic to lung cells. Acidic particles of less than 0.1 µm are supposed to provoke alveolar inflammation which causes both acute changes in blood coagulation and release of mediators to provoke attacks of acute respiratory illness (Spengler et al., 1990). The blood changes results in an increase in the exposed population susceptibility to acute episodes of cardiovascular disease.The health effects associated with particulate matter are not only a function of their physical properties but also of their chemical characteristics. The size of the particulate matter determines their penetration into the human respiratory system: once retained, the particles chemical and physical characteristics determines the biological effects (Stuart, 1983).

The aerodynamic properties of the particles, the physiology of respiration, and the anatomy of the respiratory tract do govern particle deposition. The three main mechanisms of particulate deposition namely, inertial impaction, sedimentation, and diffusion vary in effectiveness in different regions of the respiratory tract. That is why the task group on lung dynamics of the International Commission on Radiological Protection (ICRP II) developed a general model of particle deposition that divides the respiratory system into three distinct compartments: the nasopharynx (nose and throat), the tracheal/bronchial region and the pulmonary region (UN, 1992). In each of the individual compartments, a different deposition mechanism operates.

The nasopharyngeal and the tracheobronchial compartments contain an epithelial cell lining, which is ciliated and contains mucus-secreting cell. This mucociliary system is the primary clearance mechanism for the larger particles, often removing them within a matter of hours. Although the bronchi narrow down sequentially, the total cross section of the lung increases, and thus, the flow of air slows as it reaches the alveoli. This feature has a significant influence on particle settling rates.

The respiratory tract is therefore a highly effective particle filter for particles larger than 3 μm. Particles deposited in the nose and throat are removed via the mucociliary system. This mechanism is not available for removing particles deposited deep in the alveoli and therefore these particles may persist for periods as long as a year (Sterling and McNicol, 1984).

In the alveolar region, a significant fraction of the particles may enter the lung interstices. Particles can then be transported into the lymphatic or circulatory systems to other organs. Toxic elements adsorbed on the particles can then reach and accumulate in any target organ of the body.

Most toxic metals such as lead occur mainly in the submicrometer or fine particles size range (Winchester W.J. and Bimu-Tian 1984; Ward, 1990; Schwartz, 1993). The health effects of the finer particles are therefore enhanced by the presence of these toxic elements in the deeper parts of the lungs.

The deposition of irritant particulate matter into the respiratory tract can cause coughs, bronchial constriction and over secretion of mucus. Chronic exposures may result in the impairment of lung elasticity, gaseous exchange efficiency and increased susceptibility to infections. In extreme cases, lung tissues may become fibriotic (WHO/ECOTOX, 1992).

Depending on chemical and elemental species present, the toxicological effects of fine particulate matter can vary from insignificant to severe. In recent toxicological and epidemiological studies, observable health effects have been associated with exposure to respirable particles ($PM_{10}$) (Jakubownski, 1991; Pope et al., 1995). One study in the USA (UNEP/WHO, 1992) that followed some 150,000 people in 151 cities over 7 years found that residents of the cities most polluted with suspended matter have a 15 to 17 % higher risk of premature death from all causes than residents of the least polluted cities (UNEP/WHO, 1992).

In a report "Health costs due to road traffic-related air pollution", which is the result of a health impact assessment project carried out in Austria, France and Switzerland, it is indicated that pollution from cars kill more people (WHO, 1999). The study focused on exposure to fine particles ($PM_{10}$) from motor vehicles. The main findings of this study show that:

- One third of $PM_{10}$ air pollution is caused by road transport. In cities this percentage is higher-up to >50 %.

- Long term exposure to air pollution from cars to adults over 30 years of age in the three countries cause an extra 21 000 premature deaths per year from respiratory or heart diseases.

- Each year air pollution from cars in the three countries cause 300000 extra cases of bronchitis in children plus 15000 hospital admissions for heart diseases, 395000 asthma attacks in adults and 162000 asthma attacks in children.

- This air pollution causes about 16 million person-days of restricted activities for adults over 20 years old because of respiratory disease (days off work or inability to carry out usual activities of daily living).

- The total cost of this health impact in the three countries is EURO 27 billion per year, including the intangible costs for pain, grief, suffering and loss of quality of life from illness or premature mortality, as well as the monetary costs of medical treatment and loss of production.

- This is 1.7 % of the combined gross national product of the three countries in the study: Euro 360 per year.

From the findings of this study, it is very clear that reducing $PM_{10}$ pollution from road traffic could eventually reduce these health and economic costs. The situation in developing countries without strict environmental pollution regulations and poorly maintained vehicles is expected to be worse than that of the three European countries. It is therefore of paramount importance that data on the pollution levels be obtained and made available to the policy makers for appropriate measures to be taken on time to avert disasters like those observed in the developed countries at the beginning of last century. It is therefore the aim of this study to start accruing such data.

### Effects of Lead and other trace elements on health.

Increasing environmental pollution has given rise to concern about the accumulation of heavy metals in human. Metals such as zinc, copper and iron are essential for man. Chronic metabolic disturbances may occur from a deficiency or an excess occurrence of these metals. Metals such as lead, cadmium and mercury are considered to be non-essential and can cause profound biochemical and neurological changes in the human body even at trace levels. Continuos exposure to the toxic heavy metals results in their gradual accumulation in the body and elevated levels of these metals have been observed in many tissues and usually vary with time.

Lead is one of the most insidiously toxic heavy metal to which we are exposed, particularly in its ability to accumulate in the body and to damage the central nervous system, including the brain (Schroeder, et al. 1987). The toxicity of lead may to some extent be explained by its interference with different enzyme systems: lead inactivates these enzymes by binding to the SH-group of their proteins or by displacing other essential metal ions (HEI, 1988) . For this reason, almost all organs or organ systems may be considered potential targets for lead, and a wide range of biological effects of lead has been documented.

Children appear especially liable to suffer more or less permanent brain damage leading to mental retardation, irritability and bizarre behaviour patterns (Bellinger, 1987; WHO, 1987). Exposure of children to lower concentrations of lead has been shown to produce neurological disorders, including impairment of learning ability, intelligence and motor coordination. Needleman (1979), in a community based study of children in Boston in whom previous exposure to lead was estimated from examination of deciduous teeth, reported evidence of lead-related neurophysiological deficits. The negative association between tooth-lead and mental development was reported in subsequent studies (Winnekel 1984). Some authors (Hawk, 1986; Fulton, 1987) also reported a significant inverse linear association between cognitive ability and blood lead, with no evident threshold level of exposure. The mean blood lead level of the highest lead group in the study of Oehme, (1988) was 221µg/l, suggesting that IQ deficit is related to lead exposure of < 250µg/l. In agreement with these findings, a study conducted in Mexico City among school children, from low to medium social status, aged 9 to 12 years, showed a strong negative correlation between blood level and intellectual coefficients and teaching grading without evidence of threshold level (Munoz, et al., 1988, cited in WHO/ECOTOX, 1992).

Apart from the neurophysiological disorders observed in children exposed to high levels of lead, animal and epidemiological studies have demonstrated that lead exposure may act on different systems, principally heme biosynthesis, the nervous system and other systems such as the cardiovascular system (WHO, 1987).

Lead poisoning causes anaemia. Not only does lead reduce the incorporation of iron into protoporphyrin by suppressing the enzyme ferrochelatase, but it also renders iron less available (Butler, 1987). Iron is able to enter the developing red cells in the bone marrow but is unable to reach its site of utilization. It is trapped in inactive forms in the badly disrupted cytoplasmic organelles. Heme synthesis is therefore hindered. The presence of stripped cells is characteristic of the blood of a patient with lead poisoning.

Serious effects on the nervous system are more common in poisoning with organic compounds of lead (HEI, 1988; Oehme, 1988). The best known are tetra ethyl (TEL) and tetra methyl (TML) lead, the antiknock additives to petrol. Attention was first focused on the toxicity of TEL following its introduction in 1923, when appreciable illness and even death was found among those involved in its manufacture. The nervous system was predominantly affected and in fatal cases, a large concentration of lead was found in the brain. Neurological symptoms are still found to be prominent in this condition even when the blood lead level is not greatly elevated; unfortunately permanent brain damage may occur. The affinity of organic lead compounds for lipid, a major constituent of the brain and central nervous system (CNS), may explain the difference from inorganic lead poisoning.

The effects of lead on the CNS are seen in behavior problems characterised by convulsions or swelling of the brain. A single attack of acute ancelopathy can cause brain hemorrhage, mental retardation, and other permanent neurological injury (Oehme. 1988). Similarly repeated bouts of lead poisoning can also cause permanent brain damage ranging from subtle learning deficits to profound mental incompetence and epilepsy (WHO, 1987).

Under normal conditions, more than 90 % of the lead retained in the body is deposited in the skeleton (Purves, 1978). The amount of lead that is not retained in the body is excreted back into the gut in the bile and also excreted through urine, sweat, hair and nails. Long term exposure at low daily level of lead therefore is potentially hazardous because lead is highly accumulative. Under conditions of abnormally high calcium metabolism, such as feverish illness or during cortison therapy, lead may be mobilised and a toxic amount released from the skeleton (WHO, 1987). Only a small proportion of the total bone lead need be mobilised to add an appreciable increment to the small soft tissue pool. With the passage of time, absorbed lead becomes progressively more deeply buried in the bone matrix. This develops a potential dangerous pool of exchangeable lead, which can persist for months or even years. A cute led poisoning can then occur long after exposure to abnormal amounts of lead has ceased.

## Other Effects of Air pollution

### Acidic deposition/Acid rain

Emission of sulphur dioxide ($SO_2$) and nitrogen compounds, their chemical transformation, atmospheric transport and deposition is the cause of acid deposition. Both acidification and direct exposure to these pollutant gases are believed to play a role in forest decline and crop yield loses. Historical data indicate that acid deposition has increased over the last century and records of the nitrate component in acid rain show a tenfold increase between 1980 and 1990 for North America and Europe

(UNEP, 1996). $NO_x$ emissions contribute approximately one third of the acidity in rainfall, and even higher shares in the cases of acid fog or snowfall. Acidification of lakes by acid rainwater led to mass reduction-and in some cases extinction-of certain fish species in Sweden (UNEP, 1987). Increased nitrogen depositions due to large amounts of $NO_x$ released into the atmosphere have also been found to disrupt the nutrient balance in ecosystems apart from acidifying rain water, and are thus significant contributor to forest dieback in Europe (UNEP/WHO, 1994a).

Fine particulate, especially when it contains sulphate or nitrate, is the principal conveyor of acid in the atmosphere (UNEP/WHO, 1994a). Fine particulates could play an important role not only in air pollution degradation of materials, but in long-term impacts on the acidity of fresh water bodies and soils. These particles are known to remain airborne for a long time and travel long distances, therefore high levels of acidic gases laden particulate matter can cause enormous effects far away from their emission points (Gatebe, 1999).

### Climatic effects

Gaseous pollutants as well as particulate matter have also been shown to have global warming potential which could result in climatic changes. It is now generally accepted that an increase in atmospheric $CO_2$, together with other green house gases such as $CH_4$, $N_2O$, $O_3$ and Chloro-fluorocarbons (CFCs), leads to an increase in average global temperature. The magnitude of this increase is not exactly known. However, it is estimated that $CO_2$ concentrations double that of pre-industrial times will occur in this century resulting in global temperature of between 1.5 and 4-5°C (UNEP/WHO, 1994a). Such an increase in temperature would alter global weather patterns and ocean current circulations, thus affecting world agriculture and marine systems.

Air pollution can also cause significant effects on the light transmission characteristics of urban atmospheres. A major contribution to this change would come from fine particulate matter. Changes in the optical properties of the atmosphere are of interest because they affect visibility in scenic or natural areas and may, in fact affect the heat balance within the atmosphere. The presence of fine particulate matter in the atmosphere may also alter the fundamental chemical and physical properties of the atmosphere in ways that are not well understood. Heat transfer rates, the formation of precipitation, the static electrical properties of the atmosphere and other phenomena are all significantly changed by fine particulates.

### Impact on Plants

Many gaseous pollutants inhibit plant growth and development. Pollutants may affect plants in several ways by inhibition of the functional groups of plant enzymes by overloading metabolic pathways for transforming or detoxifying pollutants; and by damaging the integrity of the plasma and cellular membranes. These processes may inhibit cellular productivity and also root growth and function, causing reduced translocation and biomass production.

Ambient $SO_2$ can cause direct damage to leaves and in long-term stunt growth (Hameed and Dignon, 1992). It is unlikely that $NO_x$ alone has a direct toxic effect on plants; however, it may interact with $SO_2$ and $O_3$ in a synergistic way to cause more damage.

Ozone on the other hand, is the most important phytotoxic air pollutant (Thomson et al., 1990). It damages plasma and organelle membranes and thus affects cell permeability. $O_3$ also impairs adenosine triphosphate (ATP) formation, reducing the supply of photosynthate to the roots; this in turn affects roots function inhibiting water and nutrient uptake (Thomson, et al., 1990). The role of $O_3$ and hydrogen peroxide in forest decline is still unclear. However, studies by US EPA and the congressional research service suggest that photochemical oxidants reduce crop yield by between 12 and 30 % with an overall cost of between US $ 1.9 billion and US $ 4.3 billion per year (UN. 1997). The level of air pollution damage to tropical forests and crop yields in developing regions is largely unknown.

### Impact on materials

Air pollution can cause direct damage to various structures and materials. $SO_2$ and other acid gases are known to cause corrosion and tarnishing of materials, surface erosion and soiling of building stone and glasses. Cracking of rubber by ozone as well as degradation of monuments by $SO_2$ has been observed (Williams. 1987). The damage to structures and materials can result in enormous economic losses.

# CHAPTER THREE

# EXPERIMENTAL

In this chapter the principles and theoretical background of the techniques used in this study are discussed. Sampling design, as well as methods used for data analysis and quality control and assessment are also briefly described.

## Measurement of the gaseous pollutants

Because of the wide variety of analytical instruments and methods presently available for monitoring air pollutants, there is often uncertainty concerning which procedure is the best for use in determining the concentration of a given gas pollutant in the ambient air. In this work $NO_2$, NO, and $O_3$ have been assessed as explained below.

### Nitrogen dioxide ($NO_2$) and Nitrogen monoxide (NO)

Nitrogen dioxide has generally been determined by the Saltzman method (Saltzman, 1954). In this technique the gas is bubbled through an absorbing reagent at a rate of about 0.4 l/min for 10 minutes in order to concentrate the $NO_2$. The absorbing solution results in a colour change that can be related to the $NO_2$ concentration. The technique is quite reproducible but suffers interference from $O_3$ and peroxyacetyl nitrate (PAN). The primary sources of error in this method are chemical interference's, inefficiency of collection and the aging of reagents.

Over the years, more accurate and efficient techniques for the determination of $NO_x$ have been developed. Steffenson and Stedman (1974), and Hodgeson et al. (1972) for instance, have shown that NO can be determined very accurately by Chemiluminescence. In this technique the pollutant sample is exposed to excess quantity of ozone. The ozone reacts rapidly with the NO to form $NO_2$ in an excited state:

$$NO + O_3 \rightarrow NO_2^* + O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

Collapse of the excited nitrogen dioxide ($NO_2^*$) to the ground state is accompanied by emission of light, which is then measured and related to the initial NO

$$NO^* \rightarrow NO_2 + h\nu \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.2)$$

This technique is sensitive to $10^{-3}$ ppm of NO, has an over all response time of 10 seconds and require a flow rate of only 20 $cm^3$ / min. Interference can be caused by collisional deactivation of the excited $NO_2$* and by the reaction of other species present with ozone, the product of which will also Chemiluminescence. Steffenson and Stedman (1974) investigated the possibility of interference from $SO_2$, $NO_2$, $Cl_2$, $H_2O$, $CH_4$, $C_2H_4$ and $C_3H_6$ at a concentration of 100 ppm in air but found that these species did not emit a detectable amount of light in the region of $NO_2$* luminescence.

## Chemiluminescent Analysis of $NO_x$

In this work, NOx (NO and $NO_2$) were determined using the NO-$NO_2$-$NO_x$ chemiluminescent gas analyser (Model 14B). Gas phase chemiluminescence is defined as the production of visible or infrared radiation by the reaction of two gaseous species to form an excited species product that decays to its ground state by the photoemission process. Other possibilities exist for the decay of the excited species; instrumental design attempts to minimise deactivation by non-photoemissive events such as collision with a chamber wall or third body gaseous species. Chemiluminescence has been studied on a fundamental laboratory basis (Lodge, 1989) and these principles were practically implemented in the 1970s to the analysis of nitrogen oxide by Fontijn et al., (1971) and adapted to the analysis of automotive exhaust emissions by Niki et al., (1974). Further work on the application of this approach to the measurement of $NO_2$ by thermal decomposition of $NO_2$ to NO has been reported by Sigsby et al., 1972 (cited in Lodge, 1989). These analysers were developed initially for the analysis of high $NO_x$ levels from emission sources, but has now been extended to much lower levels that are typically encountered in ambient air.

Chemiluminescent analysers for gaseous analysis represent a significant advance over manual or automated wet chemical analytical techniques because no aqueous reagents are required. The instrumental determination of the species of interest is available in real time (~1-5 seconds response time), and instrumental techniques show few interference. Additional advantages are linearity, sensitivity and ease of use over a wide dynamic measurement range. The use of chemiluminescent method of sample analysis, especially when incorporated into detector systems of instruments designed to measure pollutants has therefore gained in popularity in the past years.

### Principles of Instrumental Operation

The Chemiluminescent reaction of NO and $O_3$ provides the basis for this improved group of instruments. When nitric oxide (NO), reacts with ozone ($O_3$), nitrogen dioxide ($NO_2$) and $O_2$ are formed. The nitrogen dioxide produced by this reaction is in excited state and reverts to the ground state with emission of radiation:

$$NO + O_3 \rightarrow NO_2^* + O_2 \text{..............................................} (3.3)$$

Where $NO_2$* is nitrogen dioxide in excited state

$NO_2$ is nitrogen dioxide in ground state.

The process was first investigated by Thrush and coworkers (cited in Butler, 1987) who established that the light intensity (I) emitted in the

600-875 nm spectral region is given by:

$$I_{\alpha} \frac{[NO][O_3]}{[M]} \text{..........................................................................}(3.4)$$

where [M] is air and that the rate constant, k, of the reaction is defined by

$$\frac{-d}{dt}[O_3] = \frac{-d}{dt}[NO] = k[NO][O_3] \text{.........................................}(3.5)$$

These findings form the basis of the development of the chemiluminescent determination of nitrogen oxides. Fig. 3.1 outlines the main components of the $NO$-$NO_2$-$NO_x$ analyser (embodying these principles) used in this study. The embodying principles of this analyser are as follows. A light-tight reaction chamber maintained by a red filter to cut off radiation of $\lambda<610$ nm. Ozonized air and polluted air containing nitric oxide are fed through nozzles into the reaction chamber.

The gases mix, and the light from the emitted radiation is detected by the photo multiplier tube (PMT). The signal is amplified and displayed on an output meter or recorder. Steffenson and Stedman (1974) have shown that the detector signal from the photomultiplier tube is given by:

$$Detector\ Signal = \frac{\mathrm{Re}actor\ gas\ flow}{\mathrm{Re}actor\ gas\ pressure} G\left[1 - \exp - \frac{F_{react}}{F_{poll}}\right] \text{......}(3.6)$$

where G is the geometry of photon collection of the reactor and exp [$-F_{react}$ / $F_{poll}$] is the fraction of pollutant molecules whose residence lifetime in the reactor ($F_{react}$) is shown compared with the reactive lifetime of ozone with pollutant. $F_{react}$ is defined by

$$F_{react} = \frac{Adp}{R} \sec ond \text{...........................................................}(3.7)$$

where A is the cross-sectional area of the reactor in cm$^2$. d is the reactor length in cm$^2$, p is the gas density in the reactor in molecules cm$^{-3}$

and R is the flow in molecules $S^{-1}$.

The instrument response is linear in the range $10\text{-}10^{-5}$ parts of NO. The lower limit of sensitivity is determined by the signal-to-noise ratio of the PMT. Commercial designs incorporate cooling devises to maintain the PMT temperature at around –20°C. Another refinement includes a stainless steel coil held at 700°C, through which polluted gas can be by-passed before entering the reaction chamber. This coil ensures that any nitrogen dioxide present is decomposed to nitric oxide and oxygen before the gas is analysed.

To measure NO concentrations, the gas sample to be analysed is blended with $O_3$ in a flow reactor (Fig. 3.1). The resulting Chemiluminescence is monitored through an optical filter by a high sensitivity photo-multiplier positioned at one end of the reactor. The filter transmittance-photomultiplier cathode response limits the optical bandwidth to a narrow range specific to the chemiluminescent reaction of nitric oxide and ozone; hence there is no interference.

To measure $NO_x$ concentration (i.e., NO plus $NO_2$), the sample gas flow is passed through an $NO_2$–to NO converter. The chemiluminescent response in the flow reactor thus becomes linearly proportioned to the $NO_x$ concentration entering the converter (Fig. 3.1).

NO and $NO_x$ concentrations are then alternately measured and stored in electronic circuits. These circuits automatically subtract the NO concentration from the $NO_x$ concentration and displays the $NO_2$ ($NO_x$ - NO) and display values continuously on the output. These can then be read and recorded. For quality control, this analyser was calibrated and standardised at California Air Resource Board (CARB) laboratories, before it was shipped to Kenya, where it was used for the first time after calibration in this study.

## Ozone ($O_3$) measurements

Traditionally, $O_3$ determination has been based on reaction of the species with potassium iodide (KI):

$$2KI + O_3 + H_2O \rightarrow I_2 + O_2 + 2KOH \quad ........................3.8$$

and measurement of the amount of iodine which is liberated by the reaction under controlled laboratory conditions. This method is accurate, and remains as one important method for calibrating ozone sources. However automatic monitors for ozone based on the KI reaction suffer from numerous difficulties. Several species, including $NO_2$, peroxides, and PAN, give a positive response for ozone in varying degrees, but the presence of $SO_2$ and reducing dust results in a serious negative interference. The interfering species such as $SO_2$ can be removed by chemical means (e.g. scrubbing), before the pollutant gases reach the ozone monitor. Others can be corrected for mathematically (e.g. $NO_2$), the KI method must be regarded, at best, as a method determining the total oxidants concentrations in a sample.

An additional difficulty with the method is that the oxidant must be collected in a concentration solution by bubbling gas at the rate of 1 to 2 liters per minute for 15 minutes; full development of colour requires an additional 30-60 minutes. Thus, the KI method provides a non-specific, averaged oxidant concentration with poor response.

In this study, Ozone ($O_3$) concentrations were measured using the DASIBI ultra-violet ozone monitor (Model 10003 AH). This is a self-contained instrument, which measures gaseous ozone by means of UV absorption. Ozone concentration in parts per million (ppm) is read directly on the front panel. UV light is generated by a low pressure, mercury vapor lamp. This lamp emits its strongest line at 2536.52 angstroms that coincides with the region of maximum light absorption of ozone. By measuring the amount of light absorbed by the sampled gas, the ozone concentration can be determined.

### Theory of operation

The design of the DASIBI ozone monitor is based upon the absorption of 253.7 nm light. The ozone concentration can be calculated from the following:

$$I_t / I_o = e^{-act} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.9)$$

Where $I_t$ = photo current of absorbed light

$I_o$ = photocurrent for zero.

a = absorption coefficient = $2.74 * 10^{-4}$ cm.

c = concentration of ozone in parts per million by volume.

t = length of absorption chamber in centimeters.

The manner in which the above expression is utilised in the DASIBI ozone monitor requires a variation of the expression as follows:

$$I_o - I_t = 1 - e^{-act} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.10)$$

$I_o$ is normalised to 1 by adjustment in the instrument. This is readily and simply achieved by front panel control.

### Gent Stacked Filter Unit (SFU) Air Sampler

$PM_{10}$ was determined using a 'Gent' Stacked Filter Unit (SFU) air Sampler. The Gent SFU air sampler is specifically designed using the principle of sequential filtration for the collection of airborne particulate matter in the inhalable ($PM_{10}$) size fraction. Sequential filtration is a method for size fractionation of aerosols, which exploits the well-defined geometry of nucleopore filters. The filters separate the large particles by letting the smaller particles pass on to a backup filter (Thomas et al. 1996). The sequential filtration constitutes a simple practical and economic method for fractionating aerosols in such a way that the samples are suited for further gravimetric and chemical or physical analysis The Gent SFU sampler was designed at the University of Gent, Belgium for a coordinated research project supported by International Atomic Energy Agency (IAEA) and with 20 participating countries.

The sampler uses an open face type stacked filter unit, in which two 47-mm nucleopore polycarbonate filters are employed for the collection of airborne particulate matter (APM). Separation of the APM into the size modes is done by placing the appropriate nucleopore filters in front of a final absolute filter in sequence or stacked configuration. The sampler uses two types of filters, 8.0 μm (coarse filter) and 0.4 μm (fine filter). The coarse filter collects particles larger than 2.5 μm aerodynamic diameter and the fine filter, particles of <2.5 μm. The filter unit is placed in a cylindrical container so the filters are well protected during transport and are only handled in the laboratory. The cylindrical container is fitted with a pre-impaction plate for the collection of particles larger than 10μm. The impaction plate is usually coated with oil to reduce bouncing of particles. The impaction plate uses particle inertia for collection of particles with equivalent aerodynamic diameter of more than 10 μm. This depends upon the mass and velocity efficiency of the plate and the flow rate.

The sampler is designed to operate at the flow rate of 16-18 liters min$^{-1}$ where the pre-impaction stage provides a $PM_{10}$ cut off point at standard temperature and pressure. At this flow rate, the coarse filter has a defined $d_{50}$ value of 2 μm. The variation of the cut point as a function of flow rate does not change significantly at face velocities at or below 10 litres/min (Thomas et al, 1996).

The division of the particles into two sizes resembles the human respiratory system. The coarse particles are stopped in the nasal and bronchial region while the fine particles can penetrate into the alveoli and possibly into the body systems.

The filter unit of the sampler, a pump and a timer forms an inexpensive sampling system. The same air stream passes through both filters, and is subject to fewer flow problems than other devises that rely upon either on split or parallel sampling parts (Maenhaut et al., 1995). The 'Gent' SFU has been calibrated and is now extensively used in $PM_{10}$ sampling (Maenhaunt et al., 1995). The SFU unit consists of the following components:

- a double (stacked) filter cassette.
- a black polyethylene container (which includes a pre-impaction stage for $PM_{10}$ for the stacked filter cassette).
- a transparent tubing with a Swagelock nylon connector at one end and Swagelock brass connector at the other end to connect the stacked filter cassette to the polyflow tubing.
- a rain protection cover with two PVC clamps inside for mounting the rain protection cover, and also with two steel clamps for holding the polyflow tubing.
- Poly-flow tubing (⅜" outer diameter, ¼" inner diameter) with a Swagelock brass connection from the transparent tubing to the pump set up.
- a vacuum gauge.
- a needle valve to regulate the flow rate.
- a vacuum pump (GAST diaphragm pump, Model No. DO A-P101-I D.
- a gas flow meter (rotameter DWTER VFB- 67-BV).

- a precision gas volume meter (SCHLUM-BERGER G 1.6).
- a time switch and an hour meter (both operating at 220 volts, 50 Hz).

The stacked filter cassette together with the black polythene container with a pre-impaction stage for $PM_{10}$ form a complete stacked filter unit (SFU). The stacked filter cassette itself is a double NILU type "open face" 47-mm diameter filter holder. The first filter holder of cassette (i.e., the holder that face the air intake) is loaded with a "coarse" filter while the second filter holder of the cassette is loaded with a "fine" filter. The filter area that is exposed to the airflow during sampling is 12.88 $cm^2$.

## Energy Dispersive X-Ray Fluorescence (EDXRF) Technique

In this study, EDXRF technique was used for trace elements analysis. It is a powerful technique for elemental analysis and is based on the fact that chemical elements emit characteristic radiation when subjected to appropriate excitation. The emission of characteristic radiation can be induced by either the impact of accelerated particles such as electrons, protons, alpha particles and ions; or by the impact of high-energy radiation from an x-ray tube or suitable radioactive source. Cadmium ($^{109}C$) source was used for this work.

Generally, direct electron excitation is used in electron microprobe technique, while radioisotope sources and accelerator are commonly associated with energy dispersive technique. For reasons of sensitivity and versatility, the combination of the high power sealed x-ray tube and wavelength dispersion by selected crystal remains the practical and preferred technique for quantitative x-ray fluorescence (XRF) analysis.

### Interaction of x-rays with matter

Two major processes are involved in the interaction of x-rays with matter. These are scattering and photoelectric absorption (Jenkins, 1979).

An x-ray is attenuated on passing through an absorber and the degree of attenuation depends upon both scattering and absorption processes.

Consider a parallel monochromator, i.e. monoenergetic x-ray beam of intensity $I_0$ (in photons per unit time) impinging on a given homogenous material (Fig 3.2). After the beam has passed through a thickness of $x$ of the material, its intensity is reduced to $I_x$ due to the absorption and scattering phenomena (Jenkins, 1979).

$$\frac{dI}{I} = -u_{lin}\,dx \qquad (3.11)$$

or after integration over the path length $x$.

$$I_x = I_o \exp(-u_{lin}x) \qquad (3.12a)$$

The constant $u_{lin}$ is the linear attenuation coefficient of the material at that wavelength. If we let $m = \rho x$ where $\rho$ is the material density, and $m$ the mass of the material in a unit section, the equation (3.12a) can also be written

$$I_x = I_O \exp\left[-\left({}^{\mu lin}\!/_{\rho}\right)\rho x\right] \qquad (3.12b)$$

if $\mu = {}^{\mu_{lin}}\!/_{\rho}$,

then

$$I_x = I_o \exp-(-\mu m) \qquad (3.13)$$

The constant $\mu$ is called the mass attenuation coefficient because it refers to the mass of the material per unit section. It is usually expressed in $cm^2g^{-1}$. The difference $I_o - I_x$ of the intensity that is not transmitted in the same direction of the incident photons is lost mainly as a result of two processes: absorption of a number of incident x-ray photon that are annihilated in expelling an equal number of orbital electrons from the atom; this is the photoelectric effect. The electronic arrangements that follow in the ionized atom gives rise to x-ray fluorescence emissions and auger absorption. The second process is scattering of the incident photons in all direction after collision with atoms. The scattered photons have either a longer wavelength (incoherent or compton scattering) or same wavelength (coherent or rayleigh scattering).

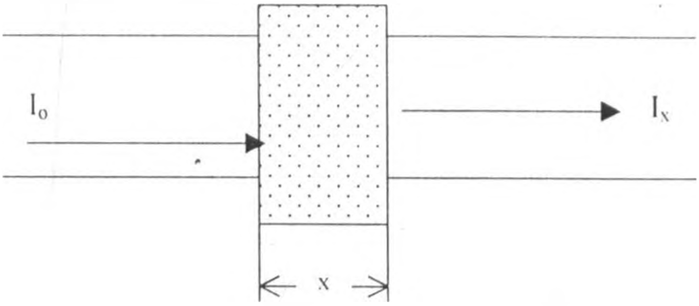


Fig. 3.2: Transmission of x-rays through a layer of material

When a beam of x-ray photons falling on to an absorber is scattered-mainly by the loosely bound outer electrons-and when no transference of energy is involved in the scattering process, the scattering is said to be coherent. The scattered wavelengths interfere with each other such that a diffraction phenomena may also occur. In x-ray spectrometry the diffraction process is of particular importance since it serves as the basis of the wavelength separation technique. Incoherent (Compton) scatter occurs where a small fraction of the energy of an incident x-ray photon is transferred to a loosely bound electron of the target element. In this instance, the wavelength of the incoherently scattered line is slightly longer than the incident wavelength (Jenkins, 1979).

Photoelectric absorption occurs when the electron of the target atom is completely removed (excited) from its initial site. The major contributions to photoelectric absorption are the inner electrons of the absorber atoms. Since binding energies of the inner electrons vary enormously with atomic number, characteristic radiation excited within a sample may be subjected to severe absorption problems. This gives rise to matrix effects, which complicates the mathematical relationship between measured characteristic wavelength intensities and chemical composition (Tertian and Claisse, 1982).

Following is a detailed discussion of the various absorption processes and their significance in the excitation efficiency of characteristic wavelengths.

## Photoelectric absorption

The photoelectric absorption of a photon can occur through an interaction with a bound electron in an atom. If the photon energy is higher than the binding energy of the electron, the electron is ejected as a photoelectron with the kinetic energy $E_{ke} = E_{in} - E_k$, where $E_k$, is the binding energy. For example, iron absorbs x-rays of energies exceeding 7112.1 eV ($\lambda = 0.1743$ nm), the energy required to remove the 1s electron. L absorption, the removal of a second shell electron (2s or 2p), is of analytical importance for elements past cesium. Lastly, the M absorption involves the removal of a third shell electron (3s, 3p or 3d) and may be used for very heavy elements. The 1s orbital are least affected by the chemical state of the atoms, and because higher energy x-rays are more penetrating, K absorption is usually the preferred mode of x-ray excitation.

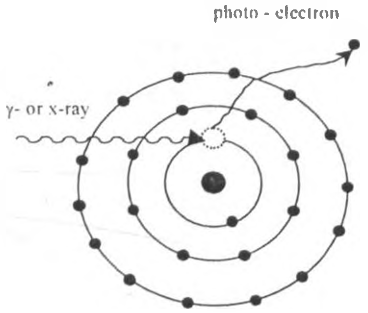


Fig.3.3: Schematic diagram showing the photoelectric effect

Example of the fluorescence process. (a) An incident photon is absorbed by the K-shell electron (b) The K-shell electron is emitted as a photoelectron and creates a vacancy in the atom. (c). The vacancy is filled by an L-shell electron. The difference in binding energy between the K and L shell ($E_k$ and $E_L$) is emitted as a characteristic x- ray photon.

The cross section for photoelectric absorption effect, $\sigma^{ph}$ in an atom is given by:

$$\sigma^{ph} = {}^{a}Z^{5}\big/(hv) \qquad \text{.......................................................(3.14)}$$

where a is the proportional constant, z the atomic number of the atom and hv is the energy of the incident radiation. For practical purposes, a more convenient quantity is the mass photoelectric absorption per unit mass, usually per one gram of the absorbent. The mass absorption coefficient μ is obtained as the product of $\sigma^{ph}$ value and the number of atoms gram of the given element. Thus

$$\mu_{ph} = \frac{aZ^{5}}{(hv)^{3}A} \qquad \text{................................................(3.15)}$$

where A and Z are the Avogadro's number and atomic weight respectively.

The probability for this process exhibits characteristic discontinuities. At these discontinuities the radiation is strongly absorbed. The discontinuities are referred to as, absorption edges and occurs at the binding energies for the electron shells in consideration. In iron for example, K absorption edge occurs at 7.1 KeV.

The maximum probability for photoelectric effect occurs when the energy is just above the electron binding energy. The magnitude of a discontinuity is the absorption jump denoted by $j_I$, where $_I$ = K, L, M depending on the electron shell in consideration. The absorption jump, $j_K$ of element I for the K shell can be approximated by:

$$jiK \equiv \frac{\sigma^{ph}\max}{\sigma^{ph}\min} \quad ........................................(3.16)$$

## Incoherent (Compton) scattering

Incoherent scattering is the result of the elastic impact of an incident photon (E = hv) on a relatively free electron i.e. an electron loosely bound to the atom.

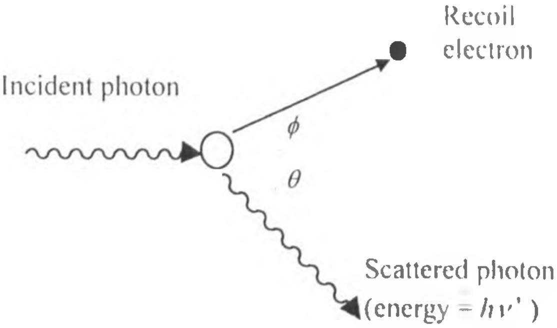


Fig.3.4: Schematic diagram of Compton Scattering

The electron recoils in the direction OA at an angle θ with the primary radiation, while the initial photon is deflected in direction OB at an angle ϕ. In the process, the photon loses some energy and takes a new frequency v' and a new energy E'. The quantities v , v' θ, $\phi$ and kinetic energy imparted to the recoil electron obey the laws of relativistic dynamics. Because of this, the principle of conservation of momentum implies that

$$\frac{hv}{c} = \frac{hv'}{c}\cos\phi + \frac{m_o v}{\sqrt{1-\beta^2}}\cos\phi \quad ........................................(3.17)$$

$$O = \frac{hv'}{c}\sin\phi + \frac{m_o}{\sqrt{1-\beta^2}}\sin\phi \quad ........................................(3.18)$$

The principle of conservation of energy is expressed as

$$h\nu = h\nu' + m_0 c^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right) \qquad (3.19)$$

where $m_0$ is the mass of the electron at rest, v is the velocity of the recoil electron, c is the velocity of light and $\beta = V/c$. Defining

$$\alpha = \frac{h\nu}{m_0 C}, \qquad (3.20)$$

and eliminating $\psi$ Z, v and β by combining equations (3.18) to (3.19)

$$\nu' = \frac{\nu}{1+\alpha(1-\cos\phi)} \qquad (3.21)$$

This relation between the modified and the initial frequencies is equivalent to the following relation between the corresponding wavelengths:

$$\lambda' = \lambda[1+\alpha(1-\cos\phi)] \qquad (3.22)$$

consequently, the combination of equations (3.20) and (3.21) results in the well-known relation for the change in wavelength

$$\lambda' - \lambda = \frac{h}{m_0 c}(1-\cos\phi) \qquad (3.23)$$

The above relationships can be used to calculate the frequency, wavelength and energy of a photon scattered in any given direction. The frequency and wavelength depends on the scattered angle ϕ. The change in wavelength however, depends on ϕ only. The constant $h/m_0 c$ has the dimensions of the length and its value is 0.02426Å. Equation 3.23 then becomes $\lambda' - \lambda = 0.0246(1-\cos\phi)$ ........................................(3.24)

There is no change in wavelength when ϕ =0; the value is 0.0242 when ϕ =90° and the maximum value is 0.0485 Å when ϕ =180°. The direction of the recoil electron is obtained by

$$\tan\psi = \frac{1}{(1+\alpha)\tan\left(\phi/2\right)} \quad \text{.........................................(3.25)}$$

The kinetic energy, hv-hv', of the recoil electron is obtained from the same equations

$$E_{kin} = h\nu\frac{\alpha(1-\cos\phi)}{1+\alpha(1-\cos\phi)} \quad \text{.........................................(3.26)}$$

## Coherent (Rayleigh) scattering

When the low energy photons are scattered by elements with higher atomic number, the probability for coherent scattering increases as more tightly bond atomic electrons are involved. Coherently scattered photons suffer no change in energy due to the fact that the mass of the electronic nucleus is much higher than that of the incident photon. the recoil of the nucleus is probably negligible.

The differential cross section for coherently scattered photons by a single atom, a, is of the form:

$$\left(\frac{d\xi}{d\Omega}\right)_a = K'\frac{(Z)^3}{h\nu_a} + F(\Psi) \quad \text{.........................................(3.27)}$$

where K' is a constant.

F (ψ) is a function of the scattering angle. From the equation (3.27) the probability of coherent scattering increases rapidly as the atomic number of the scatter increases. Similarly, the concept of mass attenuation coefficient per gram due to coherent scattering for a composite material is of the form:

$$u_{coh} = K'' \sum_{l-1}^{n} w_i \frac{Z I^3}{A_i} \qquad (3.28)$$

where K" is the constant depending on the geometry of measurement and energy of primary and secondary radiation. $W_i$ is the weight fraction of element I, $Z_i$ and $A_i$ are its atomic number and atomic weight, respectively.

## Quantitative Analysis in Energy Dispersive X-Ray Fluorescence

### General expression

Expressions for primary fluorescence intensity have been derived by many authors. The present mathematical approach is as per Sparks (1979). In x-ray fluorescence analysis it is the intensities of the radiation from a sample which is the basis of quantitative analysis. The energy spectrum consists of the characteristic x-ray lines and background contributions due to coherent and incoherent scattering. The latter tend to interfere with quantitative analysis.

The geometry of the excitation source in relation to the sample and the detector is shown in Fig 3.5.

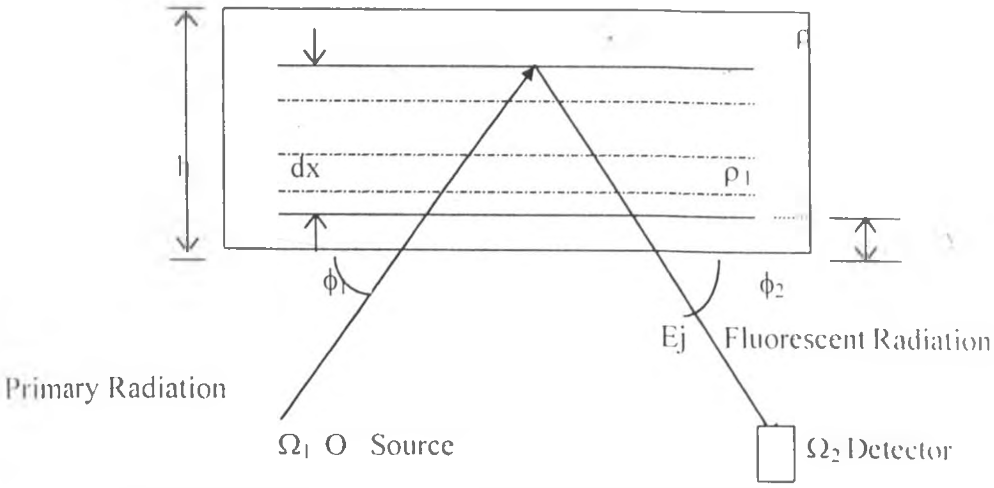


Fig. 3.5 : Geometry of the excitation source of the EDXRF

The intensities are expressed in photons or x-ray counts per second. The dependence of the intensity of fluorescence radiation of element $i$ and its mass per unit area is according to Sparks (1979) given by:

$$I_i(E_i)=G_o\cdot K_i\cdot\varepsilon(E_i)\cdot\rho_i d_i\left[\frac{1-\exp(-a_t x l)}{a_t x l}\right]\text{.............................}(3.29)$$

where $I_i(E_i)$ is the measured fluorescence intensity of element $i$

$I_o(E_i)$ is the intensity of primary exciting radiation

$G_o$ is the geometry constant which is also dependent on the source activity as is the case with radioisotope sources. $G_o$ is given by the following equation:

$G_o=\dfrac{I_o(E_O)\Omega_1\Omega_2}{\sin\theta_1}$ in which $\Omega_1$ is the solid angle of the incident primary radiation as seen by the sample. $\Omega_2$ is the solid angle of the emergent secondary radiation as seen by the detector. $K_i$ is the relative detection efficiency given by ;

$K_i=\sigma_i^{ph}(E_o)\left(1-\frac{1}{J_{is}}\right)\cdot\omega_{is}\cdot f'_s$ in which:

$\sigma_i^{ph}(E_o)$ is the photoelectric mass absorption coefficient of element $i$ at energy $E_o$

$\omega_{is}$ is the fluorescent yield for element $i$ in the shell "S".

$1-\frac{1}{J_{is}}$ is the relative probability for photoelectric effect in shell "S".

$f'_s$ is the ratio of the intensity of a given K or L line to the intensity of the whole series.

$\rho_i d_i$ is the mass per unit area of element $i$ in the sample.

$d$ is thickness of the sample and $\rho$ is its density.

$\varepsilon(E_i)$ is the relative efficiency of the detector for photons of energy $E$.

$N(O)+O \rightarrow N\overset{*}{O}_2+O$..................................(3.3) in which $\mu(E_o)$ and $\mu(E_i)$ are the total mass absorption coefficients in the sample at primary and secondary energies

$\Phi_1$ is the incident angle of primary radiation with sample.

$\Phi_2$ is the emergent angle of secondary radiation with the sample.

In the above equations, it is assumed that:

- the excitation source is a point source
- the sample is homogenous
- the primary radiation is monochromatic
- the density of element $i$, $\rho_i$, in the sample is constant over the whole sample volume and
- a fixed geometry is maintained during the intensity measurements of element $i$ in the sample, thus $\Omega_1$ and $\Omega_2$ are constant.

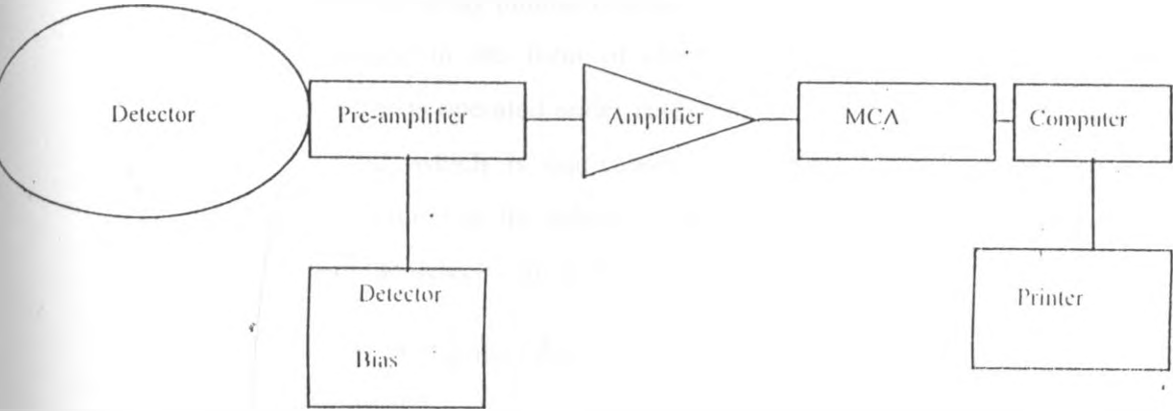
## XRFA Instrumentation

The general set up of the EDXRF used in this study is as shown in Fig. 3.6 It consists of x-ray excitation source and x-ray spectrometer. The spectrometer consists of :

- Spectroscopy amplifier; Canberra Model 2026

- Si(Li) detector, Canberra 7500
- High voltage bias supply; EG Ortex type 459
- pre-amplifier: Canberra model 11008
- Coolant liquid nitrogen in a dewar flask container
- ADC; Canberra Model 8075
- A Canberra S-PC based Multi Channel Analyser (MCA) used for data acquisition and spectrum analysis.

(a) Electronic Set up



(b) Cryostat

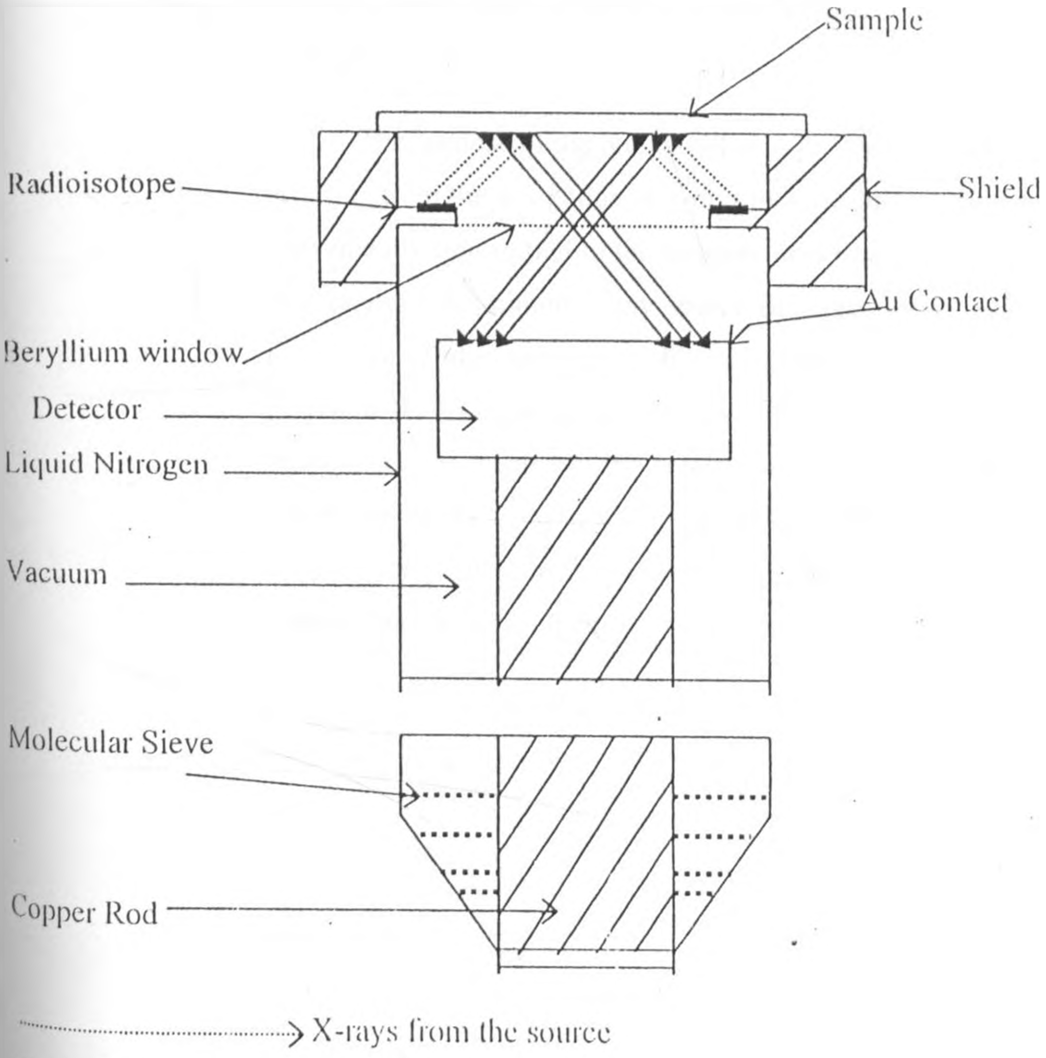


Fig. 3.6 EDXRF Experimental Setup

Source: Kinyua (1982)

The detector is a crystal of silicon that is processed to form a diode. When an x-ray photon is stopped in the detector, a cloud of ionization is produced in the form of electron-hole pairs. This happens when the detector is operated under reverse bias. The number of electron-hole pair created, which is equivalent to the total electric charge released, is proportional to the energy of the detected photon. This charge is swept from the detector diode by the high voltage applied across it.

A practical detector requires that other forces of charge carriers be minimized. This is accomplished in crystals by compensating for impurities with lithium in a process known as lithium drifting. Lithium drifted crystals are operated at liquid nitrogen temperature to reduce thermal noise.

The purpose of the pre-amplifier is to convert the bust of electrons, resulting from the absorption of x-rays into a voltage signal, which may be conveniently transmitted to the measurement system. The pre-amplifier is also required to minimise any source of noise, which may degrade the resolution of the spectrum. This is achieved by using a field effect transistor (FET) input charge sensitive pre-amplifier (Kinyua, 1982). The pre-amplifier is located at the detector to reduce capacitance of the lead, which can degrade the rise time as well as attenuate the signal. It also serves to provide a match between the high impedance out put of the detector and the low impedance of the coaxial cables to the amplifier.

A shaping amplifier follows the pre-amplifier. The amplifier serves to shape the pulse as well as to amplify it linearly and to make the pulse suitable for the precise pulse height analysis by the multichannel analyser (MCA).

Up to the input of the MCA, the signal is analog consisting of a continuum of pulse amplitudes from the amplifier output. The purpose of the multichannel analyser is to measure the pulse height of each pulse from the amplifier, record this as an integer number and store it in a particular memory channel in the MCA. This process is an analog-to-digital conversion process. The number of times a pulse of the same height has been detected is accumulated in the analyser memory to form the spectrum of pulse heights. This information is then displayed as a picture of the analysed energy spectrum. The display can then be presented with the X axis calibrated in terms of the mean energy of each interval while the Y axis display gives the number of x-ray photons counted in each energy interval during the entire data accumulation period.

The MCA usually also includes a microprocessor that is pre-programmed to perform simple data analysis operations like energy calibration, integration, and subtraction of background.

## Experimental procedures

### Sampling

Air samples were collected at the roundabout connecting University and Uhuru highways. The two highways represent one of the most busy roads in the city, at times registering some of the highest motor vehicle numbers. The sampling site and position was carefully selected to represent the area under study so as to meet the objectives of this research. The inlets of the sampling tubes were positioned at a height of about 1. 5 meters from the ground, to approximate the average human breathing level so as to estimate air that is breathed by the exposed population groups (Rao and Rao, 1992). The concentration of pollutants vary with altitude, and therefore results obtained on the roofs of tall buildings, for instance, may differ substantially from conditions at the ground or breathing level.

Sampling was done once every week for a period of three months (February to April 2000). Measurements were carried out for a duration of 8 hours (from 9:00 a.m-5:00 p.m). Background data was obtained from a location far removed from main highways in Nakuru, at an open space more than 4 km from the nearest highway. Motor vehicles density was determined using an automatic vehicle counter (Model SYX-RRL).

## Sampling of $PM_{10}$

$PM_{10}$ was determined using 'Gent' Stacked Filter Unit (SFU) air sampler, which was developed at the Gent University, Belgium. This method has been used in other studies (Maenhaunt, 1995 and Gatebe et al., 1996).

Before the start of any sampling exercise, the SFU sampler was properly cleaned with ethanol to remove any particles, which may have previously embedded inside. Filters were handled with care using clean plastic tweezers to avoid any form of contamination.

The nucleopore filter membranes were weighed in an air-conditioned laboratory at 50 % relative humidity and 20°C. Americium ($A^{241}$), an α-emitting source, (5 μCi), was used to remove electrostatic build up from the filters (Parr et al., 1996). Prior to weighing, all filters were left to equilibrate for 24 hours (Maenhaunt and Jan, 1994; Maenhaunt et al., 1995).

The fine and coarse fraction mass concentrations were obtained through gravimetric measurements of the filter membranes using a 1 μg sensitive Ainsworth (Type 24 N) weighing balance. Weighing of the filters was done prior to and after exposure and the difference in weight is the mass concentration of the fine ($PM_{2.5}$) and coarse particulates whose sum give the $PM_{10}$ concentration. The concentration in the ambient air is therefore obtained by dividing the mass of the particulates (in μg) by the total volume of air as follows:

$$\text{Concentration in } \mu g\, m^{-3} = \frac{W_f - W_i}{V} \qquad \text{.................................(3.30)}$$

where $W_F$ is the weight of the filter after exposure, $W_I$, the weight of the filter before exposure and V, the total volume of air sampled in $m^3$. V is obtained by multiplying the flow rate with the duration of sampling. The SFU sampler was operated at the flow rate of 18 litres /min and a pressure of -0.2 mbars.

### Trace elements analysis

Trace elements were anlysed using the energy dispersive x-ray fluorescence method. The loaded filters were mounted on a sample holder and held in position using thin polyester. The samples were then irradiated with $^{109}$Cd radioisotope (10 mCi) and run for 50,000 seconds to achieve reasonable statistical accuracy. Lithium-Silicon drifted Si(Li) detector with an energy resolution of between 160 and 290 eV at 5.9 keV Mn K-$\alpha$ line was used to detect x-rays. Spectrum data analysis was done using the IAEA software, AXIL (IAEA, 1992) which is based on a non linear least squares fitting procedure for optimization of the fitting model (peak energy, intensities and background parameters) for each spectrum.

Quantitative analysis was done using QXAS software program (IAEA, 1992). This program relates the spectral intensities with the elemental concentrations based on the fundamental parameters. Absorption correction of x-rays was not necessary since thin samples were used in this case.

Background contamination due to the materials and methods used in the collection and analysis of the samples was monitored routinely by using operational blanks. The operational blanks were analysed the same way as the field samples. The average concentrations of these blanks were subtracted from each sample.

Analytical precision and accuracy for trace elements was assessed by analyses of urban dust standard reference material (SRM 1648) supplied by the International Atomic Energy Agency (IAEA). The concentrations for the elements in SRM 1648 (certified values) were compared with analytical values.

### Sensitivity determination

Sensitivity of an analytical system is a measure of its ability to detect the lowest measurable concentration of a particular element in a sample (Sparks, 1979). The sensitivity curve of the EDXRF system for trace elements was generated using in-house standards. The values obtained (number of counts per second per µg for each of the K- and L-lines) were plotted against the atomic number of the elements to give the sensitivity curve.

### Detection limit

The lower limit of detection (LLD) of the EDXRF system was determined as shown in equation 3.31 using the intensity of L- and K-line peaks of the various elements analysed in this study (Sparks, 1979).

$$LLD = \frac{3}{M}\sqrt{\frac{Cb}{Tb}} \qquad \text{.........(3.31)}$$

where $C_b$ is the number of background counts, $T_b$ is the background time and M is the sensitivity of the detector in C/s/µg.

### Nitrogen Oxides Sampling and analysis

Nitrogen oxides ($NO_2$ and NO) were sampled and anlysed using a Thermo Electron's Model 14B Chemiluminescent analyser. The instrument meets a need for a more sensitive, accurate and continuos means of measuring NO, $NO_2$ and $NO_x$ for ambient air monitoring. The Chemiluminescent reaction of nitric oxide and ozone is the core of Thermo Electron's Model 14B instrument for the interference-free measurement of nitrogen oxides with eight linear, full-scale ranges from 0.05 ppm to 10 ppm.

The following parameters were checked and regulated as appropriate before the start of every sampling to confirm if the instrument was in good working condition:

- Reaction chamber gauge (the recommended value by the manufacturer is -22±2 inches of mercury.

- $NO_x$ converter temperature controller was set between 400°C and 450°C (30 minutes were allowed for the converter warm up as is recommended).

- Meter switch on "NO MANUAL" range selector to zero and full scale positions to confirm sensitivity of the instrument. With the meter switch on "NO MANUAL" and the ppm range switch at 50 ppb range. the unsuppressed photomultiplier dark current was checked / read. The recommended value by the manufacturer is < 15 ppb. The unsuppressed PM dark current is obtained by turning the background suppression photometer to the extreme counter-clockwise position.

- The reading of the concentrations of NO and $NO_2$ were obtained from the analogue-scale output at the front panel of the instrument by alternating the selector for the gases as appropriate. This was done at an interval of 1 hour through out the sampling period and the average concentration for each hour calculated and recorded.

### Ozone measurements /Analysis

Ozone measurements were obtained using DASIBI ultra-violet (UV) ozone monitor, a self contained instrument which measures gaseous ozone by means of UV absorption. The instrument was standardised by simple adjustments. Ozone concentrations in parts per million (ppm). was read directly on the front panel displayed unit. Electronic calibration and zeroing of the instrument was verified before each sampling by moving the FUNCTION switch to SPAN to display a positive reference count i.e.. the most significant five digits of six digit number as in the DASIBI ozone meter manual. The displayed number was verified to correspond to the number which is set into the four AUOTO SPAN SET switches in the access panel. The number should normally be 68.600 but could be varied to provide higher or lower readings if desired. As with $NO_x$ analyser, ozone data was taken at intervals of 1 hour.

## Meteorological parameters

### Cloud cover

The total cloud cover, is the fraction of the celestial dome covered by all the clouds visible. The assessment of the total amount of cloud therefore consists in estimating how much of the apparent area of the sky is covered with clouds. The international unit for reporting the cloud amount is the "Oktas" or eighth of the sky. In this study, the cloud cover was determined by observing the eighth of the sky within view, covered with clouds and the total amount recorded according to the scale given below:

| Scale figure | Cloud amount |
|---|---|
| 0 | None. |
| 1 | 1 Okta (1 eighth of the sky covered) or less but not 0. |
| 2 | 2 Oktas (2 eighth of the sky covered). |
| 3 | 3 Oktas (3 eighth of the sky covered). |
| 4 | 4 Oktas (4 eighth of the sky covered). |
| 5 | 5 Oktas (5 eighth of the sky covered). |
| 6 | 6 Oktas (6 eighth of the sky covered). |
| 7 | 7 Oktas (7 eighth of the sky covered) or more but not 8. |
| 8 | 8 Oktas (sky completely covered). |

An area which commands the widest possible view within the Kenya Meteorological Department (KMD) headquarters was selected as the observation point.

### Solar radiation/intensity

The determination of solar radiation was achieved by the use of Ångström pyrheliometer, which is a standard instrument for the measurement of direct solar radiation at normal incidence. Other meteorological parameters such as maximum and minimum temperature and humidity were determined using standard instruments as appropriate.

### Data analysis and graphical presentation

Statistical evaluation of data was done using Statistical Package for Social Scientists (SPSS) software (SPSS, 1998). MS-Excel spreadsheet was used for comparisons. For the apportionment of sources of the various pollutants, the raw data was subjected to correlation analysis with motor vehicle density as the determinant variable. Other statistical parameters such as mean, range, standard deviation and standard error of measurements were also determined. The graphical presentations were done using MS-Excel package.

# CHAPTER FOUR

# RESULTS AND DISCUSSION

Results of this study are presented in this chapter beginning with the quality control measures taken. Also included are the discussions of the results. Because of lack of proper means to calibrate gas analysers, concentrations reported in this study are more useful when used in a relative sense; otherwise they must be used with caution.

## Calibration and Optimisation of EDXRF System

### Quality Control

The laboratory procedure started with the optimization of the X-ray fluorescence system. This involved setting the optimum bias voltage, shaping time constant for the best detector resolution and optimum irradiation time of the loaded filters. The pulse shaping time was observed to vary with the resolution of the detector with a maximum being attained at a shaping time constant of 6 μs. The value was set and utilised for all the measurements of this study.

The energy resolution, Full-Width-at Half-Maximum (FWHM), at 5.9 keV Mn Kα peak varied from 170-200 eV for the entire analysis period. Optimum irradiation time of the filters was found to be about 50,000 secs.

An urban particulate matter Standard Reference Material (SRM-1648) from the International Atomic Energy Agency (IAEA) was analysed for trace elements following the same procedure as for the samples collected. Results are shown in Table 4.1. The results show that reliable data was obtained with the EDXRF system. Table 4.2 shows the lower limits of detection (LLD) of the EDXRF system for Ca, Mn, Fe, Cu, Zn, Br and Pb.

### Sensitivity of the EDXRF system

The elemental sensitivity (counts/sec) of the detector was found to increase with increase in atomic number of elements. A plot of sensitivity (S) against atomic number (Z) for L-and K-lines, produced an S-shaped curve (Fig. 4.1 and 4.2 respectively), which showed sensitivity to increase with increase in Z. However, the sensitivity reached a plateau between Z=83 and 92 (L-lines), probably due to high absorption of the characteristic x-rays of the elements by lower Z elements (Jenkins, 1979).

Table 4.1: SRM 1648 EDXRF analysis Results

| **Element** | **Concentration (in µg/m$^3$)** | **Certified values (in µg/m$^3$)** |
|---|---|---|
| **Fe** | **3. 820 ± 0.10** | **3.910** |
| **Zn** | **0.050 ± 0.012** | **0.061** |
| **Pb** | **0.612 ± 0.012** | **0.655** |

Table 4.2: EDXRF Detection Limit for the various Elements

| **Element** | **Detection Limit (µg/m$^3$)** |
|---|---|
| **Ca** | **0.830 ± 0.010** |
| **Mn** | **0.059 ± 0.001** |
| **Fe** | **0.051 ± 0.002** |
| **Cu** | **0.041 ± 0.015** |
| **Zn** | **0.025 ± 0.004** |
| **Br** | **0.016 ± 0.003** |
| **Pb** | **0.021 ± 0.010** |

### Suspended Particulate Matter ($PM_{10}$)

The mean weekly concentrations for suspended particulate matter, ozone and nitrogen oxides ($NO_2$ and NO) are presented in Table 4.3. There are five significant findings from these results.

First, the $PM_{10}$ levels were found to be higher than the recommended WHO guidelines; in some cases up to over 150 % or even higher (WHO, 1999). $PM_{2.5}$ levels were also higher than the WHO-24 hours standard of 15 µg/m$^3$ throughout the sampling period. The mean $PM_{10}$ level was 239 ± 126 µg/m$^3$ with a range of 66.7-444.5 µg/m$^3$. These values are higher than those obtained in most cities in developed countries, but compares closely with those

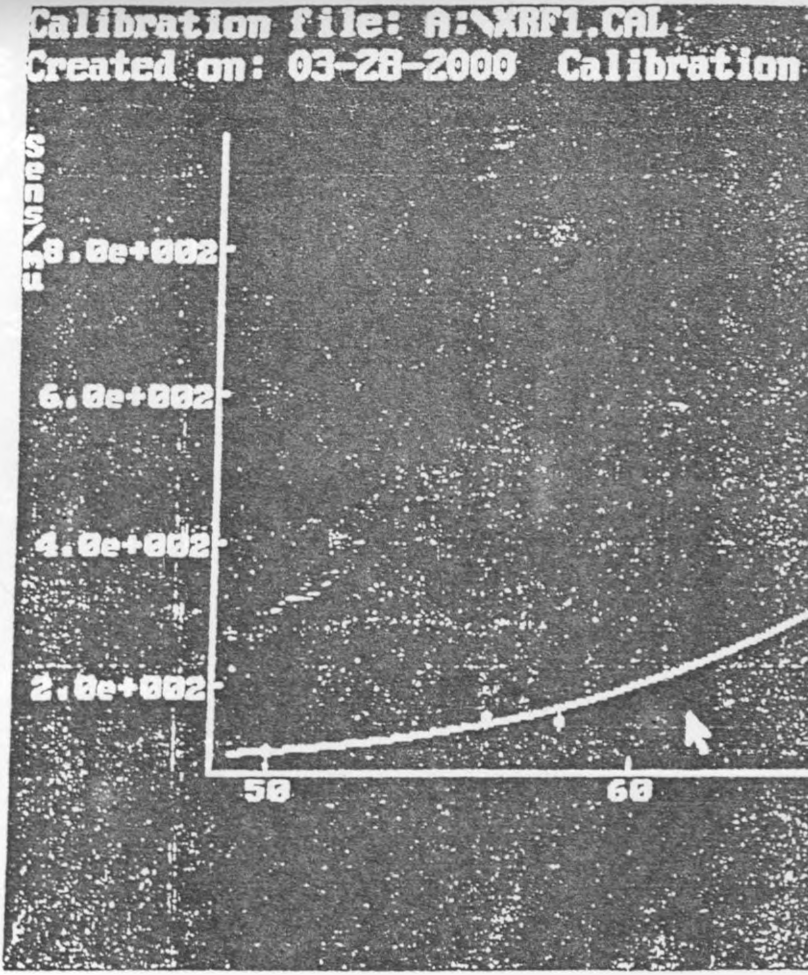
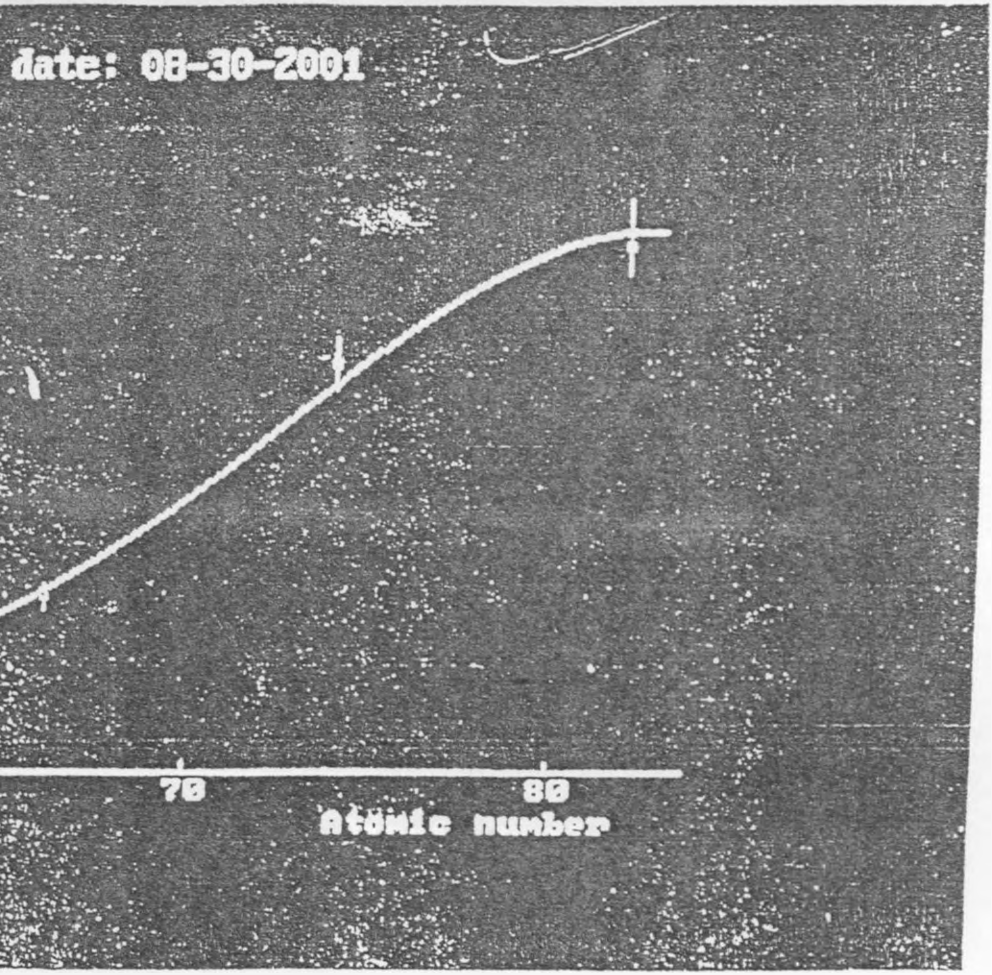


Fig. 4.1: Sensitivity curve (L-lines)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Atomic number

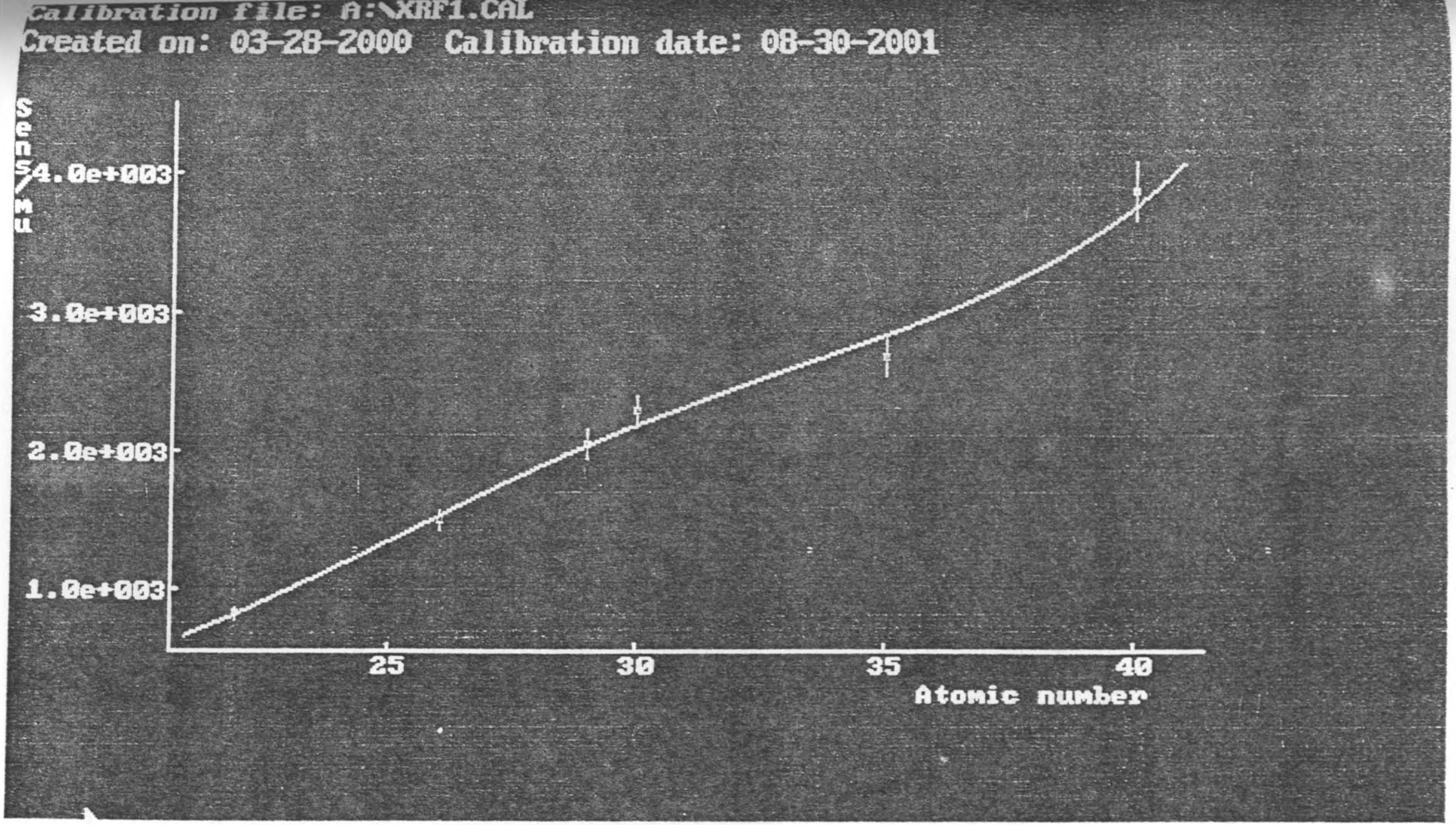

Fig.4.2: sensitivity curve (K-lines)

obtained by other researchers (WHO, 1999) in large cities in developing countries with less strict pollution control measures.

Secondly, a trend was noted on the concentration of both fine and coarse particulates. Concentration of coarse particulates were higher during the months of February and March, when they accounted for more than 70 % of $PM_{10}$.

Thirdly, there was positive correlation (r=0.3047), between vehicle density and coarse particles (Table 4.4). The correlation is however not very strong and this indicates that other sources other than the motor vehicles do contribute to these high particulate levels. At this sampling site the effect of wind blown dust was very minimal as the sampling point is well shielded by the tall buildings near by. However, resuspension of dust as a result of vehicle movements could be a big contributor to the high levels of particulate at the site.

Table 4.3: Concentrations (in ppm) of the pollutants and motor vehicle numbers.

| Sample | $O_3$ | NO | $NO_2$ | $PM_{10}$* | Fine* | Coarse* | Vehicles |
|---|---|---|---|---|---|---|---|
| FW1[#] | 0.0720 | 0.0496 | 0.0101 | 66.7 | 23.8 | 42.9 | 6301 |
| FW2 | 0.0776 | 0.0557 | 0.0182 | 165.5 | 57.9 | 107.6 | 8240 |
| FW3 | 0.0813 | 0.0590 | 0.0067 | 179.8 | 63.8 | 116 | 13218 |
| FW4 | 0.0747 | 0.0659 | 0.0062 | 259.1 | 74.1 | 185 | 10810 |
| MW2 | 0.0802 | 0.0767 | 0.0365 | 413.2 | 196.8 | 216.4 | 15204 |
| MW3 | 0.0624 | 0.0530 | 0.0117 | 162.0 | 50.9 | 111.1 | 8204 |
| MW4 | 0.0712 | 0.0607 | 0.0097 | 142.4 | 68.3 | 74.1 | 8120 |
| MW5 | 0.0682 | 0.0908 | 0.0143 | 444.4 | 206. | 238.4 | 18042 |
| AW1 | 0.0064 | 0.0928 | 0.0133 | 243.1 | 217.69 | 25.5 | 18824 |
| AW3 | 0.0490 | 0.0749 | 0.0119 | 395.8 | 155.1 | 240.7 | 13682 |
| AW4 | 0.0216 | 0.0726 | 0.0125 | 157.4 | 138.9 | 18.5 | 13214 |

* Concentrations are in $\mu g/m^3$

[#] The first letter in the sample code refers to the month in which the sample was collected and the second letter refers to the week of sampling.

Fourthly, there is high positive correlation (Table 4.4) between fine particles and motor vehicles density (r=0.9298). The high correlation (r=0.966) between fine particulates and NO also indicate that fine particulates may have similar emission source(s) to NO. This is further supported by the high correlation (Table 4.4) of NO and motor vehicles (r=0.945), $PM_{10}$ and motor vehicles (r=0.724). Motor vehicle exhausts, therefore, is the most probable source of fine particles.

Fifth, background $PM_{10}$ values obtained from Nakuru (at a site located about 4 km away from the main highway) are far below the WHO limits. They ranged from 2 μg/m$^3$ to a maximum of 27.8 μg/m$^3$. This site is situated close to the Nakuru National Park away from main anthropogenic sources of particles and gaseous pollutants. The $PM_{10}$ levels were: 2 μg/m$^3$, 10.8 μg/m$^3$, 27.8 μg/m$^3$ and 8.6 μg/m$^3$, for day 1, day 2, day 3 and day 4 of sampling, respectively. These low values can be attributed to the fact that at this site there was very little impact from vehicular exhausts. The ground at this site was also covered with grass and therefore, contribution to particles concentration by wind blown soil dust was very minimal. This shows the importance of motor vehicles as the main source of fine particulates in urban centres.

Table 4.4: Correlation matrix of the pollutants and motor vehicles.

| | $O_3$ | NO | $NO_2$ | $PM_{10}$ | Fine | Coarse | Vehicles |
|---|---|---|---|---|---|---|---|
| $O_3$ | 1 | | | | | | |
| NO | -0.5488 | 1 | | | | | |
| $NO_2$ | 0.1357 | 0.2856 | 1 | | | | |
| $PM_{10}$ | 0.0256 | 0.7326 | 0.4813 | 1 | | | |
| Fine | -0.5079 | 0.9663 | 0.4849 | 0.7805 | 1 | | |
| Coarse | 0.4690 | 0.2871 | 0.3156 | 0.8481 | 0.3307 | 1 | |
| Vehicles | -0.4745 | 0.9453 | 0.2787 | 0.7238 | 0.9298 | 0.3047 | 1 |

### Trace elements

Results for trace element analysis are presented in Table 4.5. Even though the levels of most of these metals are within the WHO limits, levels of lead (Pb) and manganese (Mn) are higher than in most urban centres in Europe and U.S.A (UNEP, 1996). The mean concentration for lead is 0.455±0.02 μg/m$^3$ with a range of 0.051 to 1.106 μg/m$^3$; Fe, 1.454±0.13 μg/m$^3$ (0.149 - 3.154 μg/m$^3$); Mn, 0.121±0.002 μg/m$^3$ (0.002 - 0.526 μg/m$^3$); Cu, 0.112±0.010 μg/m$^3$, (Lower Detection Limit (LLD) to 0.15 μg/m$^3$); Br, 0.193±0.01 μg/m$^3$ (LLD - 0.43 μg/m$^3$); Zn, 0.0972±0.02 μg/m$^3$, (LLD - 0.14 μg/m$^3$ and Ca, 3.796±0.42 μg/m$^3$ (2.18 to 5.389 μg/m$^3$). These findings agree with those previously reported in literature (Tripathi, 1992; Ward, 1990; Karue et al.; 1992). These values are also comparable particularly to those results reported from some urban centres of many

*Table 4.5: Concentrations (µg/m$^3$) of the trace elements studied.*

| Sample | Pb | Fe | Br | Zn | Cu | Ca | Mn | Pb/Br ratio |
|---|---|---|---|---|---|---|---|---|
| FW1c | 0.051±0.034 | 1.176±0.040 | BDL | BDL | BDL | 3.092±0.401 | 0.081±0.002 | |
| FW1f | 0.417±0.015 | 1.169±0.050 | 0.112±0.012 | 0.100±0.0142 | 0.092±0.008 | 2.604±0.320 | BDL | 0.268 |
| FW2c | 0.230±0.014 | 2.147±0.050 | 0.112±0.010 | 0.058±0.008 | BDL | 4.230±0.389 | 0.182±0.012 | 0.487 |
| FW2f | 0.419±0.010 | 0.149±0.055 | 0.182±0.012 | 0.102±0.012 | 0.101±0.017 | 2.982±0.402 | 0.014±0.002 | 0.434 |
| FW3c | 0.056±0.030 | 2.583±0.055 | 0.133±0.008 | BDL | BDL | 4.365±0.457 | 0.106±0.010 | 2.375* |
| FW3f | 0.453±0.015 | 0.471±0.055 | 0.176±0.010 | 0.104±0.013 | 0.113±0.015 | 4.098±0.389 | BDL | 0.389 |
| FW4c | 0.231±.013 | 2.612±0.101 | 0.097±0.008 | BDL | BDL | 4.389±0.443 | 0.012±0.004 | 0.42 |
| FW4f | 0.480±0.015 | 0.947±0.038 | 0.199±0.008 | 0.107±0.013 | 0.104±0.010 | 3.937±0.40 | BDL | 0.415 |
| MW2c | 0.268±0.013 | 2.625±0.054 | 0.104±0.013 | 0.021±0.018 | BDL | 4.390±0.374 | 0.104±0.011 | 0.388 |
| MW2f | 0.821±0.012 | 0.268±0.062 | 0.291±0.009 | 0.131±0.022 | 0.140±0.016 | 2.625±0.320 | 0.024±0.004 | 0.354 |
| MW3c | 0.276±0.013 | 2.545±0.055 | 0.199±0.010 | 0.037±0.021 | BDL | 4.313±0.382 | 0.323±0.011 | 0.721 |
| MW3f | 0.382±0.014 | 0.549±0.045 | 0.158±0.008 | 0.098±0.012 | 0.137±0.012 | 2.812±0.384 | BDL | 0.414 |
| MW4c | 0.420±0.015 | 1.898±0.049 | 0.163±0.010 | 0.102±0.012 | 0.082±0.008 | 4.310±0.382 | 0.113±0.012 | 0.388 |
| MW4f | 0.559±0.026 | 1.008±0.050 | 0.219±0.015 | 0.116±0.020 | 0.097±0.010 | 3.827±0.820 | BDL | 0.392 |
| MW5c | 0.382±0.013 | 2.756±0.085 | 0.160±0.012 | 0.049±0.010 | 0.102±0.014 | 4.593±0.424 | 0.301±0.057 | 0.419 |
| MW5f | 1.032±0.010 | 1.137±0.040 | 0.391±0.013 | 0.131±0.014 | 0.142±0.021 | 3.065±0.42 | 0.270±0.040 | 0.379 |
| AW1c | 0.401±0.018 | 1.147±0.045 | 0.134±0.008 | 0.068±0.006 | 0.091±0.024 | 4.272±0.401 | BDL | 0.334 |
| AW1f | 1.106±0.013 | 0.634±0.040 | 0.430±0.011 | 0.140±0.018 | 0.143±0.016 | 3.920±0.389 | 0.226±0.024 | 0.39 |
| AW3c | 0.423±0.015 | 3.154±0.062 | 0.176±0.012 | 0.099±0.013 | 0.061±0.012 | 5.389±0.543 | 0.526±0.041 | 0.416 |
| AW3f | 0.630±0.015 | 0.834±0.0425 | 0.190±0.010 | 0.125±0.035 | 0.133±0.021 | 2.180±0.820 | 0.083±0.010 | 0.302 |
| AW4c | 0.376±0.014 | 1.261±0.050 | 0.165±0.011 | 0.065±0.020 | 0.102±0.015 | 4.0995±0.461 | 0.283±0.011 | 0.439 |
| AW4f | 0.602±0.015 | 0.927±0.050 | 0.269±0.010 | 0.118±0.012 | 0.150±0.021 | 4.04±0.456 | BDL | 0.447 |

developing countries. Measurements in Bombay, India (UNEP, 1996) found high Pb concentrations areas with high vehicular traffic or major industrial areas (0.75-1.1 μg/m$^3$). In Taipei, Taiwan, a correlation was found between the decrease in the consumption of leaded gasoline and the monthly air lead concentrations (UNEP, 1996).

There was high correlation (Table 4.6) between motor vehicles density, lead (r =0.822), Br (r =0.826), Zn (r =0.581) and Cu (r =0.685). There was also high correlation between, Pb and Zn, (r = 0.790) and Pb and Cu (r=0.662), suggesting similar source for these elements. Since these metals also correlate well with motor vehicles, vehicular exhaust is probably their main source. Br/Pb ratios (Table 4.5) were also within the range found in gasoline (~0.3). Higher correlation values were obtained for these metals in the fine particulates. The correlation between Pb and Br in the fine particle range (Table 4.7) was, r = 0.959; Pb and Zn, 0.883; Pb and Cu, 0.623. Since the fine particles also correlate well with the motor vehicles density (0.930) (Table 4.4), motor vehicles are the most probable source of these pollutants. The fine particulate matter are known to be emitted from fuel combustion as opposed to coarse particulates which are mainly from resuspended dust particles or wind blown dust.

Some previous studies confirm that the major source of heavy metals in urban centers is vehicular emissions (UNEP 1996, Ogunsula et al., 1994). Positive correlation between vehicular density and trace elements concentration in coarse and fine filters was found between the various heavy metal levels and motor vehicle density. Table 4.7 shows the correlation matrix of some trace elements and motor vehicle density. Traffic volume and lead concentrations have a high positive correlation coefficient (r=0.8218). There was also high correlation between Pb and Br (r=0.9238), while Fe, Ca and Mn were also positively correlated with the coarse particulate matter (Table 4.7). The high correlation between Pb, Br and motor vehicles suggest their main source as motor vehicle emission. This is further supported by the Br/Pb ratio, which ranges from 0.268 to 0.721, with most values falling about ~0.386 (the Br/Pb ratio in gasoline) (Seinfeld, 1989). Calcium, iron and manganese are most probably from resuspended dust particles since they correlate well with coarse particles. Iron, calcium and manganese are poorly correlated with motor vehicles density (Table 4.6), but are well correlated with coarse particles (Table 4.7). These metals are also well correlated with one another, suggesting similar source, most probably dust particles. The correlation coefficient (Table 4.6) between Ca and Fe is, 0.726; that between Fe and Mn, 0.584 and Ca and Mn, 0.492. There is also very strong correlation between coarse particles and Fe (r= 0.910), as is, between coarse particles and Ca (r = 0.672) (Table 4.7). These metals are mainly associated with the earth crust from which the resuspended dust particles are released into the atmosphere. This can either take place through wind blowing or turbulence caused by vehicular movements.

Table 4.6: Correlation matrix of the trace elements in $PM_{10}$ and vehicles density

| | Pb | Fe | Br | Zn | Cu | Ca | Mn | Vehicles |
|---|---|---|---|---|---|---|---|---|
| Pb | 1 | | | | | | | |
| Fe | -0.507 | 1 | | | | | | |
| Br | 0.924 | -0.449 | 1 | | | | | |
| Zn | 0.790 | -0.625 | 0.645 | 1 | | | | |
| Cu | 0.662 | -0.619 | 0.660 | 0.553 | 1 | | | |
| Ca | -0.318 | 0.726 | -0.250 | -0.487 | -0.553 | 1 | | |
| Mn | 0.079 | 0.584 | 0.185 | -0.338 | -0.300 | 0.492 | 1 | |
| Vehicles | 0.822 | 0.112 | 0.826 | 0.581 | 0.685 | 0.397 | 0.435 | 1 |

Lead (Pb), zinc (Zn), copper (Cu) and bromine (Br) are mainly associated with the fine particulates, while iron (Fe), calcium (Ca) and manganese (Mn) are associated with the coarse particles. The strong positive correlation between Pb, Zn, Cu and Br, (Table 4.6), suggests that these metals are from a similar source. The elements (Pb, Zn, Cu and Br) also correlate well with motor vehicle density. This is a pointer to the fact that motor vehicles contribute majorly to their levels. Degradation of car tyres and wear of brake pads are likely sources for Cu, Zn and Mn (Ward, 1990) since the concentrations of these metals correlate well with vehicular density.

Table 4.7: Correlation matrix for the trace elements in the fine and coarse ranges

| | Pbc | Pbf | Fec | Fef | Brc | Brf | Znc | Znf | Cuc | Cuf | Cac | Caf | Mnc | Mnf | Vehicles | Coarse | Fine |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pbc | 1 | | | | | | | | | | | | | | | | |
| Pbf | 0.5620 | 1 | | | | | | | | | | | | | | | |
| Fec | 0.0620 | -0.0763 | 1 | | | | | | | | | | | | | | |
| Fef | 0.1816 | 0.1055 | -0.2171 | 1 | | | | | | | | | | | | | |
| Brc | 0.6834 | 0.1802 | 0.3903 | -0.1204 | 1 | | | | | | | | | | | | |
| Brf | 0.5965 | 0.9594 | -0.1426 | 0.0425 | 0.2854 | 1 | | | | | | | | | | | |
| Znc | 0.8536 | 0.2854 | -0.0369 | 0.0923 | 0.6102 | 0.2932 | 1 | | | | | | | | | | |
| Znf | 0.6794 | 0.8828 | -0.0131 | 0.0747 | 0.2547 | 0.8828 | 0.4428 | 1 | | | | | | | | | |
| Cuc | 0.7896 | 0.6480 | -0.2709 | 0.4899 | 0.4729 | 0.6851 | 0.7024 | 0.6775 | 1 | | | | | | | | |
| Cuf | 0.6228 | 0.6228 | 0.0975 | -0.1047 | 0.5795 | 0.6513 | 0.2513 | 0.6401 | 0 4959 | 1 | | | | | | | |
| Cac | 0.7896 | 0.2783 | 0.7426 | 0.2522 | 0.7225 | 0.2550 | 0.5061 | 0.4298 | 0.2755 | 0.4259 | 1 | | | | | | |
| Caf | 0.1138 | 0.2829 | -0.2488 | 0.2522 | 0.1989 | 0.4700 | -0.0576 | 0.1616 | 0.4486 | 0.0793 | -0.0664 | 1 | | | | | |
| Mnc | 0.4192 | -0.0560 | 0 4713 | 0.0929 | 0.5904 | -0.1194 | 0.5002 | 0.0556 | 0.2769 | 0.4273 | 0.5871 | -0.4165 | 1 | | | | |
| Mnf | 0.4906 | 0.8784 | 0.0276 | 0.2203 | 0.2299 | 0.8326 | 0.2852 | 0.7343 | 0.6206 | 0.5031 | 0.3026 | 0.2641 | 0.1193 | 1 | | | |
| Vehicles | 0.4424 | 0.8924 | 0.1327 | -0.0383 | 0.3111 | 0.8776 | 0.1491 | 0.8671 | 0.5429 | 0.7428 | 0.4714 | 0.3528 | 0.0597 | 0.4347 | 1 | | |
| Coarse | 0.1463 | 0.1880 | 0.9103 | -0.0617 | 0.1907 | 0.0712 | -0.0490 | 0.2387 | -0.1409 | 0.1674 | 0.6724 | -0.2803 | 0.4033 | 0.2345 | 0 3047 | 1 | |
| Fine | 0.6272 | 0.9341 | 0.0901 | -0 0225 | 0.3107 | 0.8931 | 0.3319 | 0.9609 | 0.6072 | 0.7817 | 0.4718 | 0.1436 | 0 1538 | 0.7532 | 0.9298 | 0.3307 | 1 |

- The letters f and c reffers to concentration of trace elements in the fine range (<PM$_{2.5}$) and coarse range (>PM $_{2.5}$) respectively.

### Gaseous pollutants (NO, $NO_2$ and $O_3$)

Figure 4.3 shows how $O_3$ concentrations varied with solar radiation and temperature. Levels of $O_3$ are seen to be high on the days when solar radiation and temperatures were also high. This is most likely due to the dependence of $O_3$ concentration on solar intensity, which plays a key role in photochemical reactions through which $O_3$ and other photochemical oxidants are formed. This agrees with the results of Pandey et al., (1991) who showed a significant positive correlation between $O_3$ concentrations, temperature and solar radiation. However, on the days when humidity levels were high (Table 4.8), ozone concentrations were low. This was also the case for the days when cloud cover was more than 5 Oktas (Table 4.9). High humidity levels in Nairobi are experienced mainly during the rainy seasons, when cloud cover is also high, hence the low ozone levels. The diurnal variations for ozone and nitrogen oxides are presented in Figures 4.4(a)-4.4(k). Most of the figures represent a typical diurnal course of $O_3$ and $NO_x$ with $O_3$ peaks noted mainly around midday and most part of the afternoon. Exceptions to this diurnal distribution were observed especially on the days when the sky was overcast (Figs. 4.4(d), 4.4(h), 4.4(i) and 4.4(j).

Highest levels of nitrogen oxides were recorded in the morning and late evening (Figs. 4.4a- 4.4k). Peaks of NO occurred during the morning (around 9:00 a.m) and evening (4:00-5:00 p.m). This coincides with the morning and evening rush hours to and from the city. Motor vehicles are mainly the source of these gaseous pollutants; directly for $NO_x$ and indirectly for ozone, by way of photochemical reactions on $NO_x$ (Seinfeld, 1989). The concentrations of ozone increased with decrease in concentrations of NO. This could be as a result of the scavenging effect of NO on ozone at high NO level. NO is also used up in the photochemical production of ozone hence low concentrations at high ozone levels (Seinfeld, 1989).

The high correlation (Table 4.4) between NO and motor vehicle density (r=0.9453) is a further indication that motor vehicle exhaust contributes a very high proportion of NO. The strong correlation between fine particles and NO (r = 0.966) also shows traffic being a common source for both fine particles and NO.

Ozone and $NO_2$ however, show weak or inverse correlation with vehicle density, with coefficient of correlation for ozone being r = -0.474 and that of $NO_2$, 0.279 (Table 4.4). This could be as a result of the fact that these two pollutants are not directly emitted from motor vehicle exhausts, but are secondary pollutants, formed by the reaction of the gases emitted directly from the exhaust.

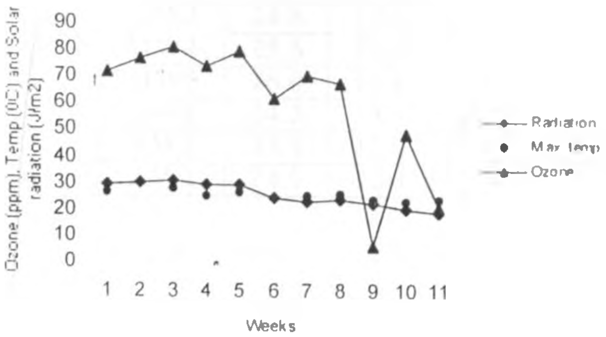

Fig 4.3: Variation of ozone with maximum temperature and solar radiation.

Compared to other gaseous pollutants, $NO_2$ recorded low concentrations throughout the sampling period. This is contrary to what is expected since higher $NO_2$ emissions are expected at roundabouts and on approaching traffic lights due to idling vehicles which lead to higher emissions of $NO_2$ than from fast flowing traffic (Lenner et al., 1983). Slow conversion of NO to $NO_2$ could be the reason for this.

Table 4.8: Other meteorological data

| Sample Code | Temp °C Max/ Min | | Humidity (%) | Rainfall (mm) | Radiation (MJ / $m^2$) |
|---|---|---|---|---|---|
| FW1 | 26.7 | 10.2 | 54 | NIL | 29.63 |
| FW2 | 30.5 | 15.2 | 30 | NIL | 30.31 |
| FW3 | 28.6 | 10.3 | 33 | NIL | 30.90 |
| FW4 | 25.4 | 10.8 | 42 | NIL | 29.88 |
| MW2 | 27.1 | 11.8 | 52 | NIL | 29.80 |
| MW3 | 24.8 | 13.5 | 46 | Trace* | 24.94 |
| MW4 | 25.5 | 12.3 | 60 | NIL | 23.45 |
| MW5 | 26.0 | 12.6 | 41 | 1.0 | 24.04 |
| AW1 | 24.2 | 14.0 | 56 | 2.5 | 22.53 |
| AW3 | 23.5 | 12.0 | 55 | NIL | 20.77 |
| AW4 | 24.0 | 12.8 | 69 | 15.6 | 19.01 |

*Less than 0.1 mm.

Table 4.9: Cloud cover data (in Oktas)

| Sample Code | 03* | 06* | 09* | 12* | 15* | 18* | 21* |
|---|---|---|---|---|---|---|---|
| FW1 | 6 | 5 | 4 | 4 | 4 | 5 | 6 |
| FW2 | 5 | 4 | 4 | 3 | 0 | 5 | 5 |
| FW3 | 2 | 4 | 3 | 1 | 1 | 3 | 4 |
| FW4 | 6 | 5 | 4 | 4 | 4 | 5 | 6 |
| MW2 | 4 | 5 | 3 | 2 | 3 | 4 | 3 |
| MW3 | 7 | 6 | 5 | 4 | 5 | 6 | 6 |
| MW4 | 5 | 5 | 5 | 4 | 3 | 4 | 4 |
| MW5 | 6 | 5 | 5 | 4 | 4 | 5 | 6 |
| AW1 | 6 | 4 | 5 | 5 | 7 | 7 | 8 |
| AW3 | 6 | 6 | 7 | 5 | 5 | 7 | 7 |
| AW4 | 8 | 7 | 7 | 5 | 7 | 6 | 7 |

* Time in GMT

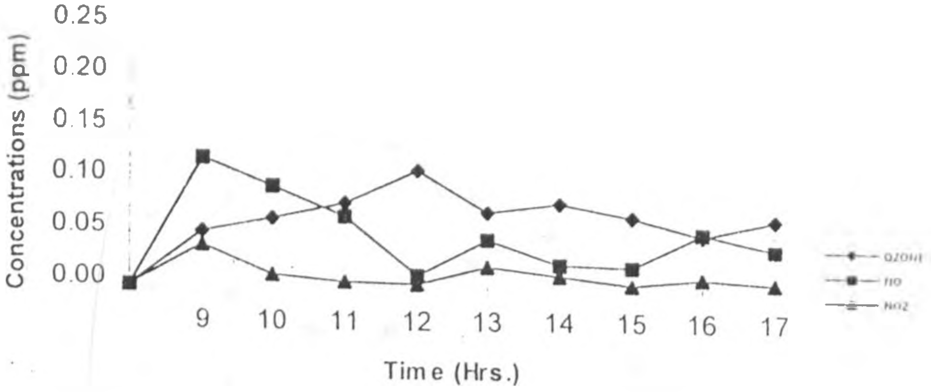

Figure 4.4 (a): Diurnal variation of ozone and nitrogen oxides (FW1)

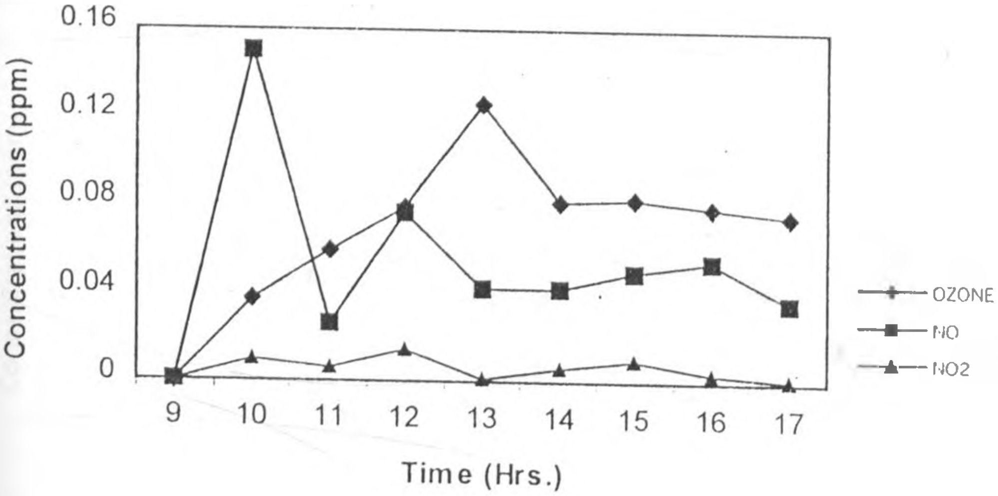

Figure 4.4 (b): Diurnal variation of ozone and nitrogen oxides (FW2)

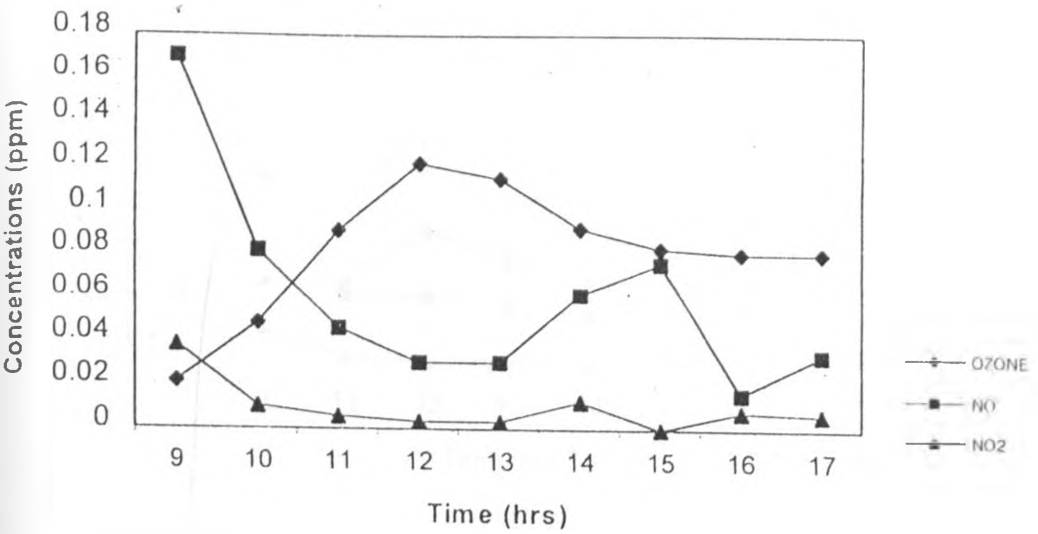

Figure 4.4 (c): Diurnal variation of ozone and nitrogen oxides (FW3)

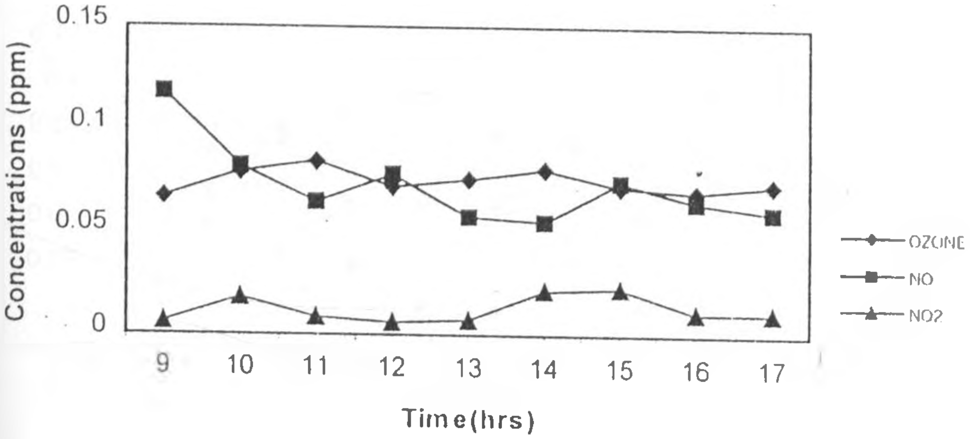

Figure 4.4 (d): Diurnal variation of ozone and nitrogen oxides (FW4)

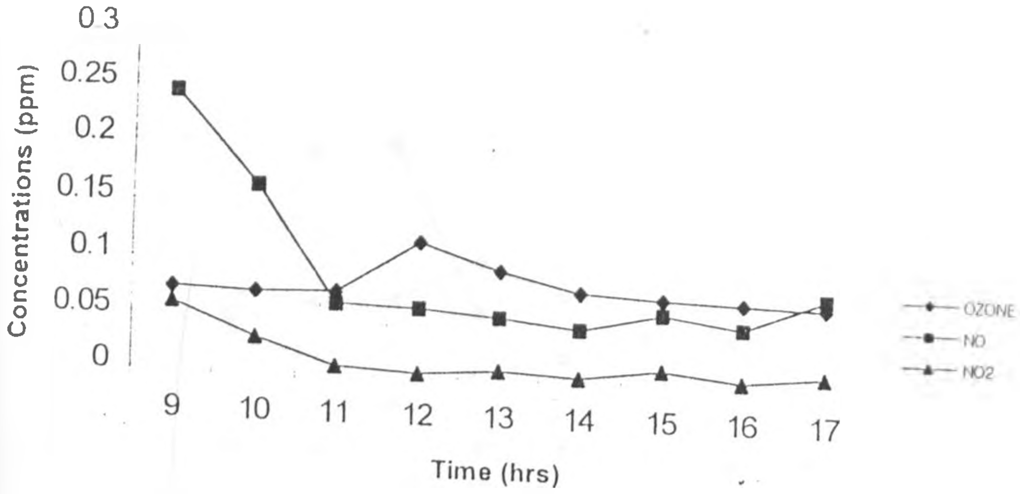

Figure 4.4 (e): Diurnal variation of ozone and nitrogen oxides (MW2)

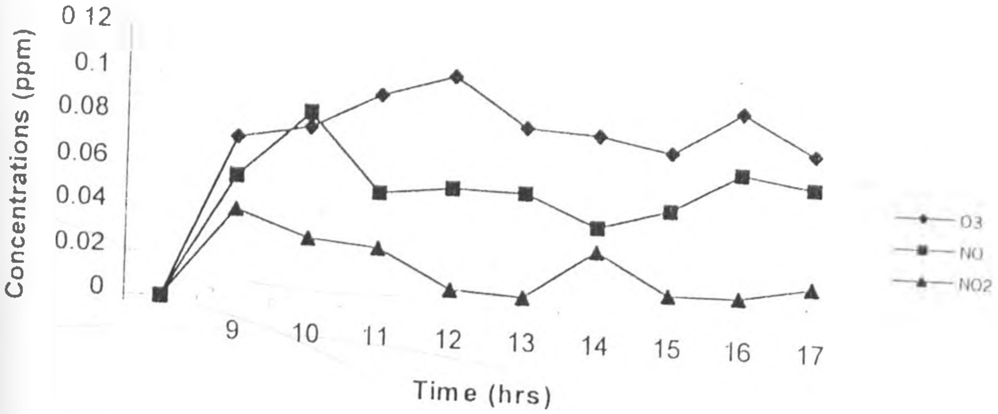

Figure 4.4 (f) Diurnal variation of ozone and nitrogen oxides (MW3)

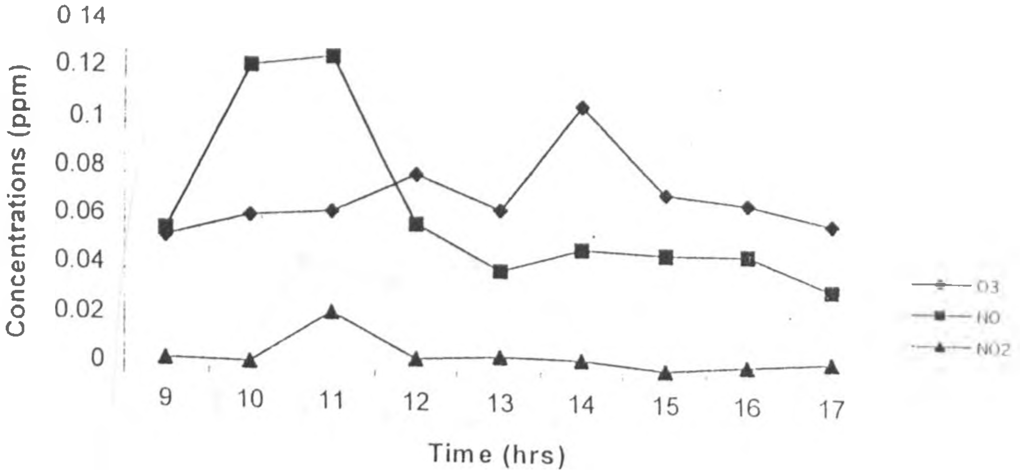

Figure 4.4 (g): diurnal variation of ozone and nitrogen oxides (MW4)

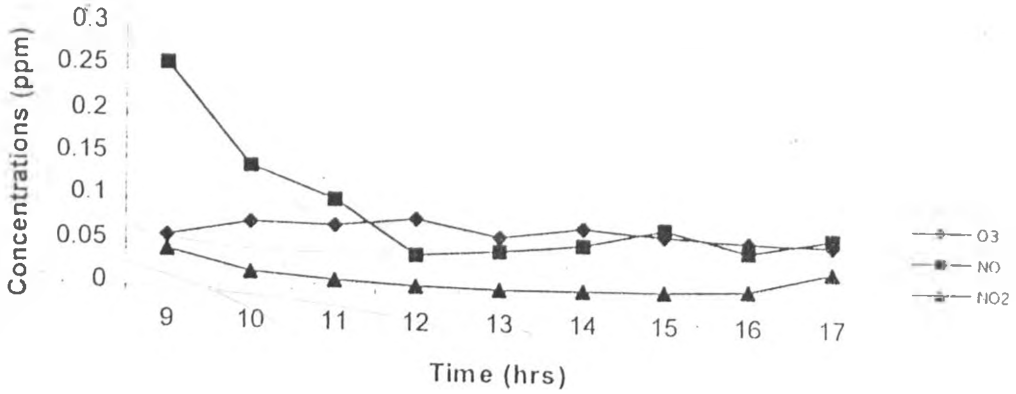

Figure 4.4 (h): Diurnal variation of ozone and nitrogen oxides (MW5)

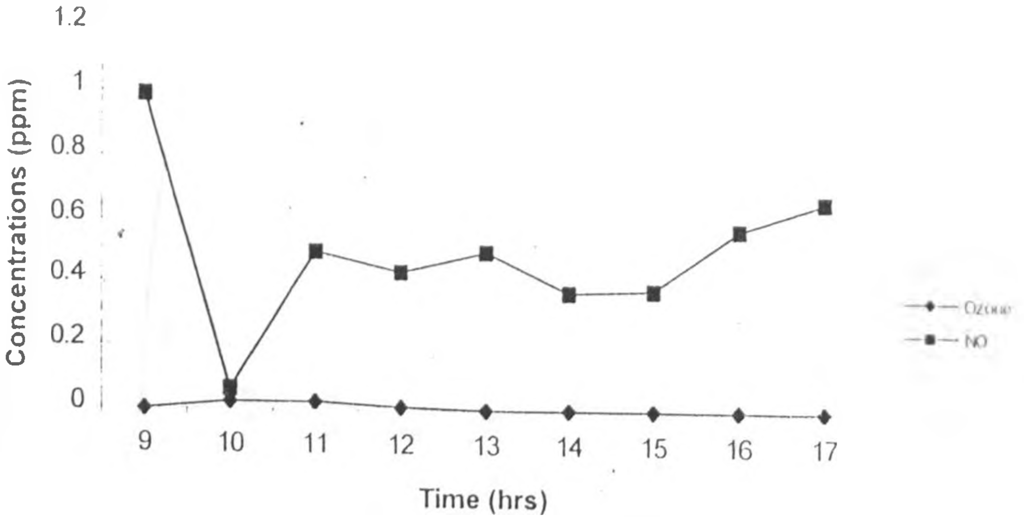

Figure 4.4 (i): Diurnal variation of ozone and nitrogen oxides (AW1)

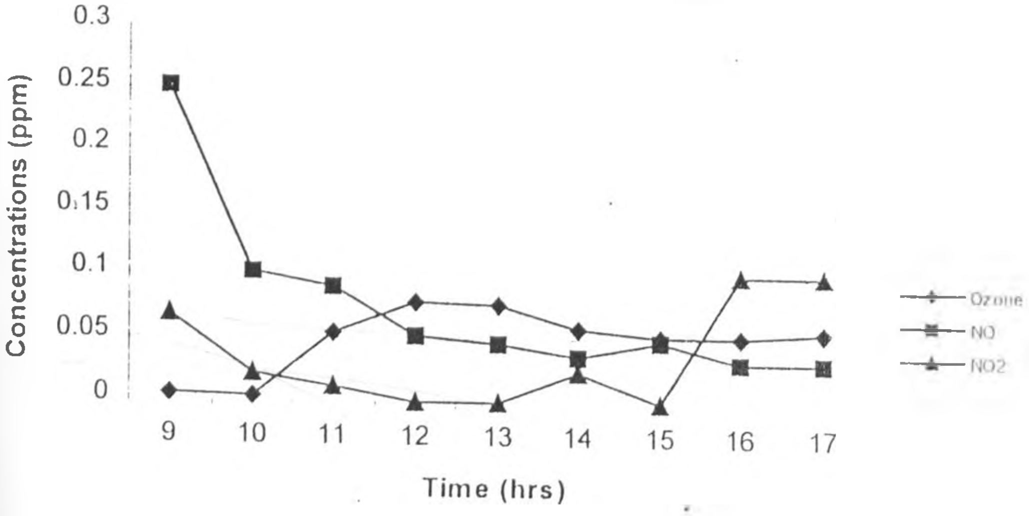

Figure 4.4 (j): Diurnal variation of ozone and nitrogen oxides (AW3)

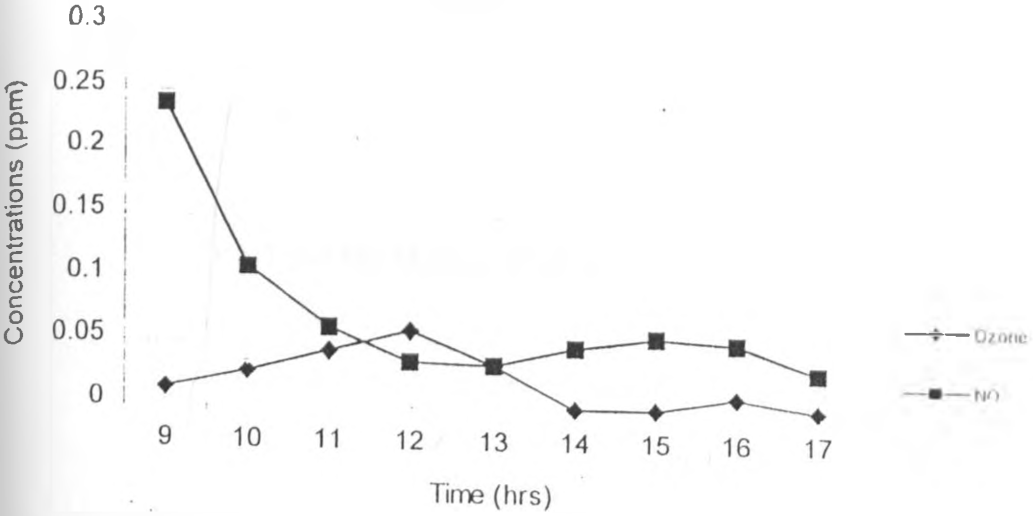

Figure 4.4 (k): Diurnal variation of ozone and nitrogen oxides (AW4)

## CHAPTER FIVE

# SUMMARY AND CONCLUSION

## Summary

### Air Particulate Matter ($PM_{10}$)

Aerosols were sampled in two size fractions, fine and coarse, at a roundabout in Nairobi. Samples were collected continuously over an eight-hour period, once a week, for three months. The samples were analysed for inorganic elemental concentrations.

- The mean level for $PM_{10}$ was 239±126 $\mu g/m^3$ while the range was 66-444 $\mu g/m^3$ (Table 4.3).

- In the dry months of February and March, coarse particulates accounted for more than 70% of $PM_{10}$ the correlation coefficient between coarse particulate and $PM_{10}$ being 0.848 (Table 4.4).

- There was strong correlation between fine particulates and motor vehicles (r=0.930), indicating that vehicular exhaust is the main source of the fine particles (Table 4.4).

### Gases

The gaseous pollutants, namely, $O_3$, $NO_2$ and NO were also measured at the same site as $PM_{10}$. The concentrations were measured at intervals of one hour for total duration of eight hours once a week throughout the sampling period (three months).

- The gaseous pollutants were for most of the times within the WHO (8-hours) guidelines, except for the peak hours when higher values were detected.

- For ozone, the mean value was 0.0618 ± 0.0012 ppm (123.6 ± 0.02 $\mu g/m^3$) (Table 4.3) with a maximum of 0.12575-ppm (236.41 $\mu g/m^3$). This is higher than the WHO-1 hour guideline of 150-200 $\mu g/m^3$ or even 100-120 $\mu g/m^3$ 8-hour guideline (WHO, 1999).

- The ozone peaks occurred mostly at noon and most of the afternoons when solar intensity/radiation was highest. Figure 4.3 shows how $O_3$ levels varied with solar intensity and temperature, confirming the importance of solar radiation in photochemical reaction through which ozone is formed.

- The levels of nitrogen oxides ($NO_x$) were low for most parts of the days except in the morning and evening when peaks coinciding with the rush hour traffic occurred. High values of NO were also recorded (Table 4.3) during these periods.

- There was also a high positive correlation (r=0.945) between NO and motor vehicles density (Table 4.4).

- $NO_2$ was however poorly correlated with motor vehicles (r= 0.279) (Table 4.4).

## Trace elements

The values obtained for trace elements are comparable to those found in other countries as well as those obtained locally (Onyari et al., 1992; WHO/UNEP, 1992; Tripathi, 1992; Karue et al., 1992). The levels obtained are within the WHO guidelines (annual).

- Lead concentrations ranged from 0.051 to 1.106 μg/m$^3$; Fe, 0.149 to 3.154 μg/m$^3$; Mn, LLD to 0.526 μg/m$^3$; Cu, LLD to 0.15 μg/m$^3$; Br, LLD to 0.43 μg/m$^3$; Zn, LLD to 0.14 μg/m$^3$ and Ca, 2.18 to 5.389 μg/m$^3$ (Table 4.5).

- There was high correlation between lead in the fine particles range (Table 4.7) and motor vehicles density (r=0.892) as there was between motor vehicles and Br (r=0.878), Zn (r=0.867) and Cu (r=0.743).

- There was also high correlation between Pb and Br (r=0.924), Pb and Zn, (r=0.790) and Pb and Cu (r=0.662), suggesting similar source for these elements (Table 4.6).

- High correlation was also observed between Pb and Br (r=0.924), which are used as octane enhancer in gasoline further (Table 4.6).

- Higher correlation values were obtained for these metals in the fine particulates (Table 4.7). The correlation between Pb and Br in the fine particle range was, r=0.959; Pb and Zn, 0.883; Pb and Cu, 0.623. Since the fine particles also correlate well (Table 4.4) with the motor vehicle (r=0.930), motor vehicles are clearly shown to be the source of these pollutants.

- Fe, Ca and Mn were poorly correlated with motor vehicles density (Table 4.6). These metals are also well correlated with one another, suggesting similar source, most probably dust particles. The correlation coefficient (Table 4.6) between Ca and Fe is, 0.7258; that between Fe and Mn, 0.5837 and Ca and Mn, 0.492.

- There was also strong correlation (Table 4.7) between coarse particles and Fe (r=0.910), as is, between coarse particles and Ca (r=0.672).

## Conclusions

From the findings of this study, Nairobi city is shown to have high levels of particulate matter ($PM_{10}$). The mean for $PM_{10}$ ($239 \pm 126\ \mu g/m^3$) is high compared to most cities of the world (UNEP, 1987). The WHO (1999) limit for $PM_{10}$ is 150 $\mu g/m^3$. Higher concentrations noted for the coarse particulates ($PM_{2.0-10}$) in the months of February and March (Table 4.3) and the high correlation between coarse particulate matter and Fe, Mn and Ca, (Table 4.7) which are associated with the earth crust, indicates that wind blown soil dust is their main source.

As for the fine particulate matter ($PM_{2.5}$), the most probable source is motor vehicles exhaust, given the high correlation (Table 4.4) between vehicles density and the fine particles (r=0.930). The high correlation between fine particles with Pb, Br, Zn and Cu, (Table 4.7) are also associated with vehicular emissions and parts degradation, is a further indication of motor vehicles as a major source for these pollutants.

The high concentrations of NO and $NO_2$ measured during the peak hour traffic (Table 4.3) is a pointer to the fact that vehicular emission is the main contributor to these gases in the ambient air of the city. $NO_2$ was however poorly correlated (Table 4.4) with motor vehicles (r=0.279). This could be because $NO_2$ is not directly emitted from the vehicle exhausts but is formed from the conversion of NO by its reaction with $O_2$ in the atmosphere. The ozone peaks occurred mostly at noon and most of the afternoons when solar intensity/radiation was highest, confirming the importance of solar radiation in photochemical reaction through which ozone is formed. This was also the same pattern for $O_3$ and temperature. Meteorological parameters were therefore found to play a significant role in the concentration of ozone.

The levels of nitrogen oxides ($NO_x$) were low for most times of the days except during the morning and evening rush hour traffic, when high values, especially for NO were recorded. This shows that within the city centre, motor vehicles are the main source of these gaseous pollutants. This is further supported by the high positive correlation (r=0.945) obtained between NO and motor vehicles density (Table 4.4). The maximum value obtained for $NO_2$ was 0.2628 ppm (494.064 $\mu g/m^3$), which is higher than the WHO 24 hour recommended value of 150 $\mu g/m^3$ and 1-hour guideline of 400$\mu g/m^3$ (WHO, 1999). $NO_2$ is associated with adverse health effects (WHO, 1987) and these values could translate to poor health for the people who might be exposed to this gas.

Analysis of the data shows strong correlation (r=0.966) between fine particles and NO (Table 4.4), indicating the importance of traffic as a common source for both fine particles and NO. $O_3$ and $NO_2$ are however, poorly correlated with motor vehicle density (Table 4.4). This, as explained above, is because $O_3$ and $NO_2$ are not directly emitted from the vehicular exhausts, but are formed from the photochemical reaction of the gases emitted directly from the exhausts. This reaction, takes some time to come to completion.

The high correlation (Table 4.7) between motor vehicles density and lead in the fine particles range (r=0.892) as well as between motor vehicles and Br (r=0.878), Zn (r=0.867) and Cu (r=0.743), suggests similar source for these elements being the vehicular exhaust. The high correlation between Pb and Br (0.930), which are used as octane enhancer in gasoline further, supports this view. Br/Pb ratios (Table 4.5) were also within the range found in gasoline (~0.3) (Seinfeld, 1989).

Several studies, especially in the USA have associated high levels of $PM_{10}$, and fine particulate matter with adverse health effects such as cardiovascular and respiratory health problems (Dockey et al., 1993; Pope, 1991; Pope et al., 1995; Schwartz, 1993, and Morgan et al., 1998). The most revealing information came from epidemiological case studies conducted in the US in which humans were exposed to particulate matter of widely differing composition in many different communities and climates (Dockey et al., 1993). These studies showed that inhaling particulate matter of 10 µm or less over long periods of time caused premature mortality, aggravation of respiratory and cardiovascular diseases, changes in lung function and structure, and changes in the ability of the lungs to fight infection. However, the mechanism through which these happens have not been well understood.

Lead has also been confirmed to have very adverse effects especially in the neuro-physiological system. Studies have for instance, confirmed lower IQ as a result of poor brain development among the children exposed to even lower levels of Pb than the ones obtained in this study (Bellinger, 1987). Apart from its effect in the neuro-physiological system, a wide range of metabolic disorders and kidney problems have been associated with environmental exposure to low levels of lead (USEPA, 1992). The most affected are children.

Considering the adverse health effects associated with these pollutants and the high levels in which they are present in ambient air in the city, it is of critical importance that appropriate measures are taken to address the problem before situations similar to the ones experienced in cities in the developed countries, such as London smog of 1952 (Cornwell, 1998) and Los Angeles occur in Nairobi. Some of the suitable measures that can be taken to alleviate this situation are discussed below.

## Recommendations

### Cleaner fuels

Alternative fuels, including compressed natural gas, liquid petroleum gas and ethanol, are receiving increased attention as potential pollution reducers. Compressed natural gas, already being used in countries such as Canada, Italy, and New Zealand, is an abundant fuel and can be particularly useful in reducing emissions of air particulate matter in the city (MacKenzie, 1994). As air particulate matter is the major pollutant in the city, and probably in other towns in the country, the possibility for the use of these alternative sources of fuel in motor vehicles should be seriously considered.

A high priority for this country should be to reduce the lead content of gasoline. In Kenya, the lead content of gasoline used in motor vehicles is 0.4 mg/l (Karue et al., 1992) which is very high compared to the developed countries like USA, Canada and Europe some of which have completely banned the use of lead as an octane enhancer in their petrol. Besides being a direct health threat, lead in gasoline prevents the use of catalytic converters in gas burning engines. Catalytic-converters help limit vehicle emissions of hydrocarbons, carbon monoxide and nitrogen oxides (Weaver et al., 1994). The ban in the use of lead in gasoline has led to great reduction of lead in the ambient air in most cities (UNEP, 1996). This subsequently leads to reduction in the lead levels in the blood of the exposed people (Eggleston et al., 1992; Jensen and Laxen, 1987).

The cost of eliminating lead from gasoline and of eliminating older vehicles have made it difficult for low income countries to switch to unleaded gasoline. In Bangkok, however, the government has supported the introduction of unleaded gasoline through a tax subsidy by taxing unleaded fuel less than leaded fuel thus the government made it cost-effective for local refineries to produce unleaded gasoline (NILU, 1996). The Kenyan government should also consider this option as this would go along way in solving the problem of high lead levels in the ambient air. It is widely felt that what is needed is, on the one hand, the use of regulation and incentives to reduce car use (e.g. promotion of the use of non-motorised and public transport systems) and, on the other, the application of traffic management measures to promote smooth traffic flow and reduce delays and start-stops in the city environment (Seinfeld, 1989). The latter has been found to have ameliorative effects on traffic-generated air pollution in several industrialised countries. Road repairs and maintenance should also be done as the poor roads condition in the city also causes traffic jams during which a lot of these pollutants are emitted.

### Vehicle Inspection and Maintenance

A high proportion of vehicles in the city are old and poorly maintained. Most of the cars sold locally are second hand, and have been in use for a number of years before resale to local buyers. Older vehicles account for a disproportionate share of air pollution. A badly maintained older vehicle can emit 100 times the pollutants of a properly maintained modern vehicle (Saville, 1993). Effective inspection and maintenance programs can help reduce emissions from older vehicles and ensure that new vehicles remain in good condition.

### Legislation

Perhaps the greatest single barrier to effectively solve air pollution problem in this country is the fact that the responsibility for urban transportation systems resides with many different entities. Typically, one institution is responsible for air quality management, another is in charge of traffic management and enforcement, a third manages public transportation, and a fourth manages infrastructure. Without clear lines of authority and strong coordination, any attempts to improve urban transportation systems will inevitably fall short.

There is also very little in the way of formal legislation or policy with which to manage air quality in Kenya, and Nairobi specifically. New legislation has been passed in parliament and received presidential assent. There are also no set of air quality standards in the country, nor are there formal emission limits for stationary or mobile sources, although vehicles can be declared unfit to drive owing to their emission levels. The owners can only pay a fine. But it is not clear how excessive emissions are defined. There should therefore be clear cut policies governing this. This can only be done when specific air quality guidelines are in place and proper enforcement of the legislation.

## Further research

This study mainly investigated the levels of nitrogen oxides ($NO_x$), ozone ($O_3$), trace elements and air particulate matter ($PM_{10}$). The focus was on motor vehicles emission. Other equally important urban air pollutants such as carbon monoxide (CO), hydrocarbons, such as benzene, which are known to be carcinogenic, were not determined. Further research recommendation should therefore include:

1. Measurement of other air pollutants, some of which are more harmful to human health should be carried out not only in Nairobi city but also in other towns in the country. This kind of study should also consider other parts of the city such as the industrial area and the residential estates.
2. Epidemiological case studies to assess health problems associated with air pollutants among the exposed population in the city should also be done. Health data on illnesses such as acute respiratory infections, asthma, emphysema, e.t.c, should be obtained and correlated with air pollution data to confirm if there are any causal relationships between the diseases and levels of the air pollutants measured.

3. Studies on the blood lead levels especially among those living close to busy highways should be carried out to check any effects and/or relationships between the lead levels in the ambient air and that in their blood.
4. Studies have confirmed the health effects of fine particles, especially the ultrafine particles. However, the mechanisms through which the particles induce the associated health effects are not well understood. Further research studies should therefore be carried out to find out about these mechanisms.

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